

A case study of the usefulness of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for PM source apportionment under different meteorological conditions

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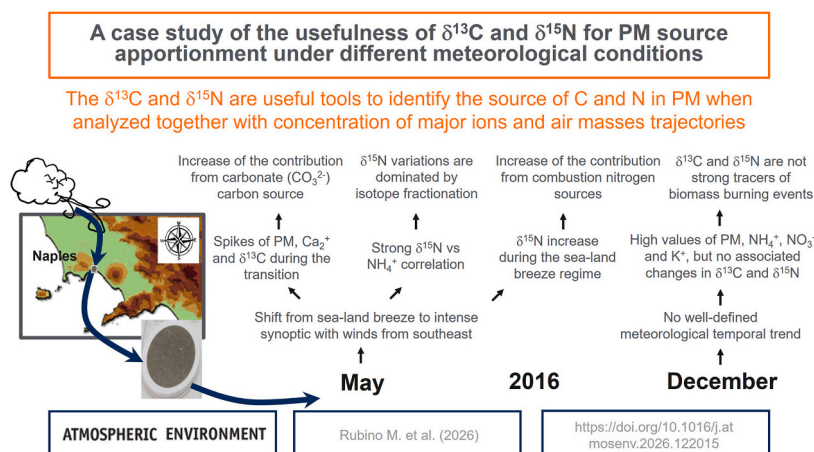
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HIGHLIGHTS

- In PM_{10} , $\delta^{13}\text{C}$ identifies an increase of CO_3^{2-} carbon sources
- In PM_{10} , $\delta^{15}\text{N}$ identifies a shift from volatilization to combustion sources
- $\delta^{15}\text{N}$ undergoes strong isotope fractionation
- Combustion sources have a higher contribution in $\text{PM}_{2.5}$ than in PM_{10} for both N and C
- Neither $\delta^{13}\text{C}$ nor $\delta^{15}\text{N}$ are useful to identify the origin of C and N during biomass burning events.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we show the strengths and limitations of using the isotopes of Carbon ($\delta^{13}\text{C}$) and Nitrogen ($\delta^{15}\text{N}$) to identify their sources in atmospheric particulate matter (PM) under different meteorological conditions. Specifically, we show they are useful to identify a shift of C sources from mostly C_3 plants/combustion to higher

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Backtrajectories
Air quality

carbonate content, and from volatilization/biological to combustion sources for N, whereas they do not help identify biomass burning events.

We collected particles with aerodynamic diameters $<2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) and $<10\ \mu\text{m}$ (PM_{10}) during May 2016 and late November 2016–early January 2017 in the city center of Naples. We measured total C and N, their $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, major ions (NH_4^+ , K^+ , Ca^{2+} , Na^+ , Mg^{2+} , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Cl^-) and analyzed wind direction, speed and back-trajectories of air masses.

May was characterized by a shift from land-sea breeze to a synoptic system with winds from southwest. We found an increase of $\delta^{13}\text{C}$ in PM_{10} during a dust resuspension event, suggesting an increase of the contribution from carbonate C from negligible to 18% of total C. $\delta^{15}\text{N}$ in PM_{10} , although significantly affected by isotope fractionation, showed a shift of total N from volatilization to combustion sources. In December, air masses mostly originated from the north, with no significant temporal pattern of wind speed and direction. We found days with elevated land-derived species (K^+ , NH_4^+ , NO_3^-) typically linked to biomass burning, but without corresponding changes in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, highlighting limitations in the isotope tracer's sensitivity. We conclude that $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ can be effective, qualitative indicators of PM origin when integrated with chemical composition and air mass trajectory analysis. However, quantitative applications require well-constrained source signatures and careful consideration of fractionation effects.

1. Introduction

Air pollution by particulate matter (PM) is an important environmental problem causing millions of deaths every year worldwide (Burnett et al., 2018; Cohen et al., 2017; Health Effect Institute, 2024; Lin et al., 2025; Yu et al., 2024). Effective mitigation strategies require robust identification of emission sources and quantification of their contributions to ambient PM (Friedrich, 2016). This task is particularly challenging in urban environments, where multiple natural and anthropogenic sources coexist and interact, producing chemically complex and highly variable mixtures (Karagulian et al., 2015).

Source apportionment is commonly addressed using receptor models, source-oriented models, and inverse modelling approaches (Belis et al., 2020; Hopke, 2016; Laupsa et al., 2009; Mircea et al., 2020; Viana et al., 2008). While powerful, these methods often require extensive input data and rely on assumptions that introduce uncertainty, leaving persistent gaps in the attribution of PM sources (Sokhi et al., 2022). Consequently, there is strong interest in complementary tracers capable of providing independent constraints. Stable isotope ratios, particularly of nitrogen ($\delta^{15}\text{N}$) and carbon ($\delta^{13}\text{C}$), have been widely explored as source fingerprints in atmospheric PM and are increasingly used alongside chemical and modelling approaches to improve source discrimination (Huang et al., 2025).

Numerous studies have applied $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, or both to investigate PM sources in urban environments (e.g., Aggarwal et al., 2013; Dong et al., 2023; Heaton, 1987; Jia and Chen, 2010; Kawashima and Kurahashi, 2011; Morera-Gómez et al., 2020; Pavuluri et al., 2010; Shi et al., 2023; Skiba et al., 2024; Wang et al., 2017; Widory, 2007; Widory et al., 2004; Xiao and Liu, 2002). However, despite clear potential, isotope-based source apportionment remains challenging and often qualitative or semi-quantitative. A growing body of literature highlights several fundamental limitations that constrain interpretation.

A primary limitation arises from overlapping isotopic end members. Many emission sources exhibit broad and partially overlapping $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures, reflecting variability in fuel composition, combustion conditions, and precursor materials (Shi et al., 2021; Wang et al., 2017). Temporal variability in source isotopic composition further complicates source attribution, as seasonal changes in emissions, atmospheric chemistry, or fuel use can shift isotopic signatures independently of source strength (Aguilera and Whigham, 2018; Chen et al., 2022). Because the number of isotopic tracers is typically small relative to the number of potential sources, the system is frequently underdetermined, limiting quantitative apportionment.

A second major limitation is post-emission isotopic fractionation. After emission, particulate and gaseous precursors undergo chemical transformation, phase partitioning, and transport processes that can modify isotopic composition independently of source contributions (Chang et al., 2018; Pan et al., 2016; Walters and Michalski, 2015).

Secondary formation pathways, gas-particle conversion, heterogeneous reactions, and volatilization–condensation cycles can all produce isotopic shifts that obscure primary source signatures. Evidence from both bulk and compound-specific isotope analyses demonstrates that atmospheric processing can substantially alter $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, particularly in secondary inorganic and organic aerosol components (Bekker et al., 2023; Dong et al., 2023; Paul et al., 2025).

A third, and comparatively less frequently addressed, limitation concerns the size-segregated behavior of isotopic composition in particulate matter. PM is not a uniform material, but a size-resolved mixture produced by different emission mechanisms and atmospheric processes. Coarse particles are typically dominated by mechanically generated material such as soil dust, sea spray, or primary biological particles, whereas fine particles often contain a larger fraction of combustion products and secondary aerosol formed through gas-to-particle conversion. Because these processes involve distinct sources and transformation pathways, isotopic composition can vary systematically with particle size (Singh et al., 2021b, 2023). Consequently, bulk isotopic measurements that integrate across size ranges may mask contrasting source contributions and atmospheric processing histories, complicating interpretation and comparison between studies that target different PM size fractions.

Interpretation is further complicated by the chemical heterogeneity of total C and total N. Both represent complex mixtures of organic and inorganic components (Correa-Ochoa et al., 2023; Duan et al., 2009; Li and Yu, 2004; Sharma et al., 2022). Total N is composed primarily of inorganic nitrate (NO_3^-) and ammonium (NH_4^+) with smaller contributions from organic N (Duan et al., 2009; Li and Yu, 2004), whereas total C is often largely organic (Correa-Ochoa et al., 2023). Isotopic compositions have therefore been investigated at multiple levels, including bulk measurements, operationally defined fractions, and individual molecular species (Bikkina et al., 2016; Chang et al., 2025; Fisseha et al., 2009; Luo et al., 2023; Paul et al., 2025; Singh et al., 2021b, 2023). These studies demonstrate both the potential of isotope measurements for source identification and the complexity introduced by atmospheric processing and compositional mixing (Singh et al., 2021a; Skiba et al., 2024; Xie et al., 2023).

Given these methodological challenges, further evaluation of isotope-based source apportionment under real atmospheric conditions is needed. Our study assesses the effectiveness of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in identifying and apportioning N and C sources in PM under contrasting meteorological conditions. To achieve this, we compared two sampling periods: May 2016, characterized by a shift from sea-land breeze to the incursion of southwesterly flows, and late November 2016–beginning of January 2017 (from now on “December”), marked by variable conditions (see section 3.1). By integrating isotopic measurements with chemical composition and air mass trajectory analysis in Naples, we build upon and expand previous research in the region. In the past, we

have studied PM chemical composition and emission characteristics (Chianese et al., 2019; Riccio et al., 2016), determined the fossil versus biogenic contribution to the carbonaceous fractions through radio-carbon (^{14}C) analyses (Sirignano et al., 2019) and investigated the influence of air mass and local wind patterns on PM concentration (Hernández-Ceballos et al., 2025; Riccio et al., 2007). Our goal is to advance a methodological framework that integrates isotopic information into routine air-quality monitoring, supporting improved identification of dominant pollution sources and more targeted mitigation strategies (Riccio and Chianese, 2024; Sebastiani et al., 2021).

2. Materials and methods

2.1. Site description and sampling method

Sampling was carried out in the historical center of Naples (south of Italy, the position of Naples is given by the white flag in Fig. 1A) on the rooftop of a university building where the San Marcellino observatory is located (40.85° N, 14.26° E, 53 m. a.s.l.) - a meteorological observational site established by the local scientific community (<https://www.meteo.unina.it/>).

Local PM emission sources include a combination of natural (e.g., marine aerosols) and anthropogenic (e.g., vehicles exhausts, domestic combustions, harbor activities and wood combustion from ovens in pizza restaurants) sources. Riccio et al. (2017) characterized specific emission factors for inorganic ions from road traffic in Naples. Regional contributions are influenced by the geography of the area. As shown in Fig. 1B, the Campania region (colored in red in Fig. 1A) is bordered by the Tyrrhenian Sea to the west (left side of Naples, the white flag on the map) and by mountains that constrain atmospheric circulation. Fig. 1C highlights the sampling location (white flag) within the urban setting.

