MISSIONE 4
ISTRUZIONE RICERCA

ITINERIS

D4.4.3: Report on the operation in the laboratory and in the field of the acquired instruments at ISAC CNR Lecce and calibration comparison with reference method [B12]

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Author(s) (Partner-OU):	Daniele Contini, Daniela Cesari, Adelaide Dinoi, Fabio Massimo Grasso, Antonio Pennetta, Ermelinda Bloise, Paola Semeraro, Florin Unga, Serena Potì, Giuseppe Deluca, Luca Cirillo Ciricugno (CNR-ISAC)
Reviewed by:	Lucia Mona, Gianluca Di Fiore (CNR-IMAA)
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INTRODUCTION

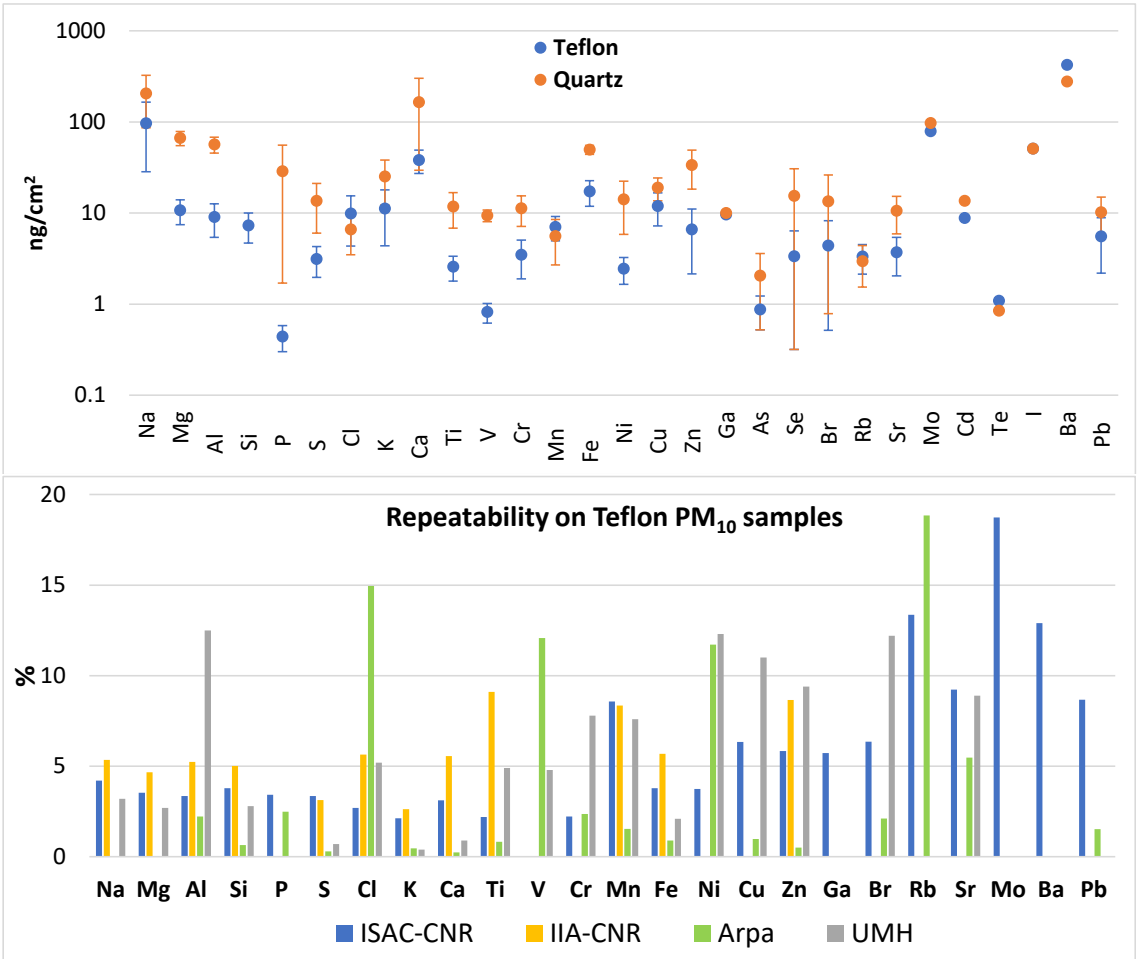
This deliverable is prepared in the context of the ITINERIS project, within the Work Package 4 that deals with the integration of Research Infrastructures working in the atmospheric domain through synergistic approaches and cross boundaries developments. This deliverable reports the progress in the implementation of the WP4.4 activities for integration and harmonization with the Italian Network of Environment RIs. The main aim of the 4.4 activity is the instrumental strengthening of the observational capacity of the facilities in Lecce, in order to reinforce the Italian contribution to ACTRIS. In particular, it is planned to extend the observation capabilities for both online and offline chemical and physical characterization of atmospheric aerosols and gases. The instrumental strengthening includes three aspects: the laboratory for aerosol characterization of ISAC-CNR in Lecce; the exploratory platform MAGA; the Environmental-Climate Observatory (ECO).

