

Project of Strategic Interest NextData:

Deliverable D1.2.7

# Report on the upgrade of GAW-WMO stations with Italian management and related to SHARE Project.

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**Partners:** CNR-ISAC, URT Ev-K2-CNR In spite of the lack of expected funds, during the third year of activity, the following activities were carried out at the Regional and Global stations led by Italian Institutions.

- Activation of continuous nitrogen oxides (NOx), nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) measurements at the Mt. Cimone GAW/WMO station.
- -Activation of continuous sulphur dioxide measurements (SO<sub>2</sub>) at the Mt. Cimone GAW/WMO station.
- Activation of continuous sulphur dioxide measurements ( $SO_2$ ) at the NCO-P GAW/WMO station.
- Activation of continuous surface ozone (O<sub>3</sub>) measurement at the Lampedusa station.
- Continuation of the implementation phase for the activation of AOD measurements at the Mt. Cimone GAW-WMO station.
- Continuation of the implementation phase for the activation of aerosol lidar measurements at the Mt. Cimone GAW-WMO station.

In the following, special attention will be paid in reporting the upgraded activities carried out at the Mt. Cimone GAW/WMO Global Station.

## Activation of Continuous nitrogen oxides (NOx), nitric oxide (NO), nitrogen dioxide (NO2) measurements.

The measuring system implemented during the second year of the Project, was successfully installed at CMN on March 2014. After two months of in-situ test under operative conditions, the measurements started on June 2014. Before installation at Mt. Cimone, the system participated to the ACTRIS UE Project round-robin experiment for NO measurements.

The system is based on a commercial chemiluminescence  $NO-NO_2$  analyser, which has been modified to specifically meet the DQOs requested by GAW-WMO and the scientific needs that are typical of a remote mountain station. In particular, as deduced by the laboratory tests, the instrumental detection limit was evaluated to be 60 ppt, which is in the typical range for similar instruments employed within the ACTRIS Project.

As already described in the deliverables D1.2.2, D1.1.1 and D1.2.5, the instrument has been modified at the ISAC laboratories to mount a photolytic converter instead of the "commercial" Molybdenum converter. While being less efficient than the Molybdenum heated converter in converting  $NO_2$  to NO (typically conversion efficiency ranged around 50% against 98% for the Molybdenum one), the photolytic converter is much more selective and the influence of "processed" nitrogen compounds (i.e. PAN) are almost completely neglected when determining the NO2 mole fraction.

The instrument was equipped with a system for the execution of automatic calibrations. To this aim, a multi-calibrator Thermo 146i has been used which allows to manage the execution of zero test, as well as to carry out span checks for NO (by diluting a flask standard) and to evaluate the conversion efficiency of the photolytic converter (by using a Gas Phase Tritation module). Currently, every 48 h, zero and span test are automatically executed. With the aim of providing reliable data in near-real time mode, the calibration data are automatically processed to provide "calibrated" NO and NO2 readings.

Figure 1 shows the daily values of NO and NO2 observed at CMN by means of this new system. It is interesting to note the frequent peaks of NO2 in Autumn and in Winter. Due to its shorter

life-time (only a few hours in Summer and 1–2 days in Winter), NO<sub>2</sub> is a good indicator for regional anthropogenic impact (Gilge et al., ACP, 2010). During the period June-December 2014, NO and NO<sub>2</sub> average values were 0.04  $\pm$  0.04 ppb and 0.18  $\pm$ 0.22 ppb, respectively. The NO<sub>2</sub> seasonal cycle, ranging from about 0.24 in Autumn-Winter to 0.13 in Summer, is well comparable with analogous observations at the Jungfraujoch station (Swiss Alps, 3580m a.s.l.), thus indicating limited impact of regional pollution at CMN.



Fig. 1: Daily values of NO (light blue) and NO2 (red) observed at CMN

Finally, we compared NO<sub>2</sub> observations carried out on Autumn 2014, with analogous measurements carried out in 2012 and 2013 at Mt. Cimone but with a system equipped with Molybdenum converter (Fig. 2). Even if furter analyses are neeeded to better understand the impact of meteorology and transport regimes on interannaul variability, the influence of the photolytic converter in selecting NO<sub>2</sub> and detecting other compounds appears to be evident.



Fig. 2: NO2 observations carried out on Autumn 2012, 2013 and 2014 at Mt. Cimone using a system equipped with different converters.

#### Activation of continuous sulhpur dioxide (SO<sub>2</sub>) measurements at Mt. Cimone

The measuring system implemented during the second year of the Project, was successfully installed at CMN on March 2014. The system is based on a commercial UV-fluorescence ultrasensitive  $SO_2$  analyser (Thermo 43i TLE). The instrument was equipped with an automatic system for the daily execution of zero and span checks. The zero air source is an external cartridge filled with activated charcoal, while the span source is a certified permeation tube (wafer type) with an emission rate set for obtaining a span point at 50 ppb with a zero air of 1 lt/min. The implementation of a system for the automatic execution of multi-point calibration (by a dilution technique) is foreseen.