PM samples were collected during two meteorologically different periods: May (1st-18th, spring) and December (18th November 2016 – 6th January 2017, late autumn to early winter). PM₁₀ and PM_{2.5} were collected over 24h intervals on pre-cleaned quartz filters (Whatman, 47 mm diameter, pre-baked at 700 °C for 2 h) using a low-volume (2.3 m³/h) dual-channel beta attenuation automatic monitor (BAM) SWAM 5a (FAI-Instruments srl). Quartz fiber filters were chosen because of their low N and C background after pre-baking, which is required for reliable $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ determination (Chow et al., 2022). Although the

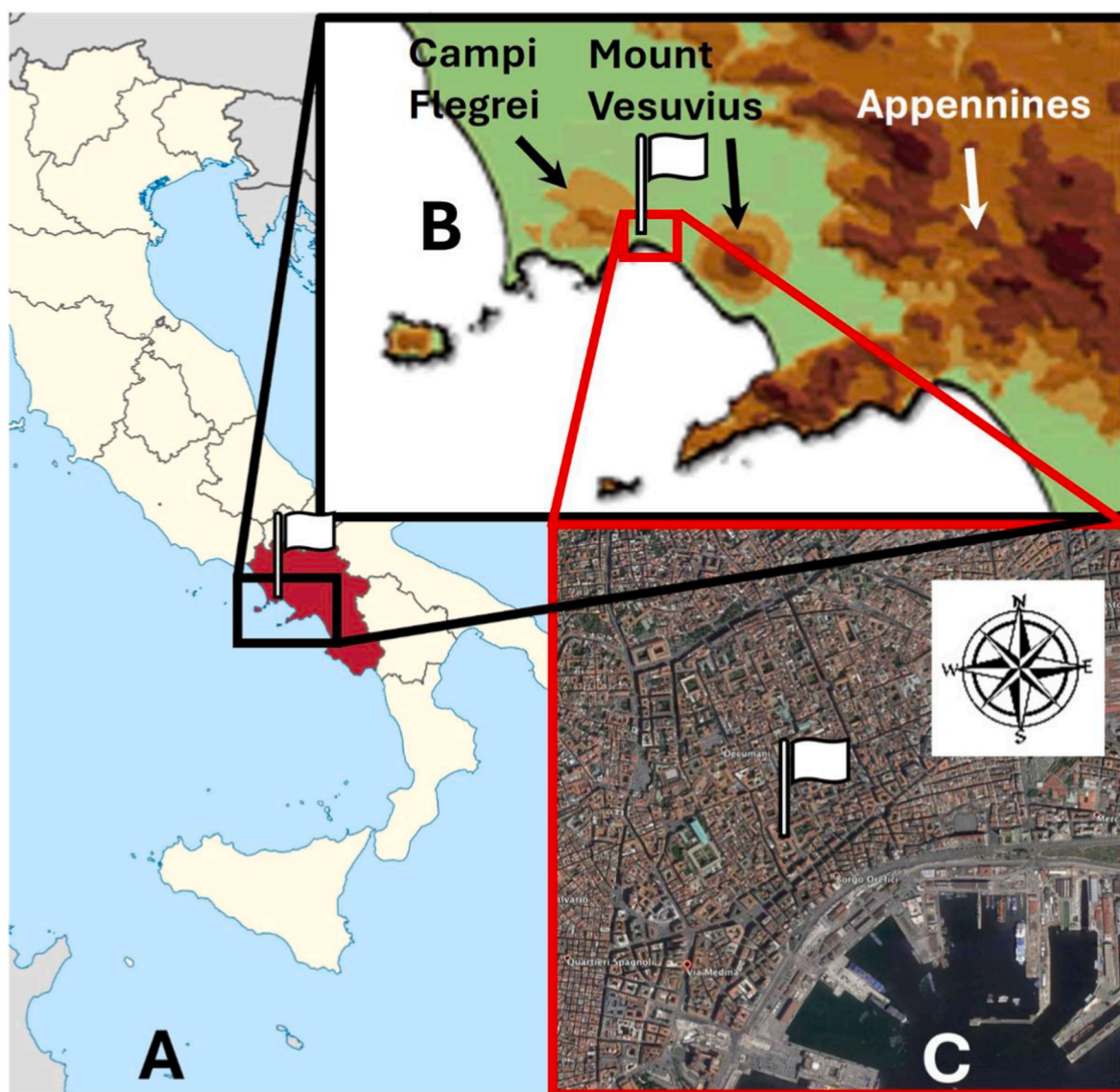


Fig. 1. A) Location of Campania region (red) on the Italian peninsula with the white flag indicating the location of the sampling site. B) Orography of the eastern part of Campania region around Naples. The main orographic features are named on the map (Campi Flegrei to the northwest, Mount Vesuvius and the Appennines to the west); C) Satellite view of the city center of Naples, with the sampling site indicated by a white flag.

use of BAM filter media for offline chemical and isotopic analysis is less standardized than dedicated sequential low-volume samplers, previous studies have demonstrated successful extraction of ionic and elemental species from BAM-collected material (Raja et al., 2017). The SWAM 5a operates at a controlled low-volume flow rate, ensuring stable flow conditions comparable to conventional low-volume reference samplers. Given the 47 mm filter diameter, the resulting filter face velocity falls within the range typical of standard filter-based PM sampling, supporting comparable particle collection efficiency and sampling artefact behavior. Sampling is performed at ambient temperature without aerosol heating, reducing thermally induced losses of semi-volatile species relative to heated instruments. The measurement uncertainty for total PM₁₀ and total PM_{2.5} concentrations is estimated to equal 0.5–0.6 µg m⁻³ (Chianese et al., 2019; Dinoi et al., 2017). Filters were stored at −20 °C between sampling and analysis to preserve sample quality.

2.2. Meteorological information

The orography of the region (Fig. 1B) constrains wind speed and direction in and around Naples. Mount Vesuvius to the southeast and the Apennines to the east prevent air circulation from east-southeast, while the hill at Campi Flegrei limits air originating from northwest. We characterized the changes over time of wind direction and speed, following what has been described in Hernández-Ceballos et al. (2025), i.e., we used the global re-analysis dataset produced by the European Centre for Medium-Range Weather Forecasts (ECMWF) Integrated Forecasting System (IFS) with spatial resolution of 9 km (0.125° × 0.125°). Backward trajectories were calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (Hysplit) at 40.85 N and 14.30 E. We used the NOAA Global Data Assimilation System (GDAS), which provides 1° lat/lon resolution and 23 pressure levels every 6 h, to characterize the air mass patterns in May and December, while the Weather Research and Forecasting (WRF) model outputs were used to calculate trajectories during the analyzed period. Hourly trajectories were calculated, over a 72 h period, with air parcels released at a final altitude of 500 m above ground level (AGL), based on time integration of the parcels' position using 3-D wind fields (Draxler and Hess, 1998). To identify the predominant air mass patterns, the clustering procedure implemented in HYSPLIT was used (Draxler, 2012; Draxler et al., 2012). The Weather Research and Forecasting (WRF) model outputs were also used to calculate hourly backward trajectories at the same receptor point during each analyzed short period. Trajectories were calculated at a final altitude of 500 m agl over a 30 h period, using 3-D wind fields. Therefore, there is no integration between trajectories driven by GDAS and those driven by WRF, and no double counting is introduced. The synoptic scenario was characterized using 500 hPa charts from the Global Forecast System (GFS) model as well as changes of Planetary Boundary Layer Height (PBLH) over the town of Naples using data collected from the Copernicus Climate Data Store with the ERA5 reanalysis dataset (Hersbach et al., 2020; Soci et al., 2024) with hourly resolution for a 0.25° × 0.25° grid cell. We also used temperature, relative humidity and cloud cover measured at the Capodichino station (Naples International Airport, approximately 5 km north-northeast of the sampling site) to speculate on the mechanisms of PM formation.

2.3. Characterization of PM composition

2.3.1. Total N and C, and their isotopic composition (δ¹⁵N and δ¹³C)

Loaded filters were divided into two halves. One half was used for isotope analysis and for the determination of C and N concentrations. Because the mass of C and N collected on filters was limited, we optimized a method for the simultaneous determination of total N and C content (%N and %C in mass) and their stable isotope composition (δ¹⁵N and δ¹³C). The method employs an Elemental Analyzer (Flash, 2000;

ThermoFisher) in combustion/reduction configuration coupled with an Isotope Ratio Mass Spectrometer (IRMS, Delta V Advantage, ThermoFisher) via the ConFlo IV interface (ThermoFisher). The δ¹⁵N and δ¹³C are defined as:

$$\delta^{15}\text{N} = \left(\frac{{}^{15}\text{R}_{\text{sa}}}{{}^{15}\text{R}_{\text{st}}} - 1 \right) \times 1000; \quad \delta^{13}\text{C} = \left(\frac{{}^{13}\text{R}_{\text{sa}}}{{}^{13}\text{R}_{\text{st}}} - 1 \right) \times 1000 \quad (1)$$

where ¹⁵R = ¹⁵N/¹⁴N, ¹³R = ¹³C/¹²C, “sa” = “sample” and “st” = “standard” (=reference material). The primary, internationally recognized standard for δ¹⁵N and δ¹³C are, respectively, N₂ in air and VPDB (Vienna-PeeDee Belemnite, a Cretaceous marine fossil – belemnite – from the Pee Dee formation in South Carolina). In our case, the greatest challenge was to analyze the δ¹⁵N of total N in PM because the quantity of total N on each filter was small and the signals obtained at the IRMS detectors (i.e. Faraday cups) were often low (below 3 V). We developed a measurement protocol followed by a selection-quality control procedure allowing us to maximize the accuracy of low-signal acquisitions and minimize the associated uncertainty. However, a significant number of δ¹⁵N values were rejected because the signals were too low to provide reliable (accurate) results (see section “Sample selection/rejection” of the Supplement for detail). Also, due to system breakdown, the δ¹³C in PM_{2.5} measured on samples collected in December were lost.

To enable proper flash combustion, the selected filter sections were cut into small pieces so that they could be placed inside tin capsules. This operation was performed using standard laboratory precision cutters. All manipulations were carried out under a clean hood. The tools used for handling and sectioning—such as tweezers, cutters, and punches—were thoroughly cleaned at each step, first with acetone and then with ethanol, to prevent contamination. Blank filters (only quartz) and blank filters with the addition of a reference material (quartz + standard) were measured to quantify the filter blank and the effect of the quartz mass in the combustion reactor. Three International Atomic Energy Agency (IAEA) reference materials for N (IAEA-N2 = ammonium sulfate: (NH₄)₂SO₄, δ¹⁵N = 20.3 ‰, IAEA-NO3 = potassium nitrate: KNO₃, δ¹⁵N = 4.7 ‰, and IAEA-600 = caffeine: C₈H₁₀N₄O₂, δ¹⁵N = 1.0 ‰) and three for C (IAEA-CH3 = cellulose: (C₆H₁₀O₅)_n, δ¹³C = −24.72 ‰, IAEA-C8 = wood, δ¹³C = −18.31 ‰ and IAEA-600 = caffeine, δ¹³C = −27.77 ‰) were used to calibrate the δ¹⁵N and δ¹³C measurements. The calibration model used was linear. Special care was taken to ensure that the signals for reference materials and unknown samples were as close as possible. This point, together with the need to remove any δ¹⁵N blank derived from the measuring system (see section “Blank of δ¹⁵N” of the supplement for more details), was crucial for δ¹⁵N measurements, given the risk of unreliable results when measuring low signals at Faraday cups (<3 V). A control sample named “UREA IVA” (IVA Analysentechnik THERMO, GmbH & Co. KG) was used as quality check (δ¹³C = −37.32 ± 0.04 ‰, δ¹⁵N = −0.45 ± 0.20 ‰). Since it was not possible to measure replicates of unknown samples because of the limited amount available for each sample, the precision was determined by measuring replicates of reference materials and UREA IVA under the same conditions as those used for unknown samples (i.e. with blank quartz filters and similar signals obtained for unknown samples). The average precision obtained was 0.25 and 0.17 ‰ for δ¹⁵N and δ¹³C respectively. The total uncertainty was derived from the calibration procedure (see section “Total uncertainty” of the Supplement) and, on average, it was 0.32 and 0.27 ‰ for δ¹⁵N and δ¹³C respectively. Blank corrections were negligible for both δ¹⁵N and δ¹³C. No significant drift was measured during the measurements period.

