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One year of aerosol chemical composition and source apportionment in Milan

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Summary. — European policy efforts to address air quality issues have led to significant reductions in pollutants over time. Despite this progress, the decrease is not homogeneous across all pollutants, as certain pollutants still exceed the thresholds set for air quality and health standards. The RI-URBANS project takes advantage of the expertise of the research infrastructures to carry out a coordinated experiment using state-of-the-art technologies in 13 European cities, where chemical composition has been studied throughout 2023. Its goal is to enhance the understanding and management of urban air quality providing a near real-time visualization and source apportionment online tool. This paper focuses on chemical characterization and source apportionment of organic aerosols, presenting data from the measurement campaign in Milan as part of the project. Innovative measurements of non-refractory aerosols using the ToF-ACSM mass spectrometer, along with black carbon concentration measurements derived from optical techniques (AE33, 7 λ), enabled continuous monitoring of various emission sources with high temporal resolution. The coordinated analysis involved Positive Matrix Factorization (PMF) and the bi-linear model for black carbon source attribution application in each city, which were then compared with the project's new tool. Results provide insight into aerosol concentrations in the urban background of Milan throughout 2023, and an initial estimation of organic aerosol sources, highlighting significant seasonal variations. Detailed analysis will be deferred in forthcoming publications.

1. – Introduction

Europe has made significant efforts to mitigate air pollution since the 1980s, resulting in an improvement in air quality in urban areas. This advancement has stimulated the consideration of new approaches to air quality management in public policy and health research. However, this reduction has not been homogeneous for all pollutants, with some still exceeding the limits established by the World Health Organization (WHO) for air quality and health standards [1]. In particular, in 2023, the European Environment Agency (EEA) reported that many European cities still had levels of air pollutants such as NO_2 , PM_{10} , $PM_{2.5}$, and O_3 outside air quality guidelines, significantly affecting the health of citizens [2]. In fact, according to the recent 2020 Global Burden of Disease assessment, air pollution was recognized as the fourth leading cause of premature deaths in 2019, with more than 0.4 million premature deaths in the EU in 2021 [2, 3]. In this context, the attribution of emission sources of organic aerosols (OA), one of the most abundant fraction of fine particulate matter (PM_1) globally, is a relevant issue. For this reason, determining the primary emission sources in urban environments has become an important focus for research, as the primary sources and secondary formation processes of organic aerosols are extremely variable and complex. In addressing this challenge, on the solid foundation of the ACTRIS Research Infrastructure, the European project RI-URBANS was born. It aims to take advantage of research infrastructures to collaborate with local agencies responsible for air quality monitoring. The main challenge of RI-URBANS is to develop innovative tools to improve urban air quality monitoring services. Task 4.1 of the project specifically focuses on developing a near real-time visualization and source apportionment online tool that offers the scientific community and the general population access to data on concentrations of key pollutants while also estimating the primary emission sources. In a complex and ever-changing urban pollution context, obtaining monitoring data on PM composition and the contributions of various sources to PM will be crucial for improving air pollution management policies and assessing health impacts across Europe. The main goal of the project is based on the idea that the use of advanced research infrastructure tools and scientific expertise can effectively supplement existing monitoring agencies tasked with regulating pollutants.

2. – Methods

2.1. The campaign. – The measurement campaign site for the RI-URBANS project consists of a mobile laboratory named *Voyager3*, currently located within the research area of the National Research Council (CNR) in Milan (Northern Italy; $45^{\circ}28'47''N$ $9^{\circ}13'54''E$; 120 m a.s.l.) (fig. 1). This location resides in the northwestern sector of the Po valley, the most densely populated and industrialized part of the well-known pollution hot spot in Europe. Specifically, the site is located within the private parking lot of the CNR research area, entirely enclosed by buildings and it is positioned between two heavily trafficked thoroughfares: Viale Abruzzi, the eastbound section of the eastward section of the city's circumferential road and the A51 highway. Notably, the site is located approximately 130 m from the ARPA (Agenzia Regionale per la Protezione Ambientale) Lombardia measurement supersite "*Milano Pascal*", categorized as an urban background station according to the criteria used by the EEA, aiming to measure urban background pollution as well. The *Voyager3* laboratory, managed by the CNR Institute of Atmospheric Sciences and Climate (ISAC) of Bologna, is equipped with advanced instrumentation for analyzing atmospheric chemistry. During the entire monitoring campaign from

