



Chemical Speciation and Source Apportionment of PM_{2.5} in Greek Urban and Suburban Areas: Insights from the PANACEA Initiative

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Abstract. This study, conducted under the PANhellenic infrastructure for Atmospheric Composition and climatE chAnge (PANACEA), examines PM_{2.5} chemical speciation and source apportionment across five Greek cities (Athens, Ioannina, Patras, Volos, and Xanthi) representing urban background, urban, and rural environments. Sampling was conducted during summer (June to August 2019) and winter (December 2019 to February 2020), complemented by an earlier campaign at Athens Thissio (December 2018 to August 2019), yielding over 545 24-hour PM_{2.5} samples. Filters were analyzed for major and trace elements, water-soluble ions, organic carbon (OC), and elemental carbon (EC). Positive Matrix Factorization (PMF) was applied separately for each site using a harmonized protocol. Seven source categories were identified across the network: biomass burning (16.2% to 50.9%), heavy oil combustion (2.5% to 15.1%), industrial emissions (3.3% to 14.4%), mineral dust (4.8% to 16.4%), sea salt (1.6% to 11.7%), secondary sulphates and organics (7.1% to 33.0%), and vehicular traffic (9.7% to 27.6%). Campaign-average PM_{2.5} concentrations in Ioannina and Volos remained above 25 µg m⁻³, pointing to severe air pollution burdens and a high risk of non-compliance with European standards. The high spatial and temporal variation in source contributions reveals that while regional background pollution strongly influences PM_{2.5} levels, localized anthropogenic activities, and particularly wintertime biomass burning for residential heating, remain a critical driver of urban air quality degradation in Greece.

1 Introduction

Particulate matter (PM) is a well-recognized atmospheric pollutant, with a multitude of studies highlighting its detrimental impacts on human health (Ostro et al., 2015; Samoli et al., 2013), the environment, and climate (Chen et al., 2021). Fine particulate matter (PM_{2.5}), consisting of particles with aerodynamic diameters less than 2.5 µm, is of particular concern due to



its ability to penetrate deeply into the lungs, leading to severe respiratory system damage ([Xing et al., 2016](#)), autoimmune conditions ([Zhao et al., 2019](#)), and even lung cancer ([Nakharutai et al., 2022](#)).

Many natural and anthropogenic sources may contribute to PM levels. The most common being biomass burning, transportation, industry, sea salt, mineral dust, the three former, together with biogenic emissions, also contributing to secondary aerosol formation ([Viana et al., 2008](#)). Given the diversity of PM emission sources, the apportionment of the observed PM concentration levels to specific sources is a key aspect of air quality management, as this information may be used as guidance for developing targeted air pollution mitigation strategies. Positive matrix factorization (PMF) is one of the most widely used receptor models for PM source apportionment ([Paatero and Tapper, 1994](#)). The objective of PMF is to quantify the contribution of the major aerosol sources to the PM concentration levels recorded at a receptor site, based on particle chemical composition and its temporal variability.

Greece, located in southeastern Europe, is a region affected by multiple aerosol pollution sources due to its geographical position, namely, anthropogenic emissions coming from the industrialized areas of N and NE Europe, the heavily polluted Balkans, and air plumes coming from the Mediterranean and N Africa, leading also to frequent desert dust transport events ([Vasilatou et al., 2017 a](#)). This regional pollution is coupled with many local anthropogenic and natural sources, and is further enhanced by the Mediterranean climate, displaying low precipitation rates and high solar radiation, which favor particle formation and accumulation. Existing studies have primarily focused on three major cities (Athens, Thessaloniki and Patras) ([Diapouli et al., 2017 a](#); [Manousakas et al., 2018](#); [Theodosi et al., 2018](#)), demonstrating similarities but also unique features in each city, depending on the geographical location and types and intensity of human activities; these findings highlight the need to investigate air quality across a broader range of urban centers, and, notably, with harmonized aerosol characterization and source apportionment methodologies. Harmonized multi-city source apportionment studies ([Amato et al., 2016](#); [Saraga et al., 2021](#)) are crucial for accurately identifying pollution sources, understanding regional pollution patterns, and formulating effective environmental policies.

The objective of this study is to provide a comprehensive and harmonized characterization of PM_{2.5} chemical composition and sources in Greek urban environments, addressing the current lack of comparable multi-city aerosol studies in the region. Specifically, this work aims to (i) quantify the chemical composition of PM_{2.5} across five Greek cities representing different urban and regional settings, including locations not previously investigated; (ii) identify and apportion the major anthropogenic and natural sources contributing to PM_{2.5} through source apportionment analysis; (iii) assess seasonal variability by conducting coordinated measurements during summer (June–August) and winter (December–February) of 2019–2020; and (iv) evaluate intra-city variability within the Athens metropolitan area through additional measurements at a second urban background site during December 2018–March 2019 and July–August 2019.