For measurements of % of C and N, Acetanilide (Thermo: C₈H₉NO, % C = 71.1 %, %N = 10.4 %) was used as a reference material, while Atropine (Thermo: C₁₇H₂₃NO₃, %C = 70.56 %, %N = 4.84 %) was chosen as a quality check because of its low %N, similar to unknown samples. The average precision was 2 % and 3 % for N and C, respectively. The average total uncertainty was not significantly different from the average precision.

2.3.2. Concentration of major ions

For the characterization of the soluble ion fractions, a quarter of each filter was first treated with 15 mL of ultra-pure water using a closed vessel microwave digestion system (Milestone StartE), following the multistep temperature ramp described in Chianese et al. (2019) and then filtered and analyzed using a Dionex ICS1100 system. We used an AS22 column and a buffer solution of 3.5 mM sodium carbonate–bicarbonate as eluent for anion detection. For cations, we used a CS12A column and 20 mM methanesulfonic acid solution as eluent. Calibration curves were built using certified multi-standard solutions.

The non-sea-salt (nss) fractions were derived using sodium (Na^+) as the reference salt ion, following the conventional seawater composition approach (Keene et al., 1986; Priyadharshini et al., 2019). Since the calculations were performed using concentrations expressed in $\mu\text{g m}^{-3}$, the applied coefficients are mass-based:

$$\text{nssK}^+ = K_{\text{measured}}^+ - \text{Na}^+ \times 0.037 \quad (2)$$

$$\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - \text{Na}^+ \times 0.252 \quad (3)$$

$$\text{nssCa}^{2+} = \text{Ca}^{2+} - \text{Na}^+ \times 0.0373 \quad (4)$$

$$\text{nssMg}^{2+} = \text{Mg}^{2+} - \text{Na}^+ \times 0.120 \quad (5)$$

Because particulate chloride is not conservative during atmospheric aging of sea-salt aerosol, especially in polluted coastal and urban plumes, chloride was treated in terms of depletion rather than as a non-sea-salt fraction:

$$\Delta\text{Cl}^- = 1.8[\text{Na}^+] - [\text{Cl}^-]_{\text{measured}} \quad (6)$$

Therefore, the total sea-salt concentration was obtained as:

$$\text{Sea salt } (\mu\text{g m}^{-3}) = [\text{Na}^+] + 1.8[\text{Na}^+] + 0.120[\text{Na}^+] + 0.037[\text{Na}^+] + 0.037[\text{Na}^+] + 0.252[\text{Na}^+] \quad (7)$$

Finally, the concentration of secondary inorganic aerosols (SIA) was determined as:

$$\text{SIA} = \text{nssSO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ \quad (8)$$

2.4. Air quality data of gaseous species

Data on major atmospheric pollutants relevant to air quality assessment - namely benzene (C_6H_6), carbon monoxide (CO), nitrogen dioxide (NO_2), and ozone (O_3) - were obtained from monitoring stations close to the sampling site. These stations include “Ferrovia”, located at the Central Railway Station in Naples, approximately 1.5 km east of the sampling site and classified as a traffic site; “Museo”, situated near the National Archaeological Museum, about 1 km northwest of the sampling site, also categorized as traffic site; and “Astronomico”, located at the Astronomical Observatory, roughly 2 km north of the sampling site, representing an urban background. For NO_2 , a chemiluminescence Nitrogen Oxides Analyzer model 200E (Teledyne, Advanced Pollution Instrumentation) is used at Astronomico, while two models 42i (Thermo Scientific) are used at Museo and Ferrovia. For CO, an infrared gas analyzer model 48iQ (Thermo Scientific) is used at Astronomico, while two models T300 (Teledyne, Advanced Pollution Instrumentation) are used at Museo and Ferrovia. For O_3 , a UV absorption analyzer (Teledyne, Advanced Pollution Instrumentation) is used at Astronomico. For Benzene, a gas-chromatograph (GC) model GC955 (Syntec), equipped with a PID (photoionization) detector, is used at Astronomico, while two GC/PID model 866 airTOXIC (Chromatotec/Airmotec) are used at Museo and Ferrovia.

2.5. Data analysis

Correlations between variables are investigated using Spearman's

rank correlation coefficient (Spearman's ρ), a non-parametric statistic used to assess the strength and direction of monotonic associations between variables, which was calculated using Origin software. In the regression plots we show linear fits with equation and correlation coefficient (R^2) as a visual guide to illustrate apparent trends in the plotted data.

Source apportionment of total C was carried out via the US Environmental Protection Agency's isotope mass balance algorithm IsoSource version 1.3 (Phillips and Gregg, 2003). Since the variability of the sources isotopic composition hinders a well constrained quantification of the contribution of each source, IsoSource is preferred to the more commonly used SIAR (Stable Isotope Analysis in R, now mixSIAR), because of its simpler approach and user-friendly interface. IsoSource has been used in the past in source apportionment studies of PM (Pan et al., 2016; Singh et al., 2021a). It calculates ranges of source proportional contributions to a mixture based on stable isotope measurements. Once the isotopic composition of each source is specified (for example, in the case of three sources δ_1 , δ_2 , δ_3), and the signature of the mixture (δ_{mix}) is measured, the calculation algorithm provides the distribution of source proportions (f_1 , f_2 , f_3) which are consistent with isotopic mass balance:

$$\delta_{\text{mix}} = f_1\delta_1 + f_2\delta_2 + f_3\delta_3$$

$$f_1 + f_2 + f_3 = 1$$

In IsoSource, each combination of possible source contribution was computed iteratively at 1% source increment with a mass balance tolerance of $\pm 0.5\%$ for predicting mixture compositions.

Published $\delta^{13}\text{C}$ signatures of major carbon sources contributing to atmospheric particulate matter were compiled from the literature to define the end members used in the mixing analysis. Reported values indicate substantial variability and partial overlap among source categories, but several broad isotopic groupings can be identified. The greatest $\delta^{13}\text{C}$ difference in nature is found between carbonates (CO_3^{2-}) and organic C compounds. Carbonates (CO_3^{2-}) have $\delta^{13}\text{C}$ around 0 ‰, whereas organic C has more negative (^{13}C depleted) $\delta^{13}\text{C}$, in the broad range -10 to -30 ‰ (Hoefs, 2021). For carbonate C, we could not find measurements of local carbonate $\delta^{13}\text{C}$ in PM, so we refer to the commonly reported range of values between -5 and $+5$ ‰ (Cerling, 1984; Vodička et al., 2025). For organic C, the $\delta^{13}\text{C}$ helps discriminate biogenic C derived from higher plants because it shows systematic differences linked to photosynthetic pathways (O'leary, 1988). Material originating from C_3 vegetation typically exhibits $\delta^{13}\text{C}$ values between approximately -30 and -20 ‰, whereas C_4 plant material is isotopically enriched, generally ranging from about -20 to -10 ‰ (Basu et al., 2015; Martinelli et al., 2002; Miyazaki et al., 2012; Mkombe et al., 2014). Direct biological particles (e.g., plant debris, pollen, surface waxes) are therefore expected to fall within these ranges. Because the present study area (Naples and surrounding region) is dominated by C_3 vegetation and the regional abundance of C_4 plants is limited, we assumed the contribution of C_4 -derived C to be negligible. In Naples, combustion processes can be a major source of PM (for example, in Naples there are hundreds of wood fire oven pizza restaurants). Several authors have argued that combustion-derived organic C - including fossil fuel emissions, traffic exhaust, and plant biomass burning - generally exhibits depleted $\delta^{13}\text{C}$ values, although reported ranges overlap those of C_3 vegetation (Aguilera and Whigham, 2018). Fossil fuel combustion products are commonly reported between roughly -30 and -23 ‰ (Cao et al., 2011; Kawashima and Haneishi, 2012; Lukens et al., 2019). Road traffic emissions typically fall between -28 and -24 ‰, while other combustion sources such as coal, charcoal, and residential heating are in the range -30 to -23 ‰, approximately (Aguilera and Whigham, 2018; Singh et al., 2021a; Widory and Javoy, 2003). Thus, individual combustion sources were grouped into a single “combustion” category because their reported $\delta^{13}\text{C}$ ranges strongly overlap and cannot be robustly separated using bulk $\delta^{13}\text{C}$ measurements alone. Marine aerosol

and mineral dust can also be an important source of PM in Naples. They are generally more enriched in ^{13}C than combustion-derived organic carbon. However, their ranges overlap those of C_3 vegetation, with reported $\delta^{13}\text{C}$ values commonly between about -25 and -18‰ , reflecting contributions from marine organic matter, carbonate material, or soil carbon (Cachier et al., 1986; Ceburnis et al., 2011; Guo et al., 2016; Turekian et al., 2003). Therefore, they cannot be clearly separated from the direct biogenic C_3 emissions.

The $\delta^{15}\text{N}$ of atmospheric particulate matter reflects contributions from multiple primary emissions as well as secondary formation processes. Reported $\delta^{15}\text{N}$ signatures of major nitrogen sources show wide variability but exhibit broad systematic differences. The two main categories that can be separated by $\delta^{15}\text{N}$, for both reduced N (NH_3 , precursor of NH_4^+ , Chen et al., 2022) and oxidized N (NO_x , $\text{NO} + \text{NO}_2$, precursors of NO_3^- , Luo et al., 2023), are volatilization/biological (^{15}N depleted) and combustion (^{15}N enriched) N emission. Agricultural emissions, particularly ammonia (NH_3) volatilized from livestock waste and fertilized soils, typically display depleted $\delta^{15}\text{N}$ values. Reported ranges for NH_3 emissions from animal waste commonly span approximately -40‰ to -10‰ , with many studies reporting values between -30‰ and -15‰ due to isotopic fractionation during volatilization (Felix et al., 2013, 2014; Heaton, 1986). Secondary particulate ammonium (NH_4^+) formed from this NH_3 may retain similarly depleted signatures, although additional fractionation during gas-particle partitioning can occur (Chen et al., 2022). Soil microbial emissions of NO_x typically show depleted $\delta^{15}\text{N}$ values (approximately -30 to 0‰),

reflecting fractionation during nitrification and denitrification processes (Bhattarai et al., 2021; Chang et al., 2018). In contrast, combustion-related NH_3 and NO_x emitted from vehicle exhaust, coal combustion, and biomass burning are generally more enriched in ^{15}N . Reported $\delta^{15}\text{N}$ values of NH_3 from coal combustion are -10 to 0‰ , whereas those from vehicle exhaust span the range 0 to 10‰ and those from biomass burning are between 10 and 20‰ (Chen et al., 2022). Similarly, NO_x from fossil fuel combustion commonly ranges from approximately -5 to $+20\text{‰}$, with vehicle emissions often clustering between 0 and $+15\text{‰}$ (Walters et al., 2015; Zong et al., 2017). However, interpretation of particulate $\delta^{15}\text{N}$ is complicated by substantial isotope fractionation during atmospheric oxidation of NO_x to nitrate (NO_3^-), gas-particle partitioning between NH_3 and NH_4^+ , heterogeneous reactions, and deposition processes (Fibiger and Hastings, 2016; Heaton et al., 1997; Walters and Michalski, 2015). These transformations can induce isotopic shifts of several per mil to more than 10‰ , often comparable to or exceeding the differences among primary sources.