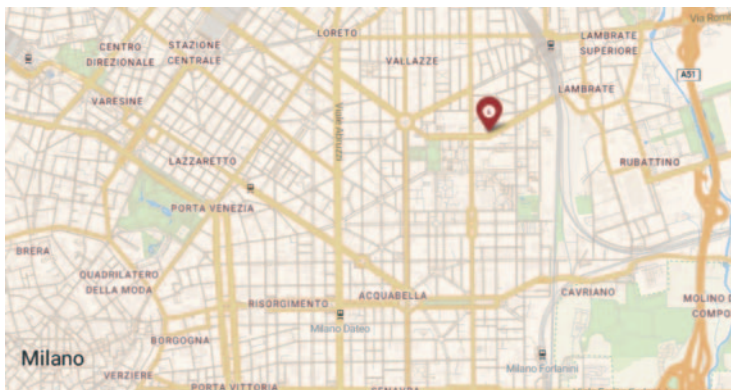


Fig. 1. – Map of the campaign measurement site with the precise location of the Voyager 3 mobile laboratory within the city of Milan.

late January 2023 to the end of 2023 (refer to fig. 2), the ToF-ACSM and the Aethalometer AE33 were utilized for comprehensive characterization of atmospheric chemistry and continuous air quality monitoring.

2.2. ToF-ACSM. – The time-of-flight Aerosol Chemical Speciation Monitor (ToF-ACSM; Aerodyne Research Inc.; [4]) is a time-of-flight mass spectrometer designed for continuous near-real-time characterization of the chemical composition of the atmosphere directly from ambient air. This instrument enables measurements of PM1 concentrations, allowing the quantification of key non-refractory aerosol components: nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-), sulfate (SO_4^{2-}), and organic aerosols (OA). Operationally, ambient air is directed through an inlet system where atmospheric aerosols are concentrated by a critical orifice and subsequently introduced into a vacuum chamber under high vacuum conditions to prevent interference from atmospheric gases. Within the chamber, the aerosols undergo flash vaporization upon impacting a vaporizer (600°C), resulting in the ionization of non-refractory particles via electron impact (70 eV). The resulting ion fragments are then analyzed by the ToF mass spectrometer, wherein the mass-to-charge ratio (m/z) is determined based on the time taken for ions to reach the detector. Subsequently, the raw time-of-flight signals are converted into spectra with Unit Mass Resolution using a fragmentation table. To convert the mass spectral signals into particle mass loading ($\mu\text{g}/\text{m}^3$), Ionization Efficiency (IE) and Relative Ion Efficiency (RIE) calibrations are conducted using 300 nm monodispersed particles of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. Additionally, a Collection Efficiency (CE) correction is applied with a value of 0.45 [5].

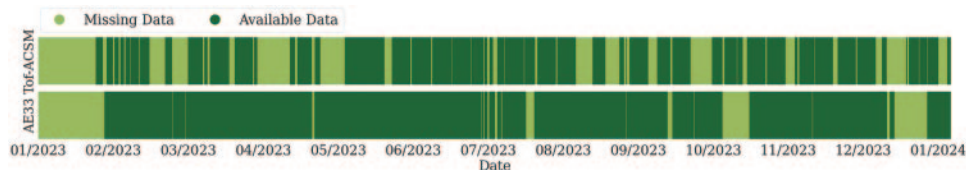


Fig. 2. – Availability of data from ToF-ACSM and Aethalometer AE33 in the 2023 measurement campaign in Milan. Approximately more than 60% of the ToF-ACSM data and more than 80% for the AE33 are available.

2.3. AE33. – In addition to the ToF-ACSM measurements, equivalent black carbon (eBC) was monitored using a seven-wavelength filter-based absorption photometer, the Aethalometer Model AE33 (Magee Scientific, Aerosol d.o.o.; [6]). eBC concentrations were derived from absorption at a wavelength of 880 nm, and the elemental eBC subfractions originating from distinct combustion sources, denoted as BC_{sf} for wood burning and BC_{lf} for fossil fuels, was achieved using the source apportionment Aethalometer model, as outlined in the methodologies detailed in Sandradewi *et al.* [7], with site specific α_{sf} and α_{lf} of 1.8 and 1.0, respectively.