Through this integrated approach, this study seeks to improve the understanding of spatial and temporal variability of PM_{2.5} sources in Southern European urban areas and to highlight the importance of including smaller urban centers and intra-city variability in air quality assessments and mitigation strategies.



65 2 Methods

2.1 PM Sampling

PM_{2.5} samples were collected at six sites, in five Greek cities (Athens, Ioannina, Patras, Volos and Xanthi), covering urban, urban background, and rural environments (**Figure 1, Table 1**). In Athens, two urban background sites were studied, one in the city center and one in a suburb of the Athens metropolitan area. Additionally, hourly meteorological data, including wind speed and wind direction, were acquired from automatic weather stations operated directly at or in close proximity to each monitoring site by the host institutions or retrieved from the automatic weather station network (NOANN) of the National Observatory of Athens. ([Lagouvardos et al., 2017](#)).



Figure 1: The six sampling locations of the PANACEA campaign.

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Table 1. Sampling stations, station characteristics, sampling periods, and number of PM_{2.5} samples collected during the warm and cold periods.

Site	Sampling location	Site type	Warm Period; No. of samples	Cold Period; No. of samples	Total Number of samples
Athens Demokritos (ATH.DEM-UB)	NCSR “Demokritos”	Urban Background	06/2019– 08/2019; 61	12/2019– 02/2020; 63	124
Athens Thissio (ATH.THIS-UB)	Thissio, NOA	Urban background	07/2019– 08/2019; 53	12/2018– 03/2019; 55	108
Ioannina (IOA-UB)	Kiafa area	Urban background	07/2019– 08/2019; 42	12/2019– 02/2020; 59	101
Xanthi (XAN-RUR)	Democritus University of Thrace campus	Rural	07/2019– 08/2019; 42	12/2019– 02/2020; 53	95
Volos (VOL-URB)	Urban area near harbor and Volos University	Urban	06/2019– 08/2019; 30	01/2020; 14	44
Patras (PAT)	ICE-HT (warm); University of Peloponnese/TEI campus (cold)	Rural (warm); Urban background (cold)	07/2019– 08/2019; 38	01/2020– 02/2020; 35	73

- **Athens Demokritos station (ATH.DEM-UB):** The Athens Demokritos urban background station in Athens is located within the NCSR “Demokritos” campus (37.99° N, 23.80° E; 270 m above sea level (m a.s.l.)). The station is a member of GAW and part of the ACTRIS and PANACEA infrastructures. It is located at a suburban zone at the northeast corner of the Athens Metropolitan area on the hillside of Hymettus Mountain. The site is mainly influenced by the outflow of the urban emissions within the Athens valley area and occasionally by incoming air from the northeast, representative of regional atmospheric aerosol conditions ([Eleftheriadis et al., 2014](#), [Eleftheriadis et al., 2021](#), [Zografou et al., 2022](#);). Sampling was performed on a 24h basis, starting at midnight, during 06/2019 – 08/2019 (warm period) and 12/2019 – 02/2020 (cold period). In total, 124 PM_{2.5} samples were collected (61 during warm and 63 during cold season) on Teflon filters (Whatman PTFE membrane filters with polypropylene support ring, 47 mm diameter, 2.0 µm pore size), by a low volume sampler (Sequential 47/50-CD, Sven Leckel GmbH, Berlin, Germany)
- **Athens Thissio station (ATH.THIS-UB):** The Thissio urban background station of the National Observatory of Athens (NOA) (37.97° N, 23.72° E; 105 m a.s.l.) is situated on the Nymphs Hill in the historic center of Athens. The monitoring site is surrounded by a pedestrian zone and a moderately populated residential area and is located approximately 0.5 km from the nearest major road. The site is a receptor of urban emissions from the central Athens basin, as well as from a variety of regional and long-range transported natural, anthropogenic and processed aerosols ([Paraskevopoulou et al., 2015](#); [Athanasopoulou et al., 2017](#); [Grivas et al., 2019](#); [Dimitriou et al., 2021](#)). 108 PM_{2.5}



samples were collected (53 during warm and 55 during cold season) on quartz fiber filters (Flex Tissuquartz, 2500QAT-UP 47 mm, Pall) during 12/2018 – 03/2019 (cold period) and 07/2019 – 08/2019 (warm period) at a 24h basis, starting from 18:00 LT, using a low volume sampler (Dichotomous Partisol – Plus, Model 2025 Sequential Air Sampler, Rupprecht & Patashnick, Co., Inc., USA).