3. Results

3.1. Meteorological conditions

Initially, we performed a meteorological characterization of the sampling periods, to show evidence of different meteorological conditions between May and December 2016. Air mass and local wind patterns in Naples as well as their influence on PM concentration have

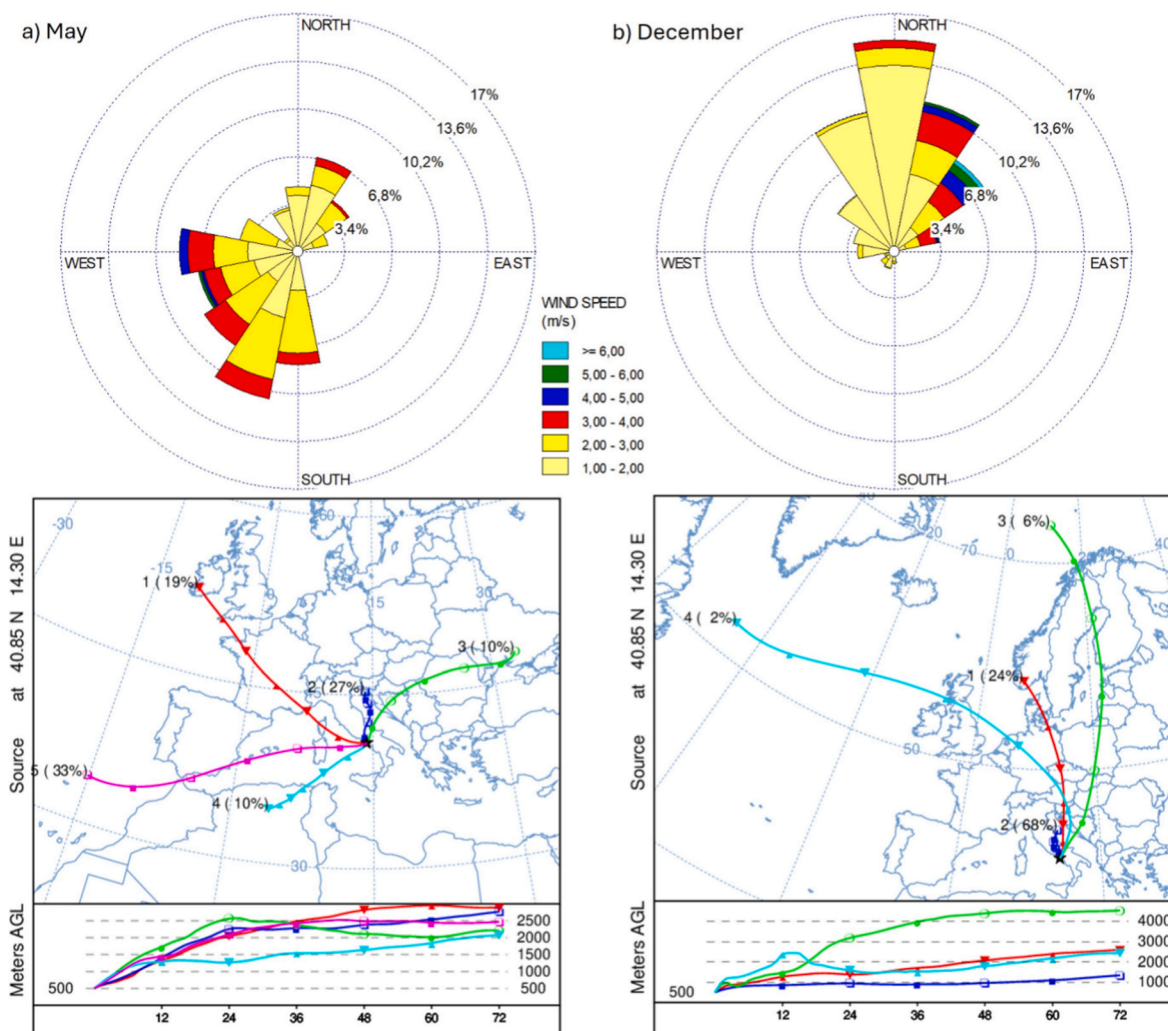


Fig. 2. Wind roses for Naples (upper plots) and Hysplit simulated back-trajectories (lower maps) for a) May (left) and b) December (right).

recently been investigated for the period 2018–2022 by Hernández-Ceballos et al. (2025). Here, we used part of the insight provided by Hernández-Ceballos to analyze the influence of meteorology on PM during the sampling period.

Differences in wind direction and speed between May and December confirmed that substantially different meteorological conditions characterized the two sampling periods. Results are presented in Fig. 2. In May, the air masses reaching Naples mostly originated from the south and west, that is from the Tyrrhenian Sea (see wind rose in Fig. 2a, with its legend providing wind speed ranges, and the underlying maps showing the simulated back-trajectories). Winds from the west had a greater speed (up to 5–6 m/s) than winds from the south (max 3–4 m/s), suggesting that air masses from the west travelled further than those originating from the south, as also shown by the back-trajectory map in Fig. 2a. On the contrary, in December air masses mostly originated from the north and northeast, with winds from northeast of Naples having greater wind speed (>6 m/s) than those from the north (max 3–4 m/s, see Fig. 2b). That means that, in December, the PM in Naples was mostly from land.

Next, we looked at the daily changes of wind speed and direction. In May, a significant shift occurred between the 10th and the 11th, transitioning from a typical land-sea breeze wind regime (with winds from northeast at night, and from south during daytime) to an intense synoptic system with winds originating from south/southwest (Fig. 3). This shift can be explained by the synoptic scenario (Fig. S2, Supplement) showing a low-pressure air mass moving from the Northern Atlantic Ocean (south of Greenland) towards southern Europe. This cold air mass reached northern Italy around the 12th–13th of May. Simultaneously, a shift in the planetary boundary layer height (Fig. S3, Supplement) occurred over Naples, with lower values on May 7th–11th and higher values thereafter.

Finally, we analyzed daily changes in wind speed and direction in December and found no significant patterns near the sampling days.

3.2. Total PM, C, N and their isotopic composition

Once we demonstrated that the two sampling periods were characterized by completely different meteorological conditions, we analyzed

the results of our measurements for the two periods separately.

3.2.1. May

Summary statistics for the species measured for the month of May and shown in Fig. 4A–E - including mean, standard deviation, and range - are presented in Table S1 of the Supplement. Here, we comment mostly on the main trends found.

Total PM

The concentrations of total PM₁₀ and PM_{2.5} (in $\mu\text{g m}^{-3}$) measured in May are shown in Fig. 4A. Both PM₁₀ and PM_{2.5} showed a general increase over the first 10 days of the month, during the sea-land breeze regime. PM₁₀ (light grey bars) fluctuated from 11 $\mu\text{g m}^{-3}$ up to 76 $\mu\text{g m}^{-3}$ (average 26 $\mu\text{g m}^{-3}$), while PM_{2.5} (dark grey bars) swayed from 6 $\mu\text{g m}^{-3}$ up to 28 $\mu\text{g m}^{-3}$ (average 14 $\mu\text{g m}^{-3}$). The spike of PM₁₀ on the 11th is hereafter named the “Event”. After the Event, the concentrations of both PM₁₀ and PM_{2.5} declined to values similar to those measured before the Event.

Each value of PM₁₀ was always higher than the corresponding value of PM_{2.5} measured on the same day. The measured values are consistent with previously reported PM₁₀ and PM_{2.5} levels in the Mediterranean region (Giannossa et al., 2022; Salameh et al., 2015; Saliba et al., 2010).

$\delta^{13}\text{C}$ and total C

The measured $\delta^{13}\text{C}$ and total C are shown in Fig. 4B and C. $\delta^{13}\text{C}$ in PM₁₀ (big, pink squares in Fig. 4B) was an average -26.2‰ ($s = 1.1\text{‰}$) and showed its highest value (-23.7‰) on the 11th, concurrently with Event, and its lowest value (-28.7‰) on the 2nd, when total C (pink bars in Fig. 4C) had its minimum. $\delta^{13}\text{C}$ in PM_{2.5} (small, red squares in Fig. 4B) was on average -26.9‰ ($s = 0.6\text{‰}$) and had its minimum (-28.6‰) also on the 2nd. Each $\delta^{13}\text{C}$ value measured in PM_{2.5} was not significantly different from the corresponding $\delta^{13}\text{C}$ value measured in PM₁₀ on the same day, except during the Event and one day after, when $\delta^{13}\text{C}$ in PM_{2.5} did not reach high values like those of $\delta^{13}\text{C}$ in PM₁₀. The trend of total C matched that of PM₁₀. During the sea-land breeze regime, both total C in PM₁₀ (pink bars in Fig. 4C) and total C in PM_{2.5} (red bars in Fig. 4C) fluctuated upward (from 2 up to 10 $\mu\text{g m}^{-3}$ and from 2 up to 8 $\mu\text{g m}^{-3}$, respectively), peaking on the 10th (one day before the Event) and decreased after that. Each value of total C in PM_{2.5} was generally lower than the corresponding value of total C in PM₁₀ measured on the same

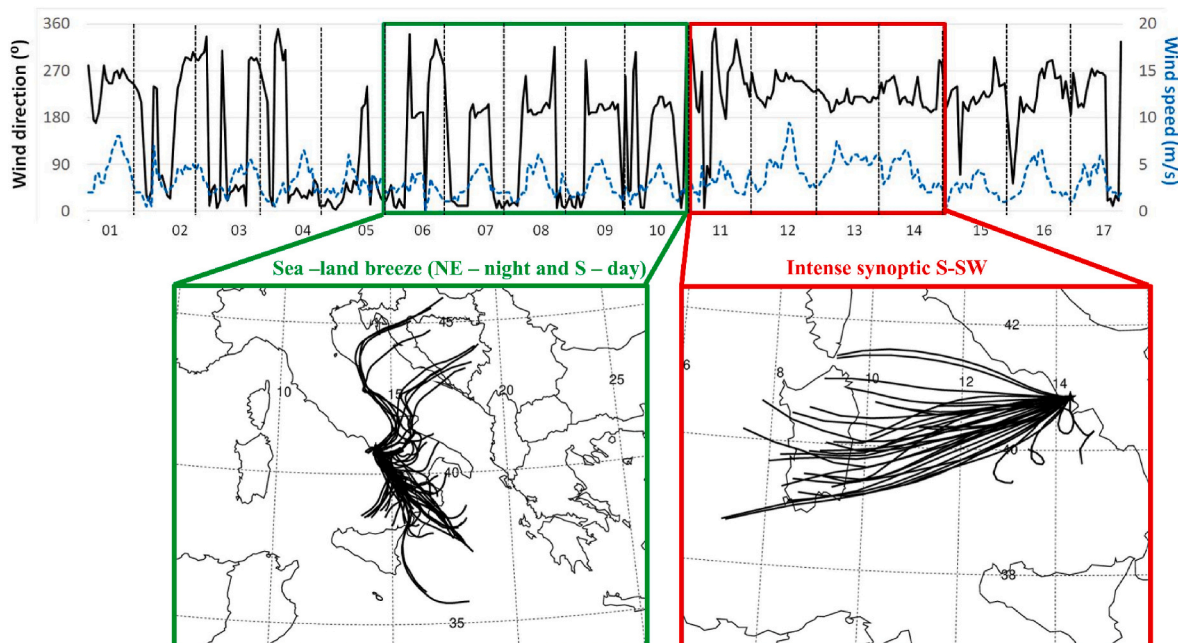


Fig. 3. Upper plot: Wind direction (black line) and speed (blue, dashed line) during the first two weeks of May 2016 (1st–17th May). Lower figures: HYSPLIT simulated back trajectories showing a change in the origin of air masses between the 5th–10th (green frame) and the 11th–14th (red frame) of May.