This document is structured in four different chapters: the introduction, and three chapters dealing with the three above-mentioned aspects. Only instruments installed and operative at the time of writing are discussed in this document.

STATUS AND OPERATIVITY OF THE INSTRUMENTS INSTALLED IN THE LABORATORY

The instrumental strengthening and operativity of the laboratory for aerosol characterization, was implemented starting from the spectroscopy room. The spectroscopy room of the laboratory (Figure 1) hosts the offline ED-XRF and the UV-VIS analyzer. The ED-XRF was used on samples collected during the ITINERIS campaigns for the activity on identification of aerosol sources for the activity 4.12. Efforts have been devoted to the evaluation of LODs and calibration of ED-XRF on quartz and Teflon samples using Micromatter standards. A collaborative work has been done between ISAC-CNR (Lecce), ARPA (Milan), IIA-CNR (Rome), UMH (Elche), and INFN (Florence) to intercompare analysis on PM samples of ED-XRF (Unga et al., 2024) and some examples are reported in Figure 2.

Figure 2: Spectroscopy room of the aerosol characterization laboratory at ISAC-CNR in Lecce.



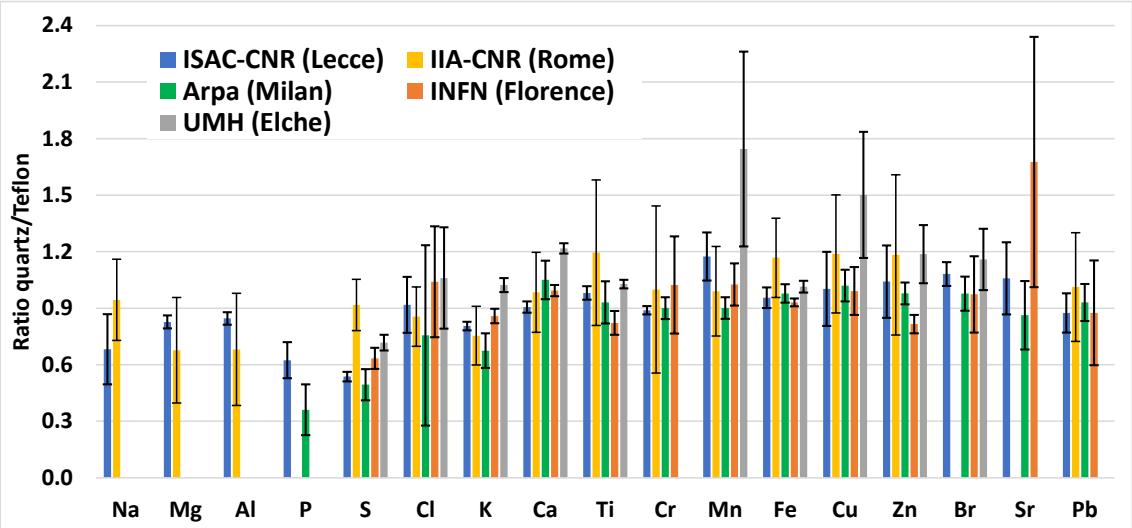


Figure 3: LODs on Teflon and quartz substrates. Repeatability of measurements on Teflon samples. Averages and standard deviations of the C_{quartz}/C_{Teflon} ratios measured by the different laboratories. Pearson coefficients were all above 0.8 with the exclusion of: P (0.72) for Arpa; Cr for INFN (0.72) and IIA-CNR (0.64) with all concentrations lower than 20 ng/cm^2; Cu for ISAC-CNR (0.72) and UMH (0.80); Sr for ISAC-CNR (0.64) and INFN (0.34) with all concentrations lower than 30 ng/cm^2; Rb (0.57, concentrations < 10 ng/cm^2) and Pb (0.49) for IIA-CNR.