- **Ioannina station (IOA-UB):** The Ioannina urban background site was located in the Kiafa area, on the outskirts of the city (39.65° N, 20.85° E; 518 m a.s.l.). The site is typically influenced by severe residential biomass burning emissions in winter (Tsiodra et al., 2025). Sampling was performed during 07/2019 – 08/2019 (warm period) and 12/2019 – 02/2020 (cold period), on a 24h basis, starting at midnight. In total, 101 PM_{2.5} samples were collected (42 during the warm and 59 during the cold season) on quartz fiber filters (Pall Tissuquartz or Whatman QM-A, 150 mm diameter) with a high-volume sampler (Digitel DH77, DIGITEL Elektronik GmbH, Austria).
- **Xanthi station (XAN-RUR):** The Xanthi station was located in a rural location, inside the Campus of Democritus University of Thrace (41.15° N, 24.92° E; 75 m a.s.l.). The ground surface around the station is mostly covered with soil and grass. A light-traffic road running in the east-west direction is located at a distance of 120 m to the south, connecting the main urban area of Xanthi with nearby villages. The distance between the station and the edge of the urban area is 1.7 km to the west. More details for the site location can be found at [Kastelis and Kourtidis, 2016](#). Sampling was performed during 07/2019 – 08/2019 (warm period) and 12/2019 – 02/2020 (cold period), on a 24h basis, starting at midnight. In total, 95 PM_{2.5} samples were collected (42 during warm and 53 during cold season) on quartz fiber filters (Pall Tissuquartz or Whatman QM-A, 150 mm diameter) by the use of a high-volume sampler (Digitel DH77, DIGITEL Elektronik GmbH, Austria).
- **Volos station (VOL-URB):** The Volos Station was established for the needs of the campaign by NCSR Demokritos and hosted by the Dept. of Mechanical Engineering, of the University of Thessaly. It was located in an urban area (39.36° N, 22.93° E; 11 m a.s.l.) and it is representative of the atmospheric urban region. Sampling was performed during 06/2019 – 08/2019 (warm period) and 01/2020 (cold period), on a 24h basis, starting at midnight. In total, 44 PM_{2.5} samples were collected (30 during warm and 14 during cold season) on quartz fiber filters (Whatman QM-A quartz microfiber filters, 150 mm diameter), by the use of an MCV high-volume sampler operating at a nominal flow rate of 30 m³ h⁻¹.
- **Patras stations (PAT):** In Patras, sampling was conducted at two different locations during the warm and cold periods, respectively, which differed in their surrounding characteristics and degree of urbanization. In the warm period, sampling was performed during 07/2019 – 08/2019, at the Institute of Chemical Engineering Sciences, ICE-HT (38.29° N, 21.80° E; 90 m a.s.l.), which is 8 km (northeast) away from the city center and 1km (south) from the Patras – Athens' highway. The ICE-HT site is situated in a relatively rural environment and is therefore considered a rural sampling site. During the cold period (01/2020 – 02/2020) the sampler was housed inside the campus of the Technological Educational Institute (TEI) of Patras (38.22° N, 21.75° E; 47 m a.s.l.). The TEI is in the southwest of the city, surrounded by moderately trafficked streets and residential areas. This site is considered an urban background



location. In total 73 PM_{2.5} samples were collected (38 during warm and 35 during cold season) on Quartz fiber filters (Pallflex Tissuquartz 2500QUAT-UP, Pall), on a 24h basis, starting at midnight, by the use of a low volume sampler (Leckel SEQ47/50 or LVS6-RV, Sven Leckel, flow rate: 2.3 m³ h⁻¹).

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Prior to weighing, the filters were equilibrated for 48 h under controlled temperature and relative humidity conditions (20 ± 3 °C and 40 ± 5 % RH for Ioannina; 20 ± 3 °C and 45 ± 5 % RH for Thissio). Filter masses were determined using a BP 211D analytical microbalance (Sartorius; 10 µg readability) for the Ioannina samples and an MX-5 microbalance (Mettler Toledo; 1 µg readability) for all other sampling sites.

140 2.2 Sample treatment and chemical analysis

2.2.1 Elemental Analysis

Benchtop ED-XRF spectrometer with secondary targets

PM_{2.5} samples underwent analysis for both major and trace elements using the Epsilon 5 (PANalytical) high-resolution energy dispersive X-Ray fluorescence 3-D optics spectrometer. This spectrometer is comprised of a side-window X-ray tube with a W/Sc anode. The characteristic X-ray emissions from the sample were detected by a Germanium (Ge) detector, achieving a measured energy resolution of approximately 150 eV FWHM at Mn-K α (5.89keV). The spectrometer offers a choice of 9 secondary targets (Al, CaF₂, Fe, Ge, Zr, Mo, KBr, Al₂O₃, LaB₆) capable of polarizing the X-ray beam. Consequently, 9 distinct measuring conditions were employed to optimize the analysis of the aerosol samples. Analysis was carried out on both PTFE and Quartz fiber filters, conducted under vacuum conditions, with each sample requiring an approximate total analysis time of 90 minutes. The detailed methodology employed for elemental characterization is thoroughly described in [Manousakas et al. \(2018\)](#). In total, 23 elements were identified using the benchtop ED-XRF spectrometer, including Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Cs, Ba, and Pb. The detection limits (LOD) (ng m⁻³) for Quartz and Teflon filters are given in **Table S1**.