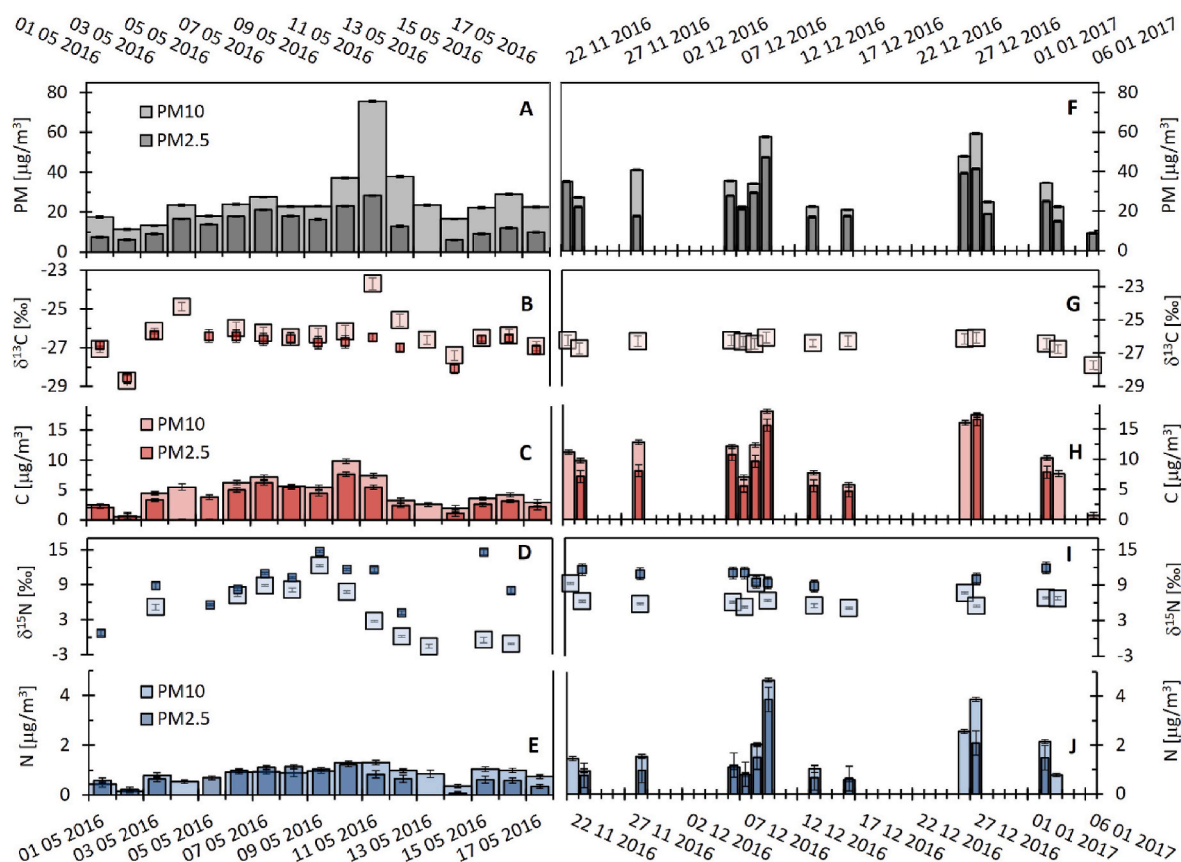


Fig. 4. Species are grouped according to the following scheme: total PM, total C and total N are bars. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are squares. PM₁₀ are lighter, thicker bars or bigger squares, whereas PM_{2.5} are darker, thinner bars or smaller squares. A and F) PM₁₀ (light grey bars) and PM_{2.5} (dark grey bars). B and G) $\delta^{13}\text{C}_{\text{PM}_{10}}$ (light red squares) and $\delta^{13}\text{C}_{\text{PM}_{2.5}}$ (dark red squares). C and H) Total C_{PM₁₀} (light red bars) and total C_{PM_{2.5}} (dark red bars). D and I) $\delta^{15}\text{N}$ in PM₁₀ (light blue squares) and PM_{2.5} (dark blue squares). E and J) Total N_{PM₁₀} (light blue bars) and total N_{PM_{2.5}} (dark blue bars). Left side (A-E): May. Right side (F-J): December.

day, except for a few days (7–9th) before the Event when they were not significantly different. The values measured for total C matched those measured in other Mediterranean cities (Salameh et al., 2015). The $\delta^{13}\text{C}$ measured was also within the range of values found in previous studies in different regions and cities around the world (Mkoma et al., 2014; Morera-Gómez et al., 2020; Vodička et al., 2019), but towards its lower end.

$\delta^{15}\text{N}$ and total N

The measured $\delta^{15}\text{N}$ and total N are shown in Fig. 4D and E. During the sea-land breeze regime, $\delta^{15}\text{N}$ of PM₁₀ (light blue squares) increased from 5 ‰ on the 3rd to 12 ‰ on the 9th. Around the Event, it declined and reached −2 ‰ on the 13th. $\delta^{15}\text{N}$ of PM_{2.5} (blue squares) also increased from 0 ‰ on the 1st to 15 ‰ on the 9th. Around the Event and during the intense synoptic with winds from the sea, $\delta^{15}\text{N}$ of PM_{2.5} varied significantly, showing no clear temporal trend. Each $\delta^{15}\text{N}$ value measured in PM_{2.5} was higher than the corresponding $\delta^{15}\text{N}$ value measured in PM₁₀ on the same day, with only one exception on the 6th. Total N followed a similar trend to that of PM₁₀. Both total N in PM₁₀ (light blue bars) and total N in PM_{2.5} (blue bars) fluctuated upward from 0.6 $\mu\text{g m}^{-3}$ on the 1st to 1.2 $\mu\text{g m}^{-3}$ on the 10th and decreased after that. During the sea-land breeze regime, each value of total N in PM_{2.5} was not statistically different from the corresponding total N measured in PM₁₀ on the same day, whereas it became lower after the 10th. The values measured for total N matched those previously reported in other studies in Mediterranean cities (Salameh et al., 2015). The $\delta^{15}\text{N}$ measured is also similar to values previously found by other studies around the world (Morera-Gómez et al., 2020; Widory, 2007), but it never reached the extreme values (either high - positive or low - negative) found in some cases (Mkoma et al., 2014; Vodička et al., 2019; Wang et al., 2017).

3.2.2. December

Summary statistics for the species measured in December and shown in Fig. 4F–J - including mean, standard deviation, and range - are presented in Table S2 of the Supplement.

3.2.2.1. Total PM. In December, the concentrations (Fig. 4F) of PM₁₀ (light grey bars) and PM_{2.5} (dark grey bars) were generally higher and more variable than those in May, with no evident temporal patterns. However, owing to the discontinuous nature of our sampling, we cannot rule out the possibility that we missed structured variability. The average values were 33 and 25 $\mu\text{g m}^{-3}$ for PM₁₀ and PM_{2.5} respectively. High concentrations were recorded on December 9th and December 26–27th (max values: 47 and 59 $\mu\text{g m}^{-3}$ for PM_{2.5} and PM₁₀, respectively). The values of PM₁₀ were generally higher than the corresponding values measured for PM_{2.5} on the same day, except for a few days when PM₁₀ and PM_{2.5} were not statistically different.

3.2.2.2. $\delta^{13}\text{C}$ and total C. $\delta^{13}\text{C}$ in PM₁₀ (pink squares in Fig. 4G) did not show significant variations around the mean value of −26.4 ‰ ($s = 0.4$ ‰), except for a low value (−27.7 ‰) on January 6th, when total C (pink bars in Fig. 4H) was also very low. Unfortunately, as previously explained, the $\delta^{13}\text{C}$ of PM_{2.5} is not available in December. Total C (Fig. 4H) in both PM₁₀ (pink bars) and PM_{2.5} (red bars) was generally higher and more scattered than in May (averages $\pm$ standard deviation: 11 ± 5 and 9 ± 4 $\mu\text{g m}^{-3}$, respectively). Like for PM₁₀ and PM_{2.5}, the highest concentrations of total C were recorded on December 9th (19 $\mu\text{g m}^{-3}$) in PM₁₀ and December 26–27th (17 $\mu\text{g m}^{-3}$) in PM_{2.5}.

$\delta^{15}\text{N}$ and total N

$\delta^{15}\text{N}$ (Fig. 4I) in PM₁₀ (light blue squares) and in PM_{2.5} (blue squares)

did not show significant trends around their mean values (6.6 ± 1.4 and 10.5 ± 1.1 ‰, respectively). Each value of $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ was higher than the corresponding value measured for $\delta^{15}\text{N}$ in PM_{10} on the same day (with one exception on December 7th). Total N (Fig. 4J) in both PM_{10} (light blue bars) and $\text{PM}_{2.5}$ (blue bars) was generally higher and more scattered than in May (1.7 ± 1.2 and $1.4 \pm 1.0 \mu\text{g m}^{-3}$, respectively). The highest concentrations of total N were recorded on December 9th (4.7 and $3.9 \mu\text{g m}^{-3}$ for PM_{10} and $\text{PM}_{2.5}$ respectively).

3.3. Major ions

The concentrations measured for major ions are given in Fig. S4 of the Supplement, where major ions were clustered based on their origin - from top to bottom: Secondary Inorganic Aerosols (SIA) - NH_4^+ , NO_3^- (orange) and SO_4^{2-} (grey), crustal/terrestrial/biomass burning - Ca^{2+} , $\text{C}_2\text{O}_4^{2-}$ and K^+ (green), and marine - Cl^- , Mg^{2+} and Na^+ (blue). Fig. S5 in the Supplement shows the concentrations of SIA, sea salt and the non-sea-salt part of ions derived using equations (2)–(8). Summary statistics for the major ions shown in Figs. S4 and S5, including average, standard deviation (SD), median, minimum and maximum, are presented in tables S3 (May) and S4 (December) of the Supplement. A detailed, quantitative explanation of the results obtained can be found in the Supplement. Here, we provide a brief description of the main features and trends found.

3.3.1. May

In May, SIA and the ions of crustal origin in PM_{10} showed an increasing trend during the sea-land breeze wind regime and a decline during the synoptic with winds from the sea (figures S4 A-F). NO_3^- , SO_4^{2-} , Ca^{2+} and $\text{C}_2\text{O}_4^{2-}$ in PM_{10} all peaked concurrently with the Event (May 11th) and then declined. SIA and the ions of crustal origin in $\text{PM}_{2.5}$ showed similar trends, but less coherent among different species. A special case was NH_4^+ because its concentration in PM_{10} peaked on the 7th. Importantly, each value of NH_4^+ measured in $\text{PM}_{2.5}$, except for a few days, exceeded the value of NH_4^+ measured in PM_{10} on the same day (Fig. S4A). The trend followed by marine species was completely different than that of SIA and ions of crustal origin. Cl^- , Mg^{2+} and Na^+ in PM_{10} were low during the sea-land breeze wind regime, while they increased during the synoptic with winds from the sea (figures S4 G-I). Cl^- , Mg^{2+} and Na^+ in $\text{PM}_{2.5}$ showed a similar trend, but less pronounced than that of the same species in PM_{10} .