The laboratory for aerosol characterization was furtherly equipped (Figure 3) during ITINERIS with two laboratory refrigerators (DESMON) used to store samples (PM filters and aqueous solutions of PM extracts, aqueous solutions of analytical standards); an Ultrasonic Bath (ArgoLab-DU65) and a Bagnomaria used for the extraction of the water-soluble fraction of PM (ions, water-soluble organic and inorganic carbon); an Electronic Balance (Sartorius-Quintix 125D-1S) was installed, used for weighing chemical compounds, e.g. analytical standards, (Pennetta et al., 2024; Potì et al., 2024).

Figure 4: Refrigerators, ultrasonic bath and analytical microbalance installed and operative at the ISAC-CNR laboratory in Lecce.

Further equipment (Figure 4) installed and operative in the implementation of action 4.4 of ITINERIS includes: a spectrophotometer (Agilent Cary Series UV-Vis-NIR) used for absorption and reflectance measurements on materials of environmental interest; a stereomicroscope (Nikon SMZ25 H550 L) for observation of particulate matter collected on opportune substrates; DNA sequencers (Avantor Thermocycler XT96 Gradient CYCL08 G) with centrifuge (Avantor MEGA STAR 600R) to be used for characterization of bioaerosol.

Figure 5: Spectrophotometer, stereomicroscope, and DNA sequencers.

A Filter-based multi-mode microplate reader-FLUOstar Omega was purchased as part of the ITINERIS project. The activities carried out using this instrument is the development and application of protocols for estimating the oxidative potential (OP) of aqueous particulate matter extracts through acellular assays, comparable to methods reported in the literature, such as the dithiothreitol (DTT) assay and the ascorbic acid (AA) assay. Use of this instrument is advantageous for the multi-sample analysis in multimode microplate combined with the possibility to control the temperature as required for this protocol. Figure 5 includes some examples of applications conducted on samples collected at the Climatic-Environmental Observatory (ECO) of ISAC-CNR in Lecce. The first results obtained for oxidative potential of PM2.5 and PM10 is currently the subject of an article submitted to the Journal of Hazardous material.

