IDEAS-QA4EO DOAS-BO: TOWARDS A NEW FRM4DOAS SITE IN THE PO VALLEY

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Abstract: Pollutant gases information can be retrieved from ground-based and satellite visible and UV spectra, exploiting the Differential Optical Absorption Spectroscopy (DOAS) technique. The validation of the satellite NO2 tropospheric column shows the particular importance that should be given to measurements acquired in polluted regions.
The Po Valley (Italy) is one of these regions. Despite this, an instrument compliant with the Fiducial Reference Measurements for Ground-Based DOAS (FRM4DOAS) standards is not yet present in Po Valley. Hence, the purpose of the DOAS-BO WPs within the IDEAS-QA4EO ESA project is to make a step to close this gap.
The objectives of the IDEAS-QA4EO DOAS-BO WPs are to demonstrate the importance of the DOAS measurements in the Po Valley, re-enforce the Italian know-how on Multi-Axis (MAX)-DOAS technique and go towards the provision of standardized data for validation networks.
This work was carried out in the frame of the Instrument Data quality Evaluation and Assessment Service - Quality Assurance for Earth Observation (IDEAS-QA4EO) contract funded by ESA-ESRIN (n. 4000128960/19/I-NS).

1) Assessing the performances of an existing MAX-DOAS spectrometer (TROPOGAS) vs FRM4DOAS requirements

Instrumental guidelines	
At least one O4 band covered well	V
Quartz fiber for removal of polarization features	V
Optical low pass filter for straylight removal in UV	V
Proper time information	V
Spectral resolution better than 0.8 nm (UV) and 1.5 (visible)	V
FOV better than 1.5° in vertical direction	X
Operational guidelines	
SZA range up to 85° for MAX-DOAS and up to 94° for zenith-sky observations	V
Zenith-sky observations at least every 30 minutes during MAX-DOAS observations	V
At least one zenith-sky measurement per degree SZA at twilight	V
At least 1°, 2°, 3°, 5°, 10°, 30° elevations in scan	V
Horizon scan on a regular basis	V
Dark signal must be measured at least daily	V
The slit function must be measured on a regular basis (daily if possible)	V
Data processing guidelines	
Apply dark signal correction	V
Apply wavelength calibration	V
Apply non-linearity correction	V
Average spectra to reach SNR of at least 3000 (visible) or 4000 (UV)	V

A custom MAX-DOAS system is deployed on the roof of ISAC-CNR Bologna premises since 2018. This system is named TROPOGAS (**Fig.1)**.

The first step of the project was the assessment of TROPOGAS performances and the development of a new measurement strategy in light of the FRM4DOAS network requirements.

In **Table 1**, the compliances of TROPOGAS to FRM4DOAS standards are reported. The only criteria that is not met is the FOV aperture (about 3° for TROPOGAS).

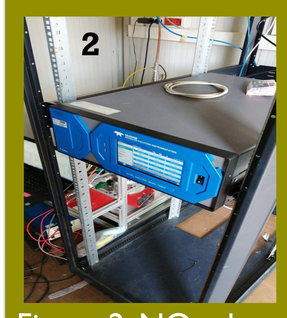
Table 1: TROPOGAS compliances. Figure 1: TROPOGAS instrument

2) Bologna measurement campaign : TROPOGAS synergies with in-situ and satellite data

The FRM4DOAS compliant measurement strategy found during the first part of the project was adopted for the TROPOGAS measurements campaign in Bologna. The campaign started in late April 2021 and ended at the beginning of June 2021. TROPOGAS data were analyzed using the QDOAS software (https://uv-vis.aeronomie.be/software/QDOAS/, see **Table 2** for analysis set-up).

Campaign results exploited satellite and in-situ synergies. A chemiluminescent analyzer equipped with photolytic converter and with an implemented correction algorithm for ozone interferences along the sampling line was used (**Fig. 2**).
NO_2 from this analyzer at surface (in-situ, blue in **Fig. 3**) were compared with surface data retrieved with a prototypal raw (no aerosol retrieval performed) algorithm for MAX-DOAS measurements analysis (red in **Fig. 3**).

Sentinel-5P TROPOMI NO2 total columns were compared with NO_2 total columns from TROPOGAS. Daily averages from ground- and satellite- based measurements are reported in **Fig. 4**. A general good agreement is found.