3.3.2. December

In December, SIA and the ions of crustal origin in PM_{10} showed high values concurrently with the high values measured for PM, total C and N (figure S4 J-Q). Specifically, the concentrations of NH_4^+ , NO_3^- , $\text{C}_2\text{O}_4^{2-}$ and K^+ in PM_{10} were all high on December 8th, 26th and 27th, and higher than the max values measured in May. SIA and the ions of crustal origin in $\text{PM}_{2.5}$ showed a similar, but less pronounced behavior. Instead, ions of marine origin did not show any significant feature (figure S4 P-R). Cl^- , Mg^{2+} and Na^+ in PM_{10} were, on average, lower than in May. Cl^- , Mg^{2+} and Na^+ in $\text{PM}_{2.5}$ showed higher values toward the end of the sampling period.

4. Discussion

The following sections discuss the two sampling periods (May and December) separately. We first identify the main features found for PM, total C, N and the major ions measured. Then, we discuss the additional insight provided by $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Our analysis explores correlations among chemical species and their relationships with meteorological and air quality parameters (data shown in Fig. S6 of the Supplement). The statistical interpretation in the text is based on Spearman's ρ and the corresponding p values. The figures display straight line fits and corresponding R^2 values, but these fits are used only as visual aids to summarize the plotted patterns. However, the reported associations are

interpreted as monotonic rather than linear relationships. The correlations found are discussed in the context of air mass origin, as determined through trajectory analysis.

4.1. May

The sea-land breeze regime, with its poor air circulation, tends to accumulate PM in Naples (Hernández-Ceballos et al., 2025). Accordingly, PM, total C and N, as well as SIA and ions of crustal origin, showed a fluctuating increase in the first half of the sampling period. At the Event, there were spikes of PM and Ca^{2+} . After the Event, the meteorological conditions changed completely because air from the sea blew over Naples. All species decreased, except marine species (Cl^- , Mg^{2+} and Na^+) which increased significantly toward the end of the sampling period.

4.1.1. $\delta^{13}\text{C}$ in PM_{10}

The $\delta^{13}\text{C}$ in PM_{10} reached its highest value (-23.7 ‰) at the Event and shows its strongest positive Spearman correlation with nss-Ca^{2+} in PM_{10} ($\rho = 0.81$, $p < 0.01$, large, white squares in Fig. 5A). In addition, there is a clear shift of $\delta^{13}\text{C}$ in PM_{10} toward more negative values as the C concentration decreases (see values below $3 \mu\text{g m}^{-3}$, large, white squares in Fig. 5B).

On the contrary, we find no significant correlation between $\delta^{13}\text{C}$ in PM_{10} and any of the parameters available from meteorological and air quality data. Since meteorological (temperature, humidity, etc ...) data can influence the transformations of PM, and air quality data, especially ozone, can provide an idea of the results of those transformations, this could suggest that the changes in $\delta^{13}\text{C}$ did not depend strongly on secondary processes and were mostly associated with changes of the sources of total C in PM_{10} .

Based on what discussed in section 2.5 ("Data analysis"), we interpret the three highest values of $\delta^{13}\text{C}$ in PM_{10} (> -26 ‰) as being influenced by a significant contribution of carbonate C (CO_3^{2-} with $\delta^{13}\text{C}$ around 0 ‰). During the event, the high $\delta^{13}\text{C}$ values correspond to high concentrations of nss-Ca^{2+} (Fig. 5A), which is often associated with CO_3^{2-} to form CaCO_3 , hence our hypothesis of the influence of CO_3^{2-} on $\delta^{13}\text{C}$. Also nss-SO_4^{2-} in PM_{10} (Fig. S5C) showed high values at the Event, suggesting gypsum (CaSO_4) to be present in significant concentrations in PM_{10} . All the high $\delta^{13}\text{C}$ values occurred in days (May 4th, 11th and 12th) when the PBL was low (Fig. S3). Since resuspension of dust (including i. e., CaCO_3 and CaSO_4 from quarries) can be very high under conditions of low PBL, we interpret the highest $\delta^{13}\text{C}$ values as being influenced by a significant contribution of CO_3^{2-} resuspended together with dust, as discussed in Shen et al. (2013) and in Vodička et al. (2025). On the other hand, we interpret the decreasing trend of $\delta^{13}\text{C}$ in PM_{10} with decreasing total C in Fig. 5B as an indication of increasing contribution of combustion derived C (fossil and/or biomass burning) in samples with low amounts of total C in PM_{10} , so we identify the C baseline as of mainly combustion origin (intercept of the best fit line in Fig. 5B: -29 ‰). The strong positive Spearman correlation of total C with nss-K^+ and NH_4^+ in PM_{10} ($\rho = 0.90$ and 0.81 , respectively with $p < 0.01$, Fig. S9A and B) supports this interpretation, as both nss-K^+ and NH_4^+ can be associated with combustion processes. Finally, as total C increases, its $\delta^{13}\text{C}$ stabilizes at a value around -26.2 ‰ (Fig. 5B), which can be typical of C_3 plants.

To quantify the contributions of the different sources to total C in the coarse fraction ($\text{C}_{\text{coarse}} = \text{C}_{\text{PM}_{10}} - \text{C}_{\text{PM}_{2.5}}$), we first derive its $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{coarse}}$), according to the following isotope mass balance equation (Mkoma et al., 2014):

$$\delta^{13}\text{C}_{\text{coarse}} = \delta^{13}\text{C}_{\text{PM}_{10}} \left(\frac{\text{C}_{\text{PM}_{10}}}{\text{C}_{\text{PM}_{10}} - \text{C}_{\text{PM}_{2.5}}} \right) - \delta^{13}\text{C}_{\text{PM}_{2.5}} \left(\frac{\text{C}_{\text{PM}_{2.5}}}{\text{C}_{\text{PM}_{10}} - \text{C}_{\text{PM}_{2.5}}} \right) \quad (9)$$

and then run IsoSource with 3 C sources derived through the considerations made above: combustion at -29 ‰ (the intercept in Fig. 5B), C_3

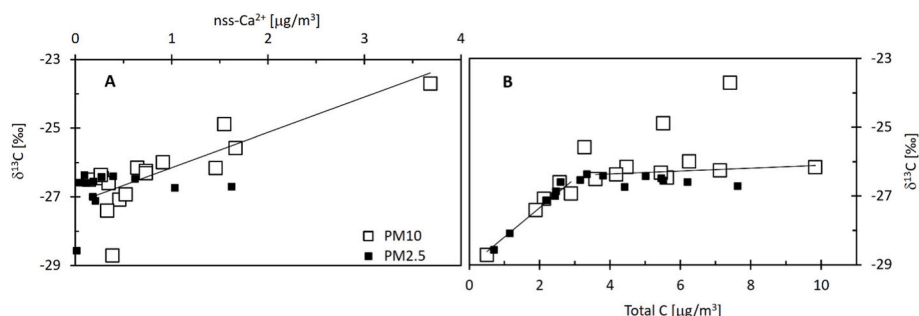


Fig. 5. Correlations of $\delta^{13}\text{C}$ in both PM_{10} (big, white squares) and $\text{PM}_{2.5}$ (small, black squares) vs A) nss-Ca^{2+} and B) total C. The correlation in A) between $\delta^{13}\text{C}$ and nss-Ca^{2+} in PM_{10} ($y = 1.03x - 27.2$, $R^2 = 0.66$) is driven by the values in the high range of $\delta^{13}\text{C}$ (> -26 ‰). The correlation in B) between $\delta^{13}\text{C}$ and total C for both PM_{10} and $\text{PM}_{2.5}$ ($y = 0.85x - 29.0$, $R^2 = 0.92$) is significant only in the low range of $\delta^{13}\text{C}$ (< -26.5 ‰).

plants at -26.2 ‰ (the $\delta^{13}\text{C}$ value at high total C in Fig. 5B) and carbonate at 0 ‰ (range: $[-5 + 5]$ ‰, as in Vodička et al., 2025). The results of IsoSource for total C_{coarse} in May show that most C derived from combustion (0–83%) or C_3 plants (0–89 %) sources. The contribution of carbonate C is generally minor (0–5 %), except during the Event when it provides between 11 and 18 % of total C in PM_{10} (see section “Isotope source apportionment with IsoSource” and Fig. S8 of the Supplement). IsoSource also shows that the C baseline, with the lowest measured $\delta^{13}\text{C}$ of -28.7 ‰ on the 2nd of May, was mostly derived from combustion sources (83–100 %), while the contribution of C_3 (0–15 %) is minor and that of CO_3^{2-} (0–2 %) is negligible. A sensitivity analysis performed by varying the $\delta^{13}\text{C}$ of the carbonate ($\delta^{13}\text{C}_{\text{CO}_3^{2-}}$) source from -5 to $+5$ ‰ shows small changes in the estimated sources contributions. For example, the carbonate contribution on the 11th May increases to 12–23 % when the $\delta^{13}\text{C}_{\text{CO}_3^{2-}}$ is taken = -5 ‰, whereas it decreased to 8–16 % when the $\delta^{13}\text{C}_{\text{CO}_3^{2-}}$ is taken = $+5$ ‰.

4.1.2. $\delta^{13}\text{C}$ in $\text{PM}_{2.5}$

Similarly to $\delta^{13}\text{C}$ in PM_{10} , the lowest values of $\delta^{13}\text{C}$ in $\text{PM}_{2.5}$ occurred on the same days (2nd and 14th) when the lowest concentrations of total C in $\text{PM}_{2.5}$ (C_{fine}) was measured (Fig. 5B). This suggests that, similarly to C_{coarse} , at low C concentration, the C baseline of C_{fine} is mainly composed of C from combustion sources. Differently from $\delta^{13}\text{C}$ in PM_{10} , at the Event and during the transition in wind regime, $\delta^{13}\text{C}$ in $\text{PM}_{2.5}$ is significantly lower than $\delta^{13}\text{C}$ in PM_{10} . This indicates a much smaller contribution of CO_3^{2-} in $\text{PM}_{2.5}$ compared to PM_{10} and confirms that total C in C_{fine} primarily originates from combustion processes and secondary aerosol formation (as discussed in Fuzzi et al., 2007; Mkoma et al., 2014).

Total C in $\text{PM}_{2.5}$ shows strong positive Spearman correlations with NH_4^+ , SO_4^{2-} and SIA ($\rho = 0.85, 0.78$ and 0.82 respectively, $p < 0.01$, plots of the correlations are shown in figures S7B, C and D) and also with NO_2 at Astronomico ($\rho = 0.75$, $p < 0.01$). Since this latter species is the product of combustion activities, this last correlation supports the interpretation that total C in $\text{PM}_{2.5}$ had a significant contribution from combustion activities. Quantitatively, IsoSource indicates that C_{fine} , for most days in May, was mainly composed of C from C_3 plant (7–88 %) and/or combustion (10–85 %) sources, with minor contribution of CO_3^{2-} (0–9 %). On days of low total C, IsoSource shows that the C_{fine} baseline was mostly from combustion activities and had the same sources contributions as total C in PM_{10} (83–100 % combustion, 0–15 % C_3 plant, 0–15 % CO_3^{2-}) on the same days.

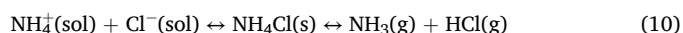
4.1.3. $\delta^{15}\text{N}$ in PM_{10}

We observe a strong positive Spearman correlation between $\delta^{15}\text{N}$ and NH_4^+ in PM_{10} ($\rho = 0.90$, $p < 0.01$, large, white squares in Fig. 6A), suggesting that variations in $\delta^{15}\text{N}$ of total N measured in PM_{10} were primarily caused by changes of the isotopic composition of NH_4^+ ($\delta^{15}\text{N-NH}_4^+$).