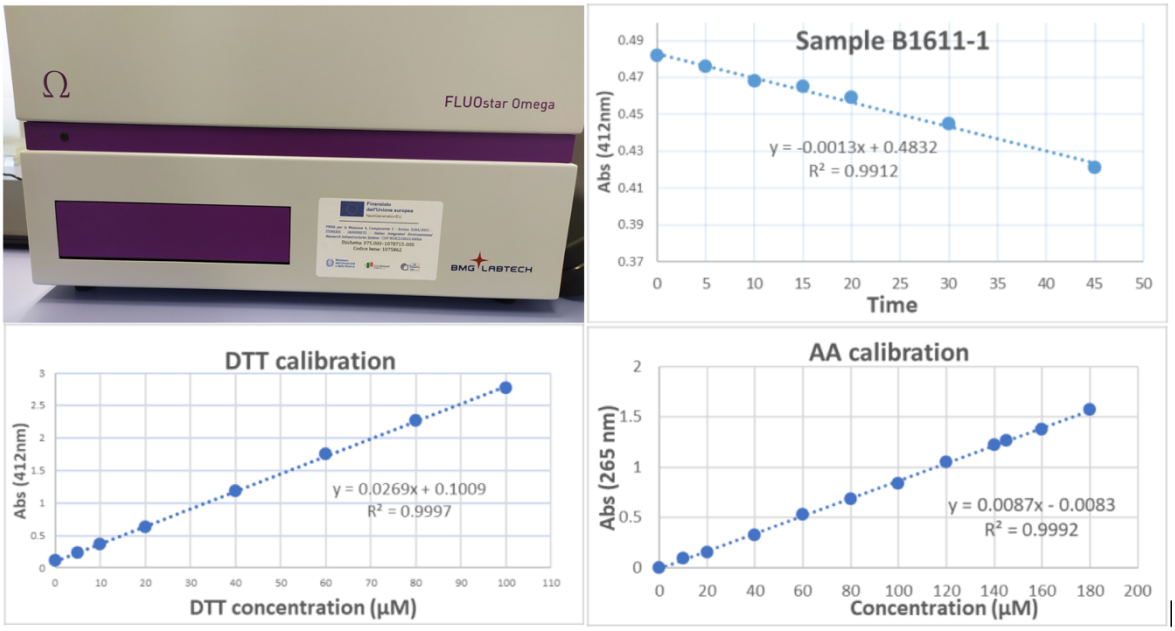


Figure 6:The plate reader and an analysis of absorbance of a real sample (B1611-1); examples of calibration for DTT at different concentrations (from 0 to 100 µM) and for AA at different concentrations (from 0 to 180µM).

STATUS AND OPERATIVITY OF THE INSTRUMENTS INSTALLED IN THE EXPLORATORY PLATFORM MAGA

The upgrades of the exploratory platform MAGA, that is the mobile laboratory showed in Figure 6 operative during a campaign performed in winter 2024, included the upgrade of the inlet system with a high-volume sampler (Figure 6) and the calibration system for gas analyzers. Specifically, the calibration lines (Figure 7) included zero, span and calibration cylinders for measurements of:

- Carbon Monoxide (CO) in air in trace levels with the Thermo Scientific™ Model 48i-TLE Enhanced Trace Level CO analyzer based on gas filter correlation and NDIR technology;
- Nitrogen Oxides (NO, NO2, NOx) in the air from sub-ppb levels up to 100ppm using chemiluminescence technology with the Model 42i (NO-NO2-NOx) analyzer;
- Sulfur Dioxide (SO2) in ambient air up to 100ppm with the Thermo Scientific™ Model 43i SO2 analyzer, using pulsed fluorescence technology.

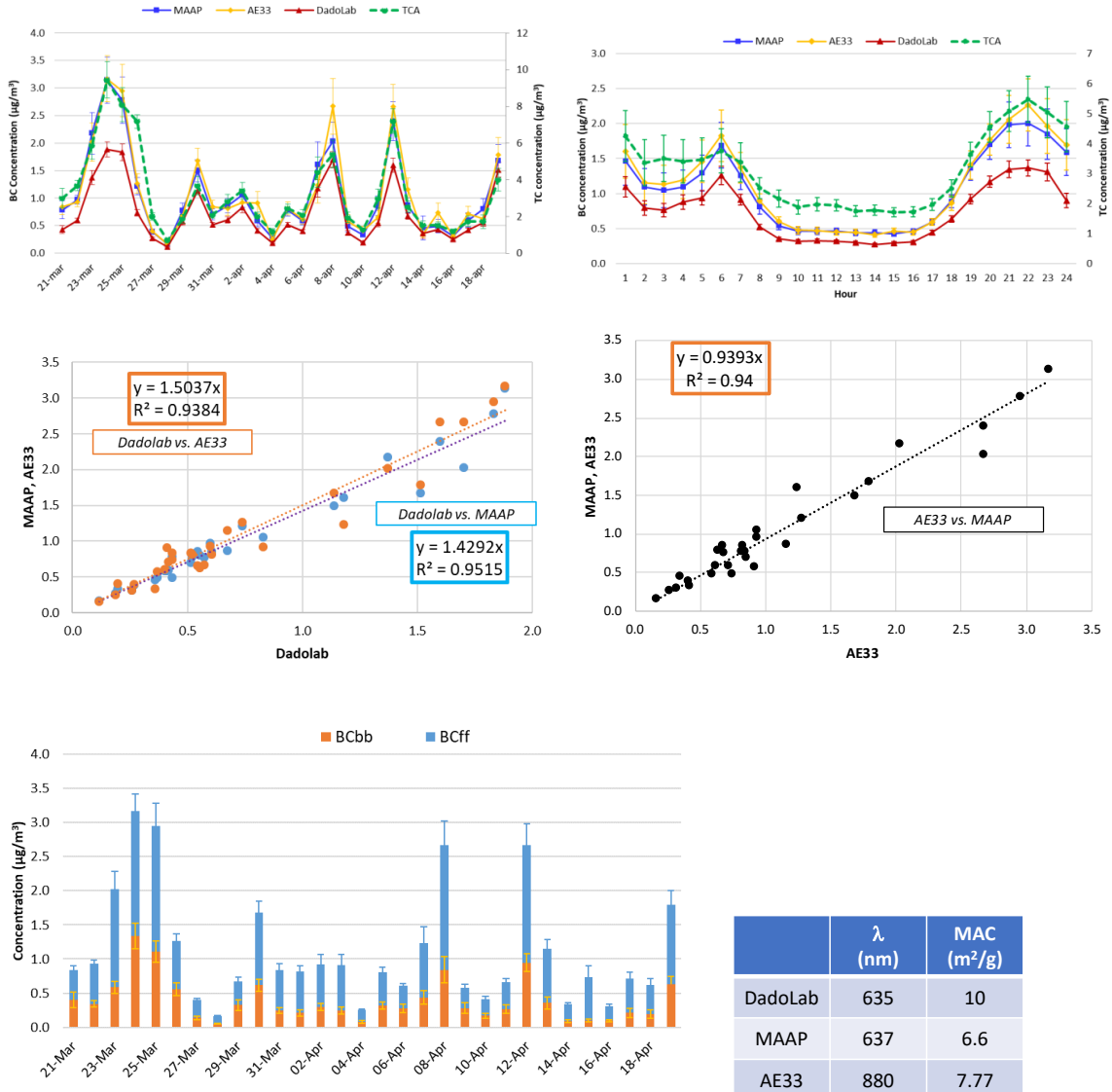
The system was used to calibrate the analyzers during the measurement campaign in summer 2024 connected to ITINERIS and TOX-IN-AIR projects. The data collected will be used in the ITINERIS project to identify the main anthropogenic sources (combustions, transport and industry) and natural, local and long-range contributing to atmospheric pollutions.