The system has been also equipped with an electronic flowmeter for monitoring the zero air source, which is a critical parameter for correctly evaluating possible span drifts. The detection limit has been assessed to be 0.11 ppb (on 1-minute average).

Figure 3 shows the daily values of  $SO_2$  observed at CMN by means of this new system. The mean average value in the period March – December 2014 was 0.04 ± 0.15 ppb (± 1s). It is interesting to note the occurrence of  $SO_2$  peaks during Autumn.



Fig. 3: Daily values of SO2 observed at CMN

However, high  $SO_2$  mixing ratios were observed, on October 22<sup>th</sup>, as shown in Fig. 4. The 30minute averaged  $SO_2$  values reached 3.7 ppb on October 22<sup>th</sup> at 6:00 and 2.4 ppb at 22:30. These  $SO_2$  peaks were not related to increases in other anthropogenic pollutants (NO, NO<sub>2</sub>, see yellow area in Fig. 4).

On August 16<sup>th</sup> the Icelandinc Bárðarbunga volcano started an intense eruption activity which is still active. FLEXTRA back-trajectories supported the transport of air-masses from Iceland, were high atmospheric SO<sub>2</sub> were detected by the OMI satellite due to volcanic emissions (see Fig. 4). This case study, clearly underline the potential of SO2 measurements at Mt. Cimone as "sentinels" of the presence of volcanic plumes.



Fig. 4: Daily values of NO, NO2, and SO2 observed at CMN



Fig. 4. On the left: 5-day air-mass back-trajectories calculated by FLEXTRA for October 22nd, 2014. Data and elaboration: NILU (curtesy By Andreas Stohl)On the right: AURA/OMI SO2 columnar integrated mixing ratio (expressed as Dobson Unit) on October 17th, 2014.

#### Activation of continuous sulhpur dioxide (SO<sub>2</sub>) measurements at the NCO-P station

A system for the continuous determination of the atmospheric SO2 mole fraction was installed at the NCO-P on October 2014. This activity is also intended to support an international experimental campaign devoted to the investigation of aerosol nucleation processes in the high Himalayan atmosphere (see D1.1.6). The system is similar to that activated at Mt. Cimone: it is based on a commercial UV-fluoresence ultra-sensitive SO2 analyser (Thermo 43i TLE). The instrument was equipped with an automatic system for the daily execution of zero checks. The zero air source is an external cartridge filled with activated charcoal. Unfortunately, due to shipping rule restrictions, the span source (permeation tube) was not sent to NCO-P. Thus at this stage no span calibration are executed at the station.

Some technical problems affected the execution of the measurements, particularly due to unexpected software acquisition failures which delayed the start of the operative measurements to November 2014, while a further unexpected stop was observed on December, 17<sup>th</sup> 2014 (the system was reactivated on January 2015).

During the first two months of operation (November – December 2014), the SO2 values were below the detection limit for almost all the measurement period (see Fig. 5). On 2015, an assessment will be carried out to evaluate the possibility to move this instrument from NCO-P to the Pakanajol station in Kathmandu, with the purpose of investigating the impact of fossil fuel emissions on atmospheric composition variability.



Fig. 5: SO2 concentration values from December 1st to December 17th, 2014 at NCO-P.

### Implementation phase for the activation of Aerosol Optical Depth measurements at the GAW-WMO Global Station Mt. Cimone

The Precision Filter Radiometer (PFR) is the instrument used in the GAW-PFR network. It acquires direct solar radiation at 4 spectral channels at 368, 412, 500 and a 862 nm and it is designed for continuous and automated operation under a broad range of weather conditions. It has a thermostatic system (Peltier) that maintains the detector at 20°C over an ambient temperature range from -20°C to 35°C. This system eliminates the need for temperature corrections and prevents accelerated aging of filters shading them by an internal shutter except for the brief measurement period. A sensor monitors the pointing quality for each measurement.

From the 4 spectral direct solar radiation measurements, the total columnar aerosol optical depth at each spectral channel is derived from the Beer-Bouguer-Lambert law, which allows to retrieve the total optical depth  $\tau$  of the atmosphere.