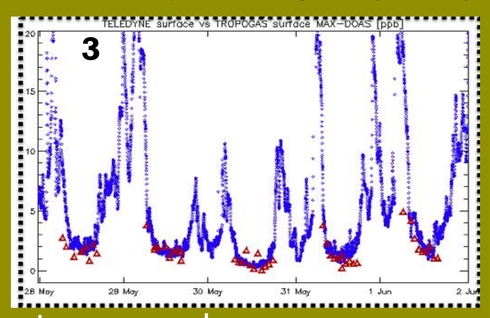


Figure 2: NO_x chemiluminescent analyzer
Figure 3: TROPOGAS vs in-situ NO_2 at surface
Figure 4: TROPOGAS vs TROPOMI NO_2 Total columns

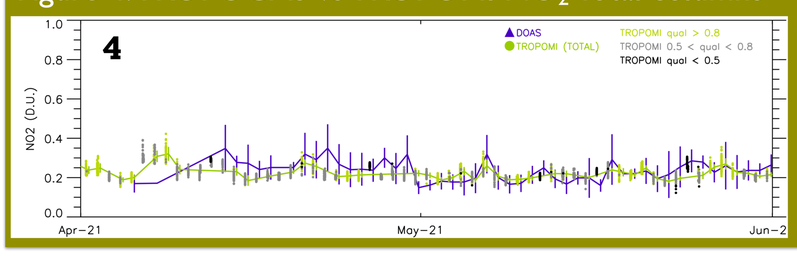


Table 2: QDOAS settings for TROPOGAS data analysis (Bologna) campaign

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)

3) A new MAX-DOAS System (SKYSPEC-2D) : Bologna inter-comparison campaign with TROPOGAS

During the project, the ISAC-CNR institute acquired, in the frame of the national founded project "Programma biennale degli investimenti del CNR", two new MAX-DOAS systems. One has as final collocation, the "Giorgio Fea" observatory in San Pietro Capofiume (BO), in the Po Valley. This instrument, is a SkySpec-2D-210 system by Airyx. These type of instruments were used in the frame of FRM4DOAS inter calibration campaigns among the reference MAX-DOAS instruments. Due to its compliances to FRM4DOAS standards and higher portability, we chose to use the SkySpec-2D system for the inter-comparison campaign at BAQUNIN foreseen for the last part of the project.

An inter comparison campaign was held in Bologna on the roof of ISAC-CNR building from 4th August to 2nd September 2021 (**Fig. 5**) with Skyspec-2D and TROPOGAS.
Results of the comparisons of NO_2 VCDs from zenith measurements for single days and averaged over the whole campaign are reported in **Fig. 6** and **Fig. 7** (SkySpec-2D in blue, TROPOGAS in red, error bars = retrieval errors in Fig.6, STD in Fig.7). On daily plots, NO_2 VCDs from TROPOMI (green) and OMI (black) are also reported.

Good agreement, both in terms of absolute values and consistent behavior, is observed despite the differences in instruments design. This can be noticed also from the scatter plot in **Fig. 8** (correlation 0.8, BIAS 3.9+/-18%)