Figure 7: Pictures of the MAGA platform during a measurement campaign in winter 2024 and of the newly installed high volume sampling system.

Figure 8: Picture of the calibration system installed and operative in the MAGA exploratory platform.

A dual channel sampler with capability to directly measure eBC on sampling filters was purchased, tested, and used during ITINERIS implementation (Figure 8). A demo version of this sampler was used during an intensive campaign in spring 2023 in which results of carbon measurements were intercompared with the other reference instruments of the observatory. The results are object of a research paper in preparation. A summary of the results is shown in Figure 9.

Figure 9: Dual Channel sampler with eBC measurements installed in Rome for a measurement campaign during autumn 2024.



	λ (nm)	MAC (m²/g)
DadoLab	635	10
MAAP	637	6.6
AE33	880	7.77

Figure 10: Inter-comparison of the eBC measurements during an intensive campaign in spring 2023 at the ECO observatory in Lecce with three different instruments: MAAP, DADOLAB, and AE33. The total carbon obtained with the TCA analyzer is also shown as daily and hourly trend (top). Center graphs shows the direct comparison of the three eBC daily measurements. The bottom graphs show the daily apportionment of eBC with AE33 due to fossil fuel (eBCff) and biomass burning (eBCbb) and the MAC used by the three instruments. The dataset is not corrected or harmonized so that the raw output from the instruments is used in the figure.

STATUS AND OPERATIVITY OF THE INSTRUMENTS INSTALLED IN THE ECO OBSERVATORY

At ECO (shelter 1) the inlet line for gas measurements has been upgraded (Figure 10) with a new system that is electronically controlled, and data of the line is automatically collected in realtime and stored. This is the inlet at which the new instrument Picarro G4201 purchased during ITINERIS implementation is connected. The Picarro performs continuous measurements of CO, H_2O, CH_4, and CO_2 and it is fully operative and integrated with the data collection of the observatory (Figure 10).