In contrast, the association with NO_3^- is weaker and negative

($\rho = -0.48$), suggesting a more limited influence on $\delta^{15}\text{N}$. Here we assume that the $\delta^{15}\text{N}$ of organic N did not change significantly. Changes in $\delta^{15}\text{N-NH}_4^+$ may have been caused by variations of its sources or by isotopic fractionation associated with the transformations of NH_4^+ (for a review of the use of isotopes to investigate atmospheric processes of reactive nitrogen, see Elliott et al., 2019). In the past, several studies have found significant correlations between $\delta^{15}\text{N}$ of total N and concentrations of NH_4^+ . For example, during a year-round monitoring in the Czech Highlands (central-east Europe), Vodička et al. (2019) found that low $\delta^{15}\text{N}$ values for total N in PM_1 were associated with enhanced NH_4^+ . Instead, Morera-Gómez et al. (2020) found a strong positive relationship between $\delta^{15}\text{N}$ of total N in PM_{10} and NH_4^+ , during an 18-month monitoring study in the town of Cienfuegos (Cuba). Singh et al., 2021b found that $\text{NH}_4^+\text{-N}$ controlled the $\delta^{15}\text{N}$ of total N in $\text{PM}_{2.5}$ in a wintertime investigation in Kanpur (India). All these studies acknowledge the possible influence on the measured $\delta^{15}\text{N}$ of equilibrium and kinetic isotope fractionation associated with multi-phase reactions during gas to particle conversion of NH_3 ($\text{NH}_3(\text{g}) \leftrightarrow \text{NH}_4^+(\text{aq})$). The two most important factors influencing isotope fractionation of $\delta^{15}\text{N}$ are temperature and humidity.

Here, we attempt to disentangle the role of chemical transformation from that of source contribution on the measured $\delta^{15}\text{N}$ in PM_{10} . The $\delta^{15}\text{N}$ in PM_{10} shows a negative correlation with relative humidity ($\rho = -0.77$, $p < 0.01$, Fig. 6B). We also find an anti-correlation between $\delta^{15}\text{N}$ in PM_{10} and sea-salt, but only during the period of winds from the sea (11–16th May, Fig. 6C). A similar correlation was observed by Morera-Gómez et al. (2020). The relevant role of sea salt in PM has been widely discussed in previous studies (Athanasopoulou et al., 2008; Chen et al., 2020; Lewandowska and Falkowska, 2013). The presence of significant amounts of Cl^- from sea salt in PM_{10} could affect the concentration of other species, as suggested by Querol et al. (2004), and later Nicolás et al. (2009) and Chianese et al. (2019) who attributed higher concentrations of NH_4^+ in $\text{PM}_{2.5}$ compared to PM_{10} to the possible loss of NH_4Cl (gas) from PM_{10} filters during sampling, according to the following reaction:



where sol = in solution, s = solid and g = gas. In fact, our data also show that NH_4^+ concentrations in $\text{PM}_{2.5}$ were higher than those in $\text{PM}_{2.5}$ during most of the sampling period in May (Fig. S4A). This pattern suggests that reaction (10) may have occurred during sampling and/or storage. However, we tend to exclude any effects during storage because all samples were stored in freezers immediately after collection, minimizing the potential for post-sampling volatilization. Additionally, volatilization during storage would have affected also the sampled collected in December, but our datapoints do not show this effect (Fig. S4J). Therefore, we assume that NH_4^+ in PM_{10} was lost from filters during sampling. While Yeatman et al. (2001) found no significant dissociation of NH_4^+ salts that would generate sampling artifacts in

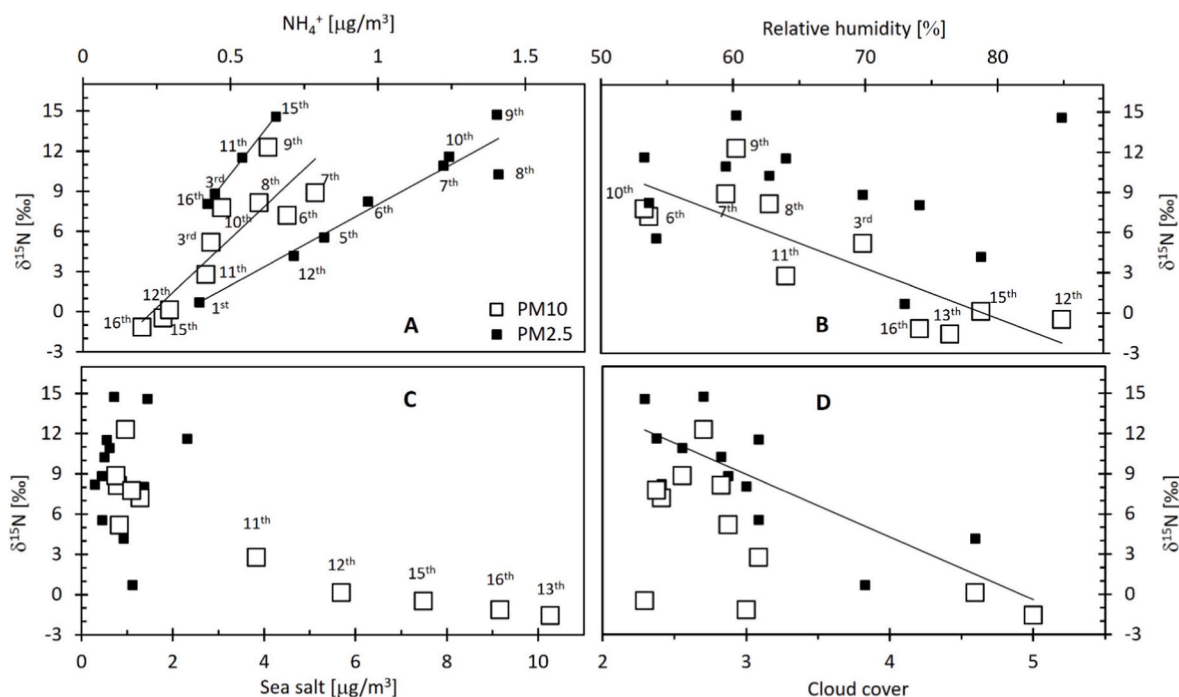


Fig. 6. Correlations of $\delta^{15}\text{N}$ in both PM_{10} (big, white squares) and $\text{PM}_{2.5}$ (small, black squares) vs A) NH_4^+ , B) relative humidity, C) sea salt and D) cloud cover. The equation of the straight line which is best fitting the correlation between $\delta^{15}\text{N}$ and NH_4^+ in PM_{10} shown in A) is: $y = 20.7x - 4.9$ ($R^2 = 0.77$). The correlation between $\delta^{15}\text{N}$ and NH_4^+ in $\text{PM}_{2.5}$ shown in A) is divided into two clusters: 8 datapoints on the right side of the plot (toward high NH_4^+) have best fitting line with equation: $y = 12.1x - 4.1$ ($R^2 = 0.92$), whereas 4 datapoints on the left side of the plot (low NH_4^+) have best fitting line with equation: $y = 28.3x - 3.9$ ($R^2 = 0.999$). The equation of the line interpolating the $\delta^{15}\text{N}$ vs RH correlation in PM_{10} shown in B) is: $y = -0.37x + 29.6$ ($R^2 = 0.68$). The equation of the line interpolating the $\delta^{15}\text{N}$ vs cloud cover correlation in $\text{PM}_{2.5}$ shown in D) is: $y = -4.7x + 23.0$ ($R^2 = 0.56$). Fig. 6A) and B) and C) show the dates of sampling as data label for each datapoint.

course mode NH_4^+ , Ianniello et al. (2011) measured that up to 53 % of fine particulate NH_4^+ evaporated from Teflon filters in annular denuder systems during summer sampling in Beijing. In response to these challenges, Walters et al. (2019) developed a specialized denuder-filter pack method to enable accurate $\delta^{15}\text{N}$ - NH_4^+ analysis while minimizing losses. Our results highlight the importance of using optimized sampling protocols that preserve N-containing species. Although we cannot directly test the hypothesis that NH_4^+ was lost from PM_{10} during sampling, indirect evidence supports this possibility. However, the influence of reaction (10) on the measured $\delta^{15}\text{N}$ in PM_{10} seems to be significant only in the period 11–16th May when there is a clear trend showing a $\delta^{15}\text{N}$ vs sea salt correlation (Fig. 6C).

Instead, if the datapoints corresponding to the intense southwesterly synoptic pattern (May 11–16th) are excluded, the observed correlations between $\delta^{15}\text{N}$ in PM_{10} vs NH_4^+ (Fig. 6A), relative humidity (Fig. 6B) and sea salt (Fig. 6C) disappear. Therefore, we assume that the $\delta^{15}\text{N}$ measured on May 3rd–9th is unaffected by isotope fractionations due to sampling artifacts, and interpret the increase in $\delta^{15}\text{N}$ in PM_{10} during the period 3rd–9th May as being caused mostly by variations of N sources. Based on what discussed in section 2.5 (“Data analysis”), the detected increase in $\delta^{15}\text{N}$ from ~ 5 ‰ on May 3rd to ~ 12 ‰ on the 9th (Fig. 4D) is consistent with a shift of N sources from volatilization to combustion, as described by Chen et al. (2022) for NH_4^+ and by Zong et al. (2017) for NO_3^- . This shift of N source occurred during a period dominated by the land-sea breeze wind regime (Fig. 3) and may be explained by accumulation of combustion emissions (vehicle exhaust, wood fire ovens, biomass burning) due to recirculation of local air masses. This interpretation is supported by the positive Spearman correlations between $\delta^{15}\text{N}$ in PM_{10} and several gaseous species measured for air quality purposes – namely benzene, CO and N_2O at Astronomico site ($\rho = 0.83, 0.71$ and 0.75 respectively, $p < 0.01$). As benzene, CO and N_2O are commonly linked to combustion, these associations are consistent with a combustion-related influence on $\delta^{15}\text{N}$ in PM_{10} .

We also find a strong positive Spearman correlation between total N and SO_4^{2-} ($\rho = 0.93$, $p < 0.01$, Fig. S9A), indicating that higher total N generally occurred together with higher sulfate concentrations. This pattern is consistent with an important contribution from secondary PM production. Additional support for this interpretation comes from the positive Spearman correlation between total N and temperature ($\rho = 0.71$, $p < 0.01$, Fig. S9B), suggesting that higher temperature were associated with higher total N and may have favored the formation of secondary PM components.

4.1.4. $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$

At first glance, the $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ does not show a statistically significant overall monotonic association with NH_4^+ (Spearman's $\rho = 0.50$, Fig. 6A). Nevertheless, Fig. 6A suggests the possible presence of two groups of observations. The first group includes eight $\delta^{15}\text{N}$ measurements. The second group includes only four $\delta^{15}\text{N}$ measurements and is characterized by more ^{15}N enriched values at comparable NH_4^+ concentrations. The linear fits and R^2 values shown for these two subsets in Fig. 6A are retained only to visualize their apparent orientation and should not be interpreted together with Spearman's ρ as a single statistical result. Within both groups, $\delta^{15}\text{N}$ appears to increase with NH_4^+ although this pattern should be interpreted cautiously, particularly for the smaller group because of its limited number of observations. This apparent behavior may be discussed in the context of the conceptual framework proposed by Heaton et al. (1997), who suggested that an increase in the $\text{NH}_4^+/\text{NH}_3$ ratio should be associated with a decrease of $\delta^{15}\text{N}$ (for the reader's convenience, Fig. 2a from Heaton et al., 1997 has been reported as Fig. S10 in the Supplement under section “Correlation of $\delta^{15}\text{N}$ vs $\text{NH}_4^+/\text{NH}_3$ ”). However, because NH_3 concentrations were not available in the present study, the comparison with the Heaton framework should be regarded as conceptual. The formation of ammonium is greatly enhanced by the availability of water. In Fig. S10, “wet atmosphere” and “dry atmosphere” conditions are regarded as typifying

conditions of high and low $\text{NH}_4^+/\text{NH}_3$ ratio, respectively.