(1)

(2)

$$S(l)=S_0(l)exp(-m\tau)$$

where S(l) is the direct sun signal at ground level at wavelength l, S0(l) is the extraterrestrial signal of the instrument, corrected by the Earth-Sun distance and m is the optical air mass in the measurement path. The aerosol optical depth  $\tau_a$  is determined then by subtracting the contributions of the molecules (Rayleigh optical depth  $\tau_r$ ) and absorbing gases (gaseous optical depth  $\tau_g$ )

$$\tau_a = [\ln(S_0(l)/S(l)) - \tau_r - \tau_g]/m$$

The channels used for aerosol investigation are located in spectral regions with weak absorption by atmospheric gases. To account for small absorptions by ozone, NO2, etc., effective absorption coefficients for each channel are calculated using the filter transmission curves. Amounts of these species were obtained from different sources: satellites (e.g. OMI), co-located ground-based measurements (e.g. Brewer) or monthly climatologies retrieved

from measurements/models. The Ångström exponent (AE), indicative of size predominance between fine and coarse, is obtained from the AOD at different wavelengths according to the Ångström law:

 $\tau_a = bl^{-a}$ 

(3)

The sunphotometer is currently at ISAC-CNR laboratories in Bologna (Fig. 6): it is necessary to assemble a power box that makes the system resistant to the atmospheric conditions of the Mt. Cimone station.



Fig. 6: The sunphotometer currently located at the ISAC-CNR laboratories in Bologna

In particular, a IP65 box is going to be setup with the needed dual powering system (with +/-12V and 5 V, 3A max) that will power both the instrument and the Campbell Scientific CR10X datalogger. A special LEMO brand panel connector was ordered as required to interface the datalogger with PFR.

Special attention will be paid to the sun-tracker deployment. The system will be based on one of the following solution: i) a testing system made available within an agreement with NESA s.r.l. that is developing a brand new sun tracking system or ii) by a full upgrade of the electrical and motor driving parts of the sun trackers that operated at Mt. Cimone for several years. In both cases an active solar tracking will support the astronomical positioning.

A site testing of at least one month (May, 2015) is scheduled in Bologna, in order to optimize the setup and to perform a full intercomparison with a collocated sun photometer (Cimel/Prede or Yesdas MFR7). Data will be analyzed following the procedure descripted in Mazzola et al. (2010) and in Mazzola et al. (2012).

It is worth to plan a final deployment of the system during early June 2015. The datalogger will be equipped with a CS/IO-network interface - Tibbo or similar, that will allow direct management from Bologna through the Ethernet connection. Local data backup will be guaranteed by a 16MByte Campbell storage module.

#### Implementation phase for the activation of aerosol lidar measurements at the Mt. Cimone GAW-WMO station

During the third year of activities, several efforts have been carried out for implementing the aerosol lidar measurements at the Mt. Cimone GAW/WMO station. Once operative, this system will allow obtaining the following parameters:

- Range corrected signal (colour plots of aerosol and cloud distributions).

- Attenuated backscatter coefficient (calibrated range-corrected signal).

- PBL depth.
- Aerosol backscatter coefficient.
- Aerosol type discrimination (dust, anthropogenic).
- Aerosol extinction coefficient (estimate), optical depth, column lidar ratio.

During the execution of the first in-situ tests at the Mt. Cimone station, a major failure affected the lidar laser source which was repaired by the manufactory. This event delayed the start of the in-situ operations. After the re-installation at Mt. Cimone, some inaccuracies in the design of the external quartz window holder was pointed out. This led to "spurious" back signals. For this reason, the window holder was dismounted and rearranged at the ISAC laboratories in Bologna. This new system was mounted at Mt. Cimone on November 2014. The optical alignment and the resulting calibration of the system is not a trivial task and several nigh-time measurements under clear sky conditions are required. This strongly affects the possibility of making the lidar system operative before Summer 2015.

#### Activation of continuous surface ozone (O<sub>3</sub>) measurement at the Lampedusa station

During the third year of activity, a new programme for measuring surface ozone at the regional GAW/WMO station at Lampedusa has been activated in agreement with the upgraded plans recommended during the first year of NextData activity (see D1.2.1).

The instrument was equipped with systems for the automatic execution of zero and span check every 24h. The internet connection, available at the station, allows the remote control of the instrumentation status. On a monthly basis ISAC-CNR staff executes a check of the data and metadata (internal parameters) provided by the instrument and stored by the acquisition system on a local PC. Standard Operating Procedures (SOP) were defined by ISAC-CNR in collaboration with ENEA-UTMEA.

An UV-absorbtion analyser Thermo 49i was installed at the "R. Sarao" station by ENEA-UTMEA on July 2014. The instrument has been provided by ISAC-CNR together with a dedicated acquisition and management software. Figure 7 shows the time series of hourly averaged values from July to December 2014. An average ozone level of 43.3 ±7.3 ppb has been observed.



Fig. 7: Time series of hourly averaged Ozone values from July to December 2014

As deduced by the monthly percentile analysis shown in Fig. 8, a seasonal declining trend is present from July to December, especially for the upper values (75<sup>th</sup> monthly percentiles declined from 69 ppb in July to 50 ppb in December).



Fig. 8: monthly percentile analysis for Ozone measurements at the Lampedusa station.