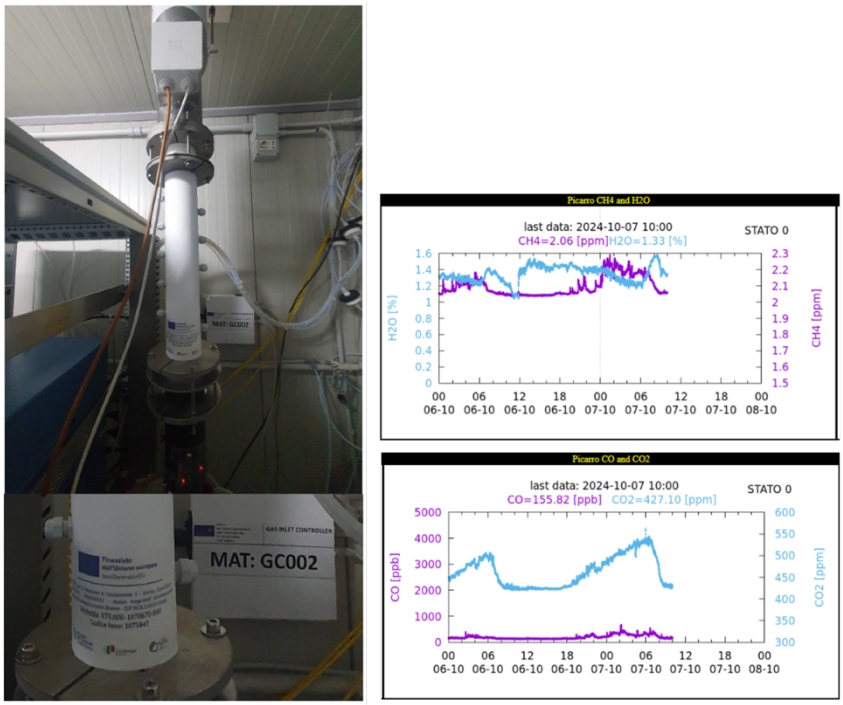


Figure 11: Inlet line for gas sampling and an example of measurements of Picarro G4201.

In addition, the air conditioning of shelter 1 has been upgraded and a new compressor with filter and dehumidification has been installed to use as zero air for some of the aerosol instruments.

Implementation of the activities of ITINERIS project required the installation of a second shelter (shelter 2) at ECO observatory dedicated to the ACTRIS component aerosol in situ. The new shelter was realized and installed dedicated to the main aerosol in situ component. This is shown in Figure 11. It is realized with two independent rooms: one dedicated to the compressor and the pumps; and the other dedicated to instruments. Both rooms are conditioned and kept at a comparable temperature. The power supply includes lines with UPS (20 KVA) and standard lines connected to the main electrical supply of ISAC-CNR.

Two aerosol inlets have been installed and made operative. One inlet has a PM10 cut-off and operates at 2.3 m^3/h. It has an isokinetic splitter (stainless steel) to serve the MAAP, the AE33, the Aurora3000, and the APS. Each instrument has its own nafion dryer, system for measurement of temperature and relative humidity, and a differential pressure measurement system is used to automatically detect eventual non-operating instruments and automatically adjust the excess flow. The second inlet has a PM2.5 cut-off and operates at 1 m^3/h. It also has an isokinetic splitter (stainless steel) to serve the SMPS+CPC and the TOF-ACSM. The SMPS+CPC and the TOF-ACSM have their own nafion dryer on the inlet and measurement of temperature and relative humidity. In addition, a total pressure (for SMPS+CPC) and a differential pressure (for TOF-ACSM) measurement is used to automatically detect eventual non-operating instruments and automatically adjust the excess flow. All the nafion dryers are connected to a distribution line for the counter-flows and served by a compressor able to provide filtered and dehumidified (dew point < -20°C) flow up to 160 L/min. This allows to use serve all nafion tubes with counter-flows between 2 and 3 times the inlet flow. The inlets system is connected to a PC that continuously monitors (and records) the data from the different sensors of the lines; the conditions (pressure, temperature, and relative humidity) at the two splitters; temperature, humidity and pressure inside the shelter. Figure 12 reports some photos including an overview of the solution adopted at the Observatory and the details of the PM2.5 and PM10 inlets. An example of data collected in the different lines is reported in Figure 13.