2.4. Positive Matrix Factorization. – The Positive Matrix Factorization (*PMF*) [8] is a multivariate statistical technique which allows the identification of covariances in time between spectral patterns and concentration contributions from the total organic aerosol. From the following equations:

$$(1a) \quad x_{ij} = \sum_{k=1}^p g_{ik} \times f_{kj} + e_{ij},$$

where x_{ij} is the organic aerosol measurements matrix at the i -th time point and the j -th m/z ratio, g_{ik} is the factor time series for the k -th factor, f_{kj} represents the factor profiles, and e_{ij} represents the residuals, summed over the total number of factors, p . The *PMF* finds the model solution minimizing the objective function Q :

$$(1b) \quad Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2,$$

where σ_{ij} is the measurement uncertainty. While effective, the *PMF* model encounters the challenge of rotational ambiguity, where different combinations of matrix rotations can yield the same result. For this reason for the the *PMF* analysis it was used the multilinear engine (ME-2) algorithm by Paatero [9], implemented in the SoFi (Source Finder) software in Igor Pro environment by Canonaco *et al.* [10], which introduces a priori information, such as source profiles or external data, to guide the model and reduce the unrealistic rotations. Consequently, users can exert greater control over factor solutions by imposing constraints during the least square minimization process [11].

2.5. Organic aerosol source apportionment. – The source apportionment procedure via *PMF* provides the identification of the primary emitting sources of organic aerosols, by giving an initial distinction between Primary Organic Aerosol (POA) and Secondary Organic Aerosol (SOA). The main sources of POA include hydrocarbon organic aerosols (HOA), associated with the combustion of fossil fuels typically attributed to vehicular traffic, and biomass combustion organic aerosols (BBOA), mainly attributable to the wood combustion for residential heating. SOAs, on the other hand, consist of oxygenated organic aerosols (OOAs), which include secondary formation aerosols and aged aerosols, whether local or not. Specifically, these secondary formed and/or aged aerosols can be further categorized into two factors: more oxygenated organic aerosols (MOOOA) and less oxygenated organic aerosols (LOOOA), based on their degree of oxidation and thus ageing. The identification of these factors primarily relies on analyzing their mass spectra, known as factor profiles, which exhibit distinct characteristics for each factor based on the presence and abundance of specific fragments with known nature and/or

origin: hydrocarbons fragments for HOA, biomass combustion-associated fragments for BBOA, such as m/z 60 associated to the anhydrosugars produced by the combustion of lignins (*e.g.*, levoglucosan), and fragments highlighting the oxidation degree of the factor for SOAs, in particular m/z 44, representing CO_2^+ fragment typical of all the carboxylic acids. Following factor identification, the attribution technique to specific emitting sources takes advantage of the typical diurnal variation trends of the factors and the comparison with tracer concentrations of specific emitting sources tracers, such as black carbon subfractions, BC_{sf} and BC_{lf} .

3. – Preliminary results

3.1. Online aerosol chemical composition. – The time series of non-refractory aerosol species obtained from the ToF-ACSM during the 2023 measurement campaign are shown in fig. 3. The presented data were averaged over 10-minute intervals as they did not undergo detailed quality control during the data analysis process. The data control primarily involved eliminating measurement interruptions (*e.g.*, calibrations, malfunctioning of the instrument or acquisition software). Throughout the measurement year, all non-refractory aerosol species exhibited a consistent seasonal variability, with concentrations decreasing from autumn-winter to spring-summer. This decrease is likely attributed to both the reduction in primary emissions during the summer months and the seasonal variation in atmospheric dynamics, where the increase in mixing layer height leads to a more efficient dilution of pollutants. A similar pattern was previously observed in the Po valley by Paglione *et al.* [12]. As illustrated in the figure, the seasonal variability described above is most pronounced for nitrate, which undergoes a drastic reduction during the spring-summer period, decreasing from a maximum average concentration of $6.1 \mu\text{g}/\text{m}^3$ in november to $0.16 \mu\text{g}/\text{m}^3$ in august, approximately 35 times lower. Meanwhile, the concentration of organic aerosol only decreases by a factor of 2. This discrepancy can be attributed to the semi-volatile nature of ammonium nitrate, whose stability in the aerosol phase depends strongly on temperature, resulting in a significant shift of the partitioning equilibrium to the gas phase in warm months.