Figure 5: TROPOGAS and SKYSPEC-2D at ISAC-CNR

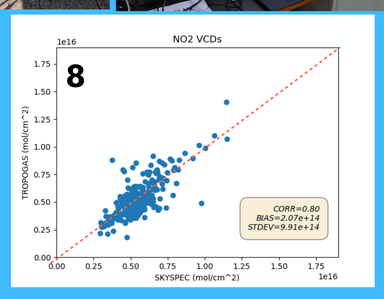


Figure 8: TROPOGAS vs SKYSPEC-2D NO_2 zenith VCDs scatter plot

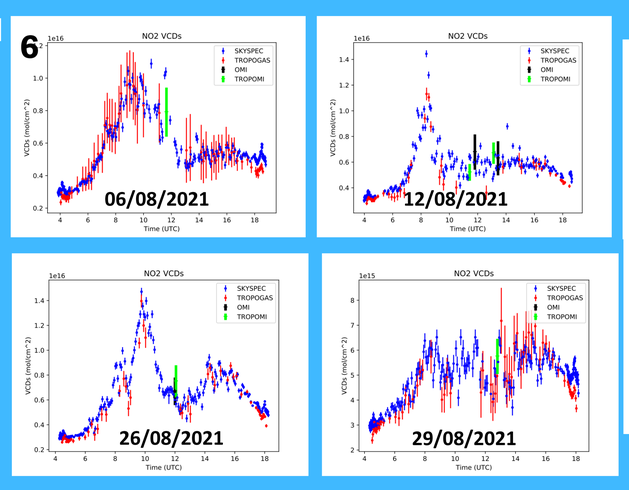
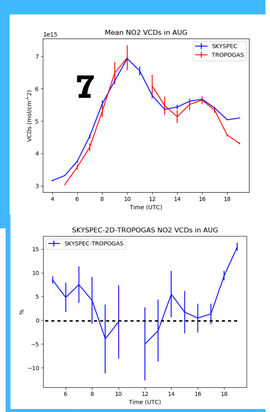


Figure 6: TROPOGAS (red) vs SKYSPEC-2D (blue) during the Bologna inter-comparison campaign. NO_2 VCDs on 6, 12, 26, 29 August 2021



TROPOGAS vs SKYSPEC-2D NO_2 VCDs average day

4) BAQUNIN inter-comparison campaign: SKYSPEC-2D and Pandora

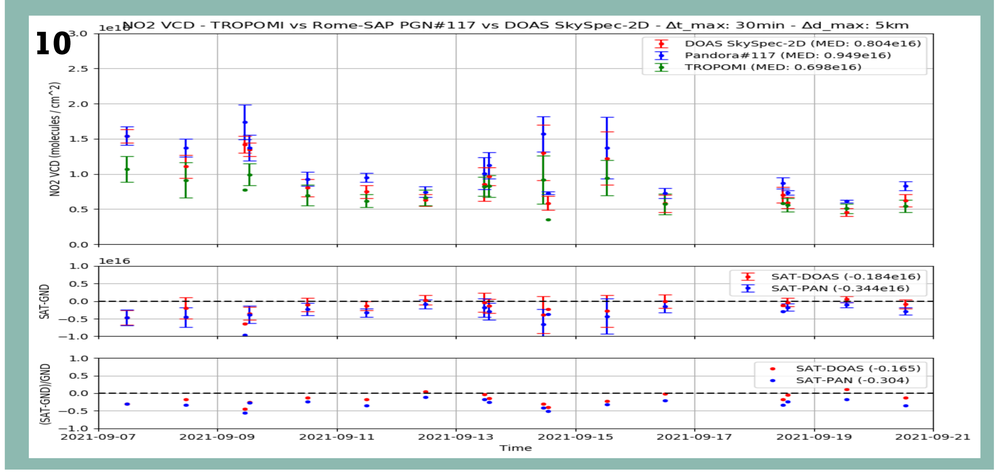
The SkySpec-2D took part in the inter-comparison campaign at BAQUNIN from the 6th to the 21st of September 2021. The instrument was placed on the roof of the "La Sapienza" University in Rome (**Fig. 9**). During this period, the QUATRAM3 (QUAlity and TRaceabiliy of Atmospheric aerosol Measurements) campaign was also ongoing in the same place.

The SkySpec-2D NO_2 VCDs have been compared with similar products retrieved using the Pandora #117 and the Sentinel-5P TROPOMI observations. Preliminary results of the inter-comparison are shown in **Fig. 10**.

A general good agreement can be observed, TROPOMI has a bias of -17% with respect to SkySpec-2D and of -30% with respect to Pandora#117.

Figure 9: SKYSPEC-2D at BAQUNIN

Figure 10: SKYSPEC-2D vs Pandora and TROPOMI NO_2 VCDs



Conclusions

During the IDEAS-QA4EO DOAS-BO WPs, we make a step towards the closure of the gap of MAX-DOAS measurements in the Po valley:
1) We assess the performances of TROPOGAS in Bologna and make its measurement configuration compliant with FRM4DOAS requirements
2) After the acquisition of a new fully FRM4DOAS compliant MAX-DOAS system, we compare its performances with TROPOMI, TROPOGAS, in Bologna, and Pandora, in BAQUNIN
3) The new system is now placed in the "Giorgio Fea" meteorological station (St. Pietro Capofiume), ensuring two MAX-DOAS systems operating in the Po Valley (with verified performances)