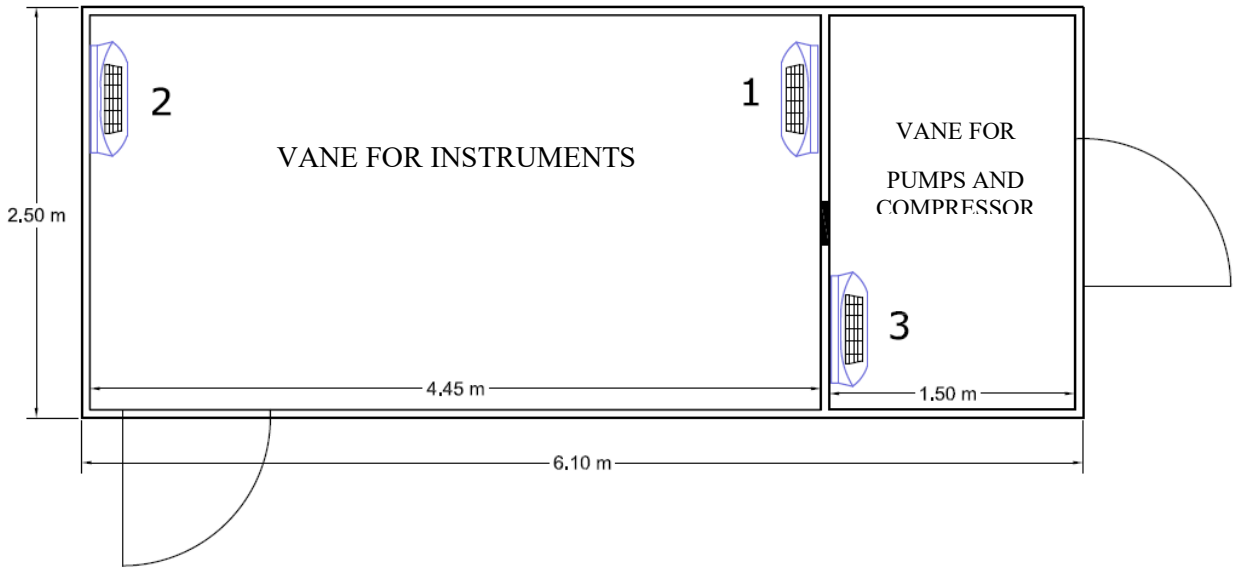


Figure 12: Pictures of the installation of the shelters and its internal organization with the position of the air conditioners.

Figure 13: Pictures of the interior of the new shelter and details of the PM10 and PM2.5 inlets.

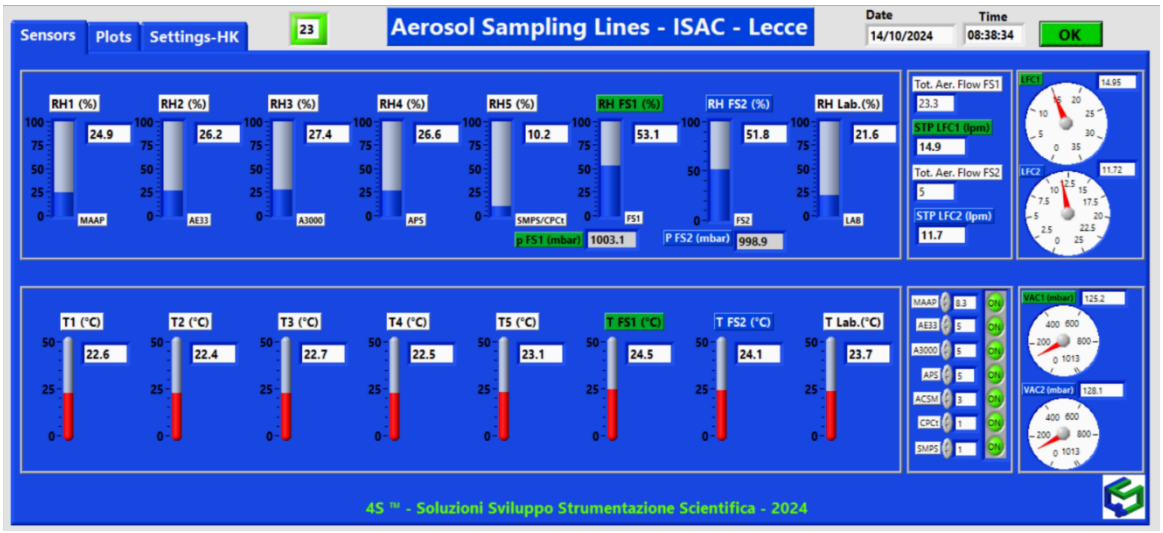


Figure 14: A screenshot of the realtime monitoring and data collection system of the two aerosol inlets.