3.2. Source apportionment. – The apportionment process of the primary emitting sources of organic aerosol involves several phases of analysis of factors obtained from

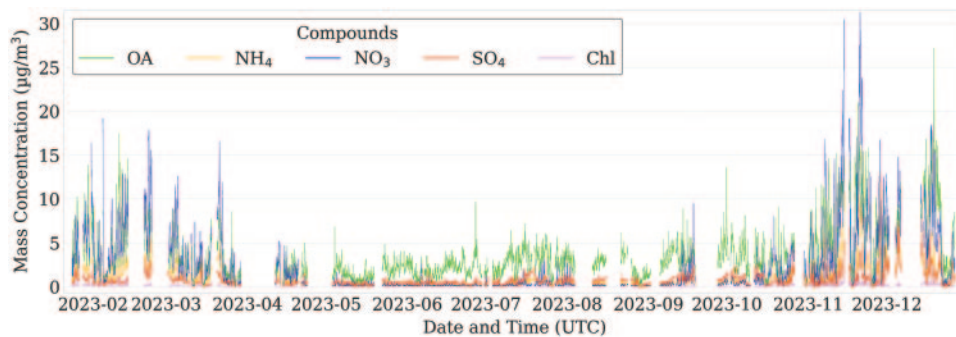


Fig. 3. – Time series of all the compounds measured by the ToF ACSM during the measurements campaign in 2023, UTC, 10 minutes averaged data: organic aerosols (OA), ammonium (NH_4^+), nitrate (NO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-).

PMF. These phases include examining factor profiles to identify known mass spectra, correlating the time trends of the factors with tracer compounds, and assessing diurnal variations in factors. The black carbon measurements available during the campaign was an important added value for attributing the factors to their respective sources, enabling comparisons of time series and correlations between the black carbon sub-fractions, BC_{sf} and BC_{lf} , used as tracers for BBOA and HOA, respectively (*e.g.*, fig. 4).

Analyzing the daily trends of the factors provides a more reliable attribution of main sources. During the campaign, the diurnal variability of each organic aerosol component has shown typical features associated with their respective sources (fig. 5). HOA exhibits a daily trend featuring two peaks, one in the morning and one in the evening, corresponding to the so-called “rush hours,” when vehicular traffic is most intense, as typical of urban environments. BBOA, on the other hand, shows a daily variability with a nearly constant peak during the night and early morning hours, followed by a gradual decrease until reaching a minimum during the central hours of the day. This pattern is likely influenced by the mixing layer dynamics, favoring pollutant accumulation during the night and a tendency of stronger heating source during colder nighttime hours. Finally, SOAs show a mostly flat daily trend with potential peaks during central day-light hours as photochemistry intensifies with maximum insolation, thereby enhancing secondary formation processes.

Based on preliminary analyses and initial source apportionments conducted monthly during the measurement campaign, the contributions of the main organic aerosol components identified for a representative month of each season are reported in fig. 6. The graphs show distinct seasonal patterns, particularly for the primary components. The contribution of HOA to the organic aerosol mass remains relatively stable throughout each season, approximately 15–18%. In contrast, the interseasonal contribution of BBOA exhibits significant seasonal variability, with a maximum contribution in winter at 22.1%, decreasing to 14–15% in transitional seasons and it is virtually absent in summer as it was not detected by PMF. This indicates that BBOA predominates during cold periods, exceeding fossil fuel combustion, while it plays a minimal role during warmer periods, consistent with the different usage of domestic heating across the seasons. The contribution of secondary OOA does not exhibit a well-defined pattern in seasonal variability. However, MOOOA represents the major contribution throughout the year, ranging from 61%

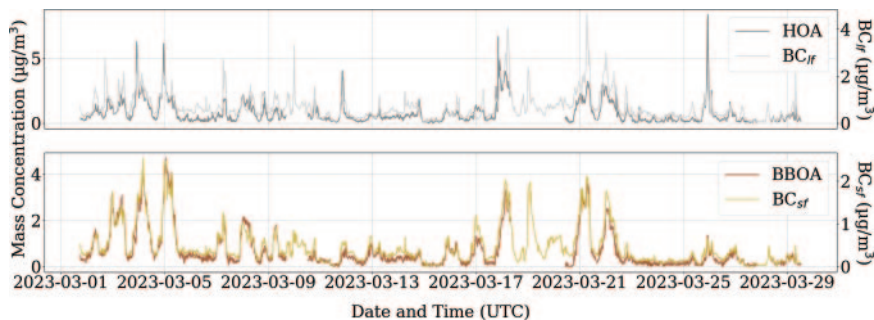


Fig. 4. – Comparison between the time series of BC_{lf} and HOA, represented at the top, and of BC_{sf} and BBOA, represented at the bottom, for the month of March 2023. The correlation between these factors showed respectively a weak correlation, $R^2 = 0.43$, and a strong correlation, $R^2 = 0.93$.