A decrease of approximately 10 ‰ in $\delta^{15}\text{N}$ of $\text{PM}_{2.5}$ was observed between May 9th (14.7 ‰) and 12th (4.2 ‰, dark blue squares in Fig. 4D). This shift coincided with the change of weather conditions from sea-land breeze to intense synoptic pattern with wind blowing from S-SW (Fig. 3) and the increase of relative humidity. Because ammonium formation is enhanced by the availability of water, this behavior is consistent with a possible role of gas-to-particle conversion of NH_3 in controlling $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$, as also discussed in Pan et al. (2016). Still, in the absence of direct NH_3 measurements, this interpretation remains tentative.

The broadly similar apparent intercepts of the two groups may reflect a comparable underlying isotopic background, whereas the different apparent slopes may indicate differences in the effective isotope fractionation behavior. However, because these features are inferred from visualized linear fits and not from a formal subgroup regression analysis reported with full statistics, they should be considered hypothesis-generating rather than conclusive. In this respect, the observations may be compared qualitatively with the results of “lab in the field experiment” by Chang et al. (2025).

Intriguingly, $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ shows a negative Spearman correlation with cloud cover ($\rho = -0.73$, $p < 0.01$, Fig. 6D), indicating that $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ might have been affected by photochemical processes.

Total N in $\text{PM}_{2.5}$ is strongly associated with SIA , NH_4^+ and SO_4^{2-} ($\rho = 0.95$, 0.95 and 0.91 respectively, $p < 0.01$, figures S9 C-D), and also with nss-K^+ and temperature, and anticorrelated with relative humidity ($\rho = 0.90$, 0.81 and -0.80 respectively, $p < 0.01$). There is also a correlation between total N and NO_2 at Astronomico. Overall, these patterns suggest that total N in $\text{PM}_{2.5}$ was influenced by both secondary processes and by the changes in precursor concentration.

On each day for which both size fractions were available, $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ is higher than the $\delta^{15}\text{N}$ measured in PM_{10} . This behavior is consistent with the decrease in $\delta^{15}\text{N}$, from fine to coarse particles, reported by Wiedenhause et al. (2021), who attributed the isotope difference to distinct fractionation processes during particle formation, including the equilibrium formation of NH_4NO_3 that enriches fine particles in ^{15}N . A similar interpretation was proposed by Mkoma et al. (2014) who related the higher $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ to ^{15}N enrichment in fine particles through isotope exchange NH_3 (g) and NH_4^+ (aq). In our dataset, such fractionation effects may have operated together with source-related differences, with $\text{PM}_{2.5}$ potentially containing a larger proportion of combustion-derived N than PM_{10} .

4.2. December

In December, the concentration of several species, including SIA and nss-K^+ , showed high values on specific days (December 9th, 26th and 27th), but no specific meteorological trend or shift was detected around those days (Fig. S11). Given the terrestrial origin of these ions and the predominance of land derived air masses in December (Fig. 2B), we attribute these high values to a terrestrial source (spikes of K^+ , but also NH_4^+ and NO_3^- are often derived from biomass burning).

4.2.1. $\delta^{13}\text{C}$ in PM_{10}

In December, the $\delta^{13}\text{C}$ in PM_{10} showed no remarkable correlation with any species or meteorological or air quality parameter, as its values remained relatively stable (Fig. 4G and Table S2). On the 6th of January 2017, $\delta^{13}\text{C}$ and total C in PM_{10} were both low (-27.7 ‰ and 0.96 mg/ m^3 , respectively, Fig. S12A), suggesting that, similarly to the pattern observed in May, the C baseline was primarily derived from combustion C sources. In PM_{10} , total C is strongly positively correlated with total PM (Fig. S13), NO_3^- , NH_4^+ and K^+ ($\rho = 0.90$, 0.86 and 0.83 respectively, Figure S14A, B and C), all of which showed elevated concentrations on December 9th and 26–27th. Also, total C in PM_{10} shows a strong negative Spearman correlation with cloud cover ($\rho = -0.93$, $p < 0.01$, Fig. S14D), which may indicate the involvement of photochemical processes in the

formation of carbonaceous compounds. Total C in PM_{10} is positively correlated with several air quality species: benzene at Ferrovia, CO and NO_2 at Museo ($\rho = 0.77$, 0.73 and 0.80 , respectively $p < 0.01$). Based on these correlations, we propose that biomass burning events could have been the major contributors to the elevated total C in PM_{10} levels. Since $\delta^{13}\text{C}$ does not change significantly, it does not provide further insight into the sources of total C. We run IsoSource with the same sources and isotopic signatures as the ones used for May, and conclude that total C in PM_{10} consisted of a mixture of combustion derived C (18–95 %) and C_3 plant derived C (0–82 %), with negligible contribution from carbonate sources (0–5 %). However, on January 6th it was mostly composed of baseline C from combustion (45–97 %), with lower contribution of C_3 plant (0–52 %) and negligible carbonate contribution (0–5 %).

4.2.2. $\delta^{15}\text{N}$ in PM_{10}

Like $\delta^{13}\text{C}$, also $\delta^{15}\text{N}$ in PM_{10} shows minimal variations in December (Fig. 4I and Table S2) and, consequently, no significant correlation with other species. Relative to the baseline range of approximately 5.5–6.5 ‰, two elevated values at around 9.3 ‰ were observed on November 22nd and December 8th. These increases may reflect a greater contribution from combustion-related sources to total N in PM_{10} during those periods.

Total N in PM_{10} is strongly correlated with NH_4^+ , NO_3^- and K^+ ($\rho = 0.95$, 0.95 and 0.93 respectively, Figure S15A, B and C) and negatively associated with cloud cover ($\rho = -0.93$, $p < 0.01$, Fig. S15D). Consistent with the discussion for total C in PM_{10} , the wind roses analysis (Fig. 2B) and the positive correlations with the air quality species (benzene at Ferrovia and NO_2 at Museo, $\rho = 0.78$ and 0.79 , respectively $p < 0.01$), suggest a terrestrial origin, supporting the interpretation that biomass burning contributed to the elevated levels observed in December. However, the $\delta^{15}\text{N}$ does not provide additional information regarding the sources of total N in PM_{10} during these high concentration events.

4.2.3. $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$

Like in May, also in December, each value measured for $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ is higher than the corresponding value measured for $\delta^{15}\text{N}$ in PM_{10} on the same day (except for the value measured on December the 8th) suggesting a greater proportion of combustion derived-N in $\text{PM}_{2.5}$.

Total N in $\text{PM}_{2.5}$ is positively correlated with NH_4^+ , NO_3^- and K^+ ($\rho = 0.87$, 0.89 and 0.79 respectively, $p < 0.01$, Figure S15A, B and C) and negatively correlated with cloud cover ($\rho = -0.96$, $p < 0.01$, Fig. S15D). This pattern suggests a terrestrial origin, and $\delta^{15}\text{N}$ itself does not appear to be a robust indicator of source changes in $\text{PM}_{2.5}$.

5. Conclusions

Our study has shown that the isotopes of C and N can be, in specific circumstances, useful tools to identify the origin of total C and N in PM. In our case-study at Naples, the $\delta^{13}\text{C}$ revealed a contribution of 11–18 % of CO_3^{2-} -C in PM_{10} during an event in May 2016, likely caused by a shift in wind regime that led to dust resuspension. The $\delta^{13}\text{C}$ values also indicated that the C baseline in both PM_{10} and $\text{PM}_{2.5}$ is primarily made of combustion derived-C.

In May, the $\delta^{15}\text{N}$ in PM_{10} showed clear evidence of isotope fractionation caused by the reaction of NH_4^+ and Cl^- during sampling. Once the $\delta^{15}\text{N}$ values of samples fractionated because of sampling artifacts were rejected, the retained $\delta^{15}\text{N}$ values suggested a shift from volatilization to combustion derived N sources, on days marked by stagnant atmospheric conditions and accumulation of urban pollutants. In $\text{PM}_{2.5}$, $\delta^{15}\text{N}$ was affected by fractionation associated with the transformation of NH_3 into NH_4^+ (and vice versa), which could provide insight into atmospheric processes. Studies addressing isotopic fractionation mechanisms of specific transformation reactions under real-world environmental conditions are needed to improve the accuracy of source apportionment results based on isotopic signatures (Chang et al., 2025;

Huang et al., 2025). Notably, the generally higher $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ (as compared to $\delta^{15}\text{N}$ in PM_{10}) suggested a greater influence of combustion derived N in the fine than in the coarse particle fraction.

The power of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ to identify the sources was very limited in December. Elevated concentrations of PM, total N, C and major ions - interpreted as resulting from biomass burning events - did not see corresponding change of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, suggesting that these isotope tracers may not reflect sources contributions under these circumstances.

The effectiveness of isotopic analysis in complex urban environments is hindered by issues like collinearity among source tracers, reliance on isotopic composition of total PM, and the need for extensive isotopic data resources. These limitations necessitate supplementary methods and a more comprehensive isotopic fingerprint database to improve source apportionment in urban settings. The ability to quantitatively apportion sources is constrained, particularly when the number of potential sources exceeded the number of available isotopes plus one (Shi et al., 2021; Wang et al., 2017). Our results also confirm the challenge of overlapping source isotopic composition (Aguilera and Whigham, 2018; Chen et al., 2022). This limitation necessitates careful consideration when interpreting isotopic signals and emphasizes the importance of constraining source signatures specific to the study area.

The limitations mentioned can be partly overcome by measuring the isotopic composition of specific fractions/molecules of total C (Elemental Carbon, Organic Carbon and/or specific carbon compounds, Zenker et al., 2020; Aggarwal et al., 2013) and total N (NH_4^+ , NO_3^- and organic N, Chen et al., 2022; Singh et al., 2021b; Zong et al., 2017; Wu et al., 2021). However, these analyses are more time consuming and expensive than those of bulk isotopic composition of total C and N.

Importantly, integration of major ions data and air masses origin analysis (eg: wind speed, direction and back-trajectories) provided essential context to interpret isotope signals. Therefore, we conclude that $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of total C and N can be effective indicators of PM origin, but only when supported by complementary datasets, particularly data of chemical composition and meteorological information.

Data statement

Data will be made available on request.

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CRediT authorship contribution statement

Mauro Rubino: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Carmina Sirignano:** Conceptualization, Methodology, Writing – review & editing. **Elena Chianese:** Investigation, Resources. **Miguel-Angel Hernández-Ceballos:** Investigation, Visualization. **Anikó Angyal:** Formal analysis, Writing – review & editing. **Fabio Marzaioli:** Investigation, Writing – review & editing. **Davide Di Rosa:** Investigation. **Giuseppe Caso:** Investigation. **Angelo Riccio:** Resources, Software, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2026.122015>.

Data availability

Data will be made available on request. Please contact mauro.rubino@unicampania.it, if interested

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