The CPC (TSI 3750) purchased during ITINERIS implementation has been calibrated at CAIS-ECAC following the ACTRIS procedures and it was installed, as a total counter, at ECO observatory connected to the existing SMPS. It is now fully operative and data are continuously collected online.

The Sun/sky/lunar photometer CIMEL model CE318-T, calibrated following ACTRIS procedure, was installed on 14 November 2023, on the rooftop of CNR-ISAC Lecce building at 12 meters altitude from ground. Prior installation, the instrument has undergone ACTRIS calibration. Since the installation, it operates continuously, day and night, providing in clear sky conditions spectral column integrated aerosol properties and water vapor. The instrument provides direct measurements at 8 wavelengths (340, 380, 440, 500, 675, 870, 1020, 1640 nm) of AOD (aerosol optical depth), which is directly linked to the amount of aerosols in the atmosphere, Angstrom Exponent between 440 and 870 nm giving information about the dominant size of aerosols, and AOD fine and coarse. By an inversion algorithm, it also provides at 4 wavelengths (440, 675, 870, 1020 nm) column integrated, Single Scattering Albedo, Complex Refractive Index (real and imaginary part), Absorption Optical Depth, Extinction Optical Depth, Asymmetry Factor, Phase Functions (from 0 to 180 degrees) and Volume Size Distribution between 0.05 and 15 µm radius.

The Sun/sky/lunar photometer CIMEL CE318-T is now installed in close proximity (1 km) to Lecce_University AERONET site for intercomparison purpose, where a long-term (~20 years) sun/sky/lunar photometer is installed. The CIMEL CE318-T is intended to be also used in mobile measurements campaigns in fixed locations, where no other sun/sky/lunar photometer exists in close proximity, and can be used for atmospheric aerosol characterization and for satellites validation. Since it's a solar powered instrument it can be installed in remote locations. The instrument is complementary to the CIMEL microLIDAR CE376 for aerosol characterization in each atmospheric layer and stratification analysis that will be installed during ITINERIS implementation.

Figure 15: View of the Sun/sky/lunar photometer CIMEL CE318-T located on rooftop of CNR-ISAC Lecce building

CONCLUSIONS

The instruments that have been installed and made operative will be the base for collecting datasets necessary to the analysis of Aerosol Sources (action 4.12). Some of the datasets are already available and preparation of publications is ongoing. Additional datasets will be available when the instruments not yet installed will be made operative. Among these, the most relevant for activity 4.12 are the offline Ion Chromatograph, the online ED-XRF, the online monitoring of fluorescent particles that will furnish the possibility to investigate the bioaerosol fraction of atmospheric particles. These instruments have all been purchased and will be installed and made operative within the end of 2024.

REFERENCES

Unga F., Calzolai G., Chiari M., Cuccia E., Colombi C., Franciosa M., Dinoi A., Merico E., Pennetta A., Gomez Sánchez N., Mapelli C., Pareti S., Perrino C., Yubero E., Contini D., 2024. Determination of aerosol composition by ED-XRF on Teflon and quartz substrates: potentialities and limits. European Aerosol Conference – EAC2024, Tampere.

Potì S,, Merico E., Conte M., Unga F., Cesari D., Dinoi A., Guascito M. R., De Bartolomeo A. R., Carlino A., Pennetta A., Bloise E., De Benedetto G. E., Ferrera R., Bompadre E., Contini D., 2024a. Variabilità spaziale e temporale del PM e della sua tossicità nell'area di Lecce. Atti del Convegno nazionale sul Particolato Atmosferico (PM2024), Torino.

Pennetta A., Bloise E., Deluca G., Merico E., Cesari D., Unga F., Potì S., Dinoi A., Contini D., 2024. Comparing methods for determination of Water-Soluble Organic Carbon. Atti del Convegno nazionale sul Particolato Atmosferico (PM2024), Torino.