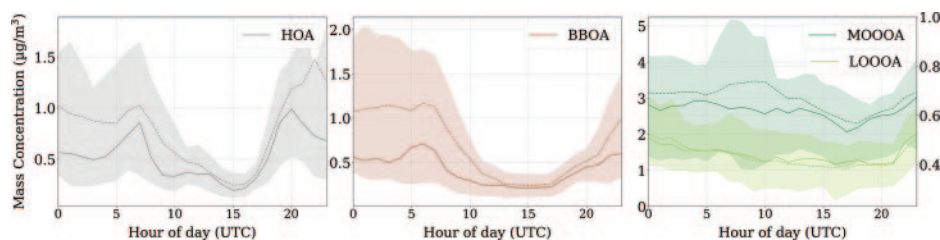


Fig. 5. – Diurnal variability of organic aerosol components for March 2023: HOA on the left, BBOA in the middle, and the OOA, MOOOA and LOOOA, on the right. The solid lines represent the median value, the dashed lines the mean and the coloured area represents the interquartile range.

to 44%, while LOOOA varies considerably and irregularly from a minimum contribution of 8% to a maximum contribution of 37%.

4. – Conclusions

The primary objective of this study is to delineate the key methodologies used for studying and monitoring air quality and atmospheric chemistry, with a particular emphasis on the efficacy of source apportionment techniques within the framework of the RI-URBANS project. Additionally, this paper provides an overview of the results, offering insights into the chemical composition of the atmospheric aerosols, with a specific focus on the non-refractory components of aerosols (*i.e.*, nitrate, sulfate, ammonium, chloride and organic aerosols) and the primary sources of organic aerosols in Milan during the whole 2023 year. The analysis revealed significant seasonal differences in all non-refractory aerosol species, with the most pronounced changes observed in nitrate concentrations. These decreased notably from an average of $6.1 \mu\text{g}/\text{m}^3$ to $0.16 \mu\text{g}/\text{m}^3$ from winter to summer. Additionally, source apportionment techniques unveiled seasonal variations for different organic aerosol components. The HOA factor (linked with traffic emissions) maintained a consistent contribution of approximately 15–18% across seasons. BBOA (linked with biomass burning) exhibited seasonal variability, peaking at 22.1% in winter but being negligible in summer. Meanwhile, MOOOA (linked with oxidized/aged

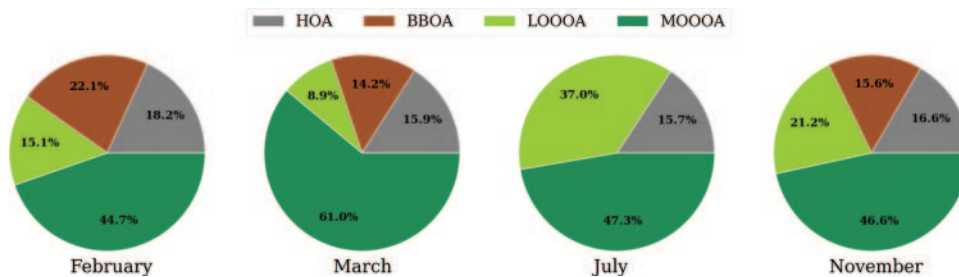


Fig. 6. – Contributions of HOA, BBOA, and OOA in representative months corresponding to different seasons: February (winter), March (spring), July (summer), and November (autumn). The total concentrations of apportioned organic aerosols for each month are respectively: $4.70 \mu\text{g}/\text{m}^3$, $2.63 \mu\text{g}/\text{m}^3$, $2.83 \mu\text{g}/\text{m}^3$ and $6.59 \mu\text{g}/\text{m}^3$.

aerosols) dominated throughout the year, ranging from 44% to 61% contribution. While these large seasonal differences have been identified and described in this paper, a more comprehensive analysis of the findings presented herein will be elaborated upon in a forthcoming publication.

* * *

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