155 Near real-time XRF spectrometer

At the ATH.THIS-UB station, the PM_{2.5} elemental composition during the summer period (07 - 08/2019) was determined using a Horiba PX-375 online ED-XRF spectrometer ([Creamean et al., 2016](#); [Grivas et al., 2020](#)). The instrument sampled through a PM₁₀ inlet followed by a very sharp-cut cyclone (VSCC) for PM_{2.5} separation. Particles were drawn at a flow rate of 16.7 L min⁻¹ and collected on a PTFE filter tape. Concentrations for an array of elements, including Al, Ti, V, Mn, Fe, Ni, Cu, Zn, and Pb, were determined at 3-hour intervals and then averaged over the 24-hour intervals of concurrently collected filter samples. The detection limits (LOD) for the Horiba Inc. PX-375 online ED-XRF spectrometer are given in **Table S2**. Details on the instrument's setup, operation during 2019-2020, and QA/QC (including comparisons with filters concurrently sampled during June 19 – July 8 and analyzed by ICP-MS) are provided by [Grivas et al. \(2026\)](#).

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165 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

PM_{2.5} elemental concentrations during the winter period at the ATH.THIS-UB station were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer, NexION 300X) after an acid microwave digestion procedure described in [Theodosi et al. \(2018\)](#). Yttrium (Y) and Indium (In) were added as internal standards, and all reported concentrations were corrected for blanks. The measured elements included: Al, Ca, Mn, Fe, V, Cr, Ni, Cu, Zn, and Pb. Limits of detection for ICP-MS are provided in **Table S3**.

2.2.2 Organic and Elemental Carbon

Elemental (EC) and organic carbon (OC) concentrations in PM_{2.5} were determined by the thermo-optical transmittance (TOT) method and the EUSAAR-2 thermal protocol ([Cavalli et al., 2010](#)). In all other stations except ATH.DEM, OC and EC levels were determined using a Lab OC-EC Aerosol Analyzer (Sunset Laboratory, Inc., Tigard, OR, U.S.A.), via the Thermal-Optical Transmission (TOT) technique and following the EUSAAR-2 protocol at ECPL, University of Crete, ([Paraskevopoulou et al., 2014](#)). The detection limits for OC and EC were estimated at 0.26 and 0.05 $\mu\text{g m}^{-3}$, respectively, with uncertainties less than 10% (5% for OC and 8% for EC). All reported concentrations were blank corrected. At the ATH.DEM-UB station, EC and OC were measured in near-real time, at 3-hr intervals, using a semi-continuous OC-EC field analyzer (Model-4, Sunset Laboratory, Inc., Tigard, OR, U.S.A.). The inlet was equipped with a PM_{2.5} cyclone and an in-line parallel carbon denuder to eliminate organic gases ([Diapouli et al., 2022](#)). The detection limit for both OC and EC was estimated at 0.08 $\mu\text{g m}^{-3}$ and the expanded uncertainties were equal to 18% for OC and 25% for EC.

2.2.3 Ionic Species

Ion chromatography (IC) was used to determine the levels of the inorganic ionic species. The major aerosol cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+) and anions (SO_4^{2-} , NO_3^- , Cl^-) were analyzed by Ion Chromatography (IC; Dionex-500; Thermo Fischer Scientific) at ECPL, University of Crete, following the methodology described in [Paraskevopoulou et al. \(2015\)](#). Prior to the analysis, the filters were extracted in ultrapure water (18.2 M Ω cm at 25 °C) under sonication for 30 min. Three replicate injections were done per sample, and the average value was reported. Depending on the measurement site, the limit of detection varied (**Table S4**). The expanded uncertainties for each ion were calculated based on the three replicate injections performed per sample. All analytical results were blank-corrected.

190 2.3 Source Apportionment

Positive matrix factorization (PMF) serves as a receptor model designed to assess sources of particulate matter (PM) based on their distinct chemical profiles and to quantify their respective impacts on observed PM concentration levels ([Paatero and Tapper, 1994](#)). The fundamental mass balance equation utilized by PMF can be represented as follows:



$$X_{mn} = G_{mp} F_{pn} + E \quad (1)$$

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Here, X denotes the concentrations of individual species (n) measured across different samples (m), G represents the contribution of each source (p) to each sample (m) as determined by the model, F denotes the contribution of each species (n) to the chemical profile of each source (p), also determined by the model, and E signifies the residual for species (n) in sample (m). The objective of PMF is to solve equation (1) by minimizing the objective function Q , defined as the sum of uncertainty-weighted squared residuals (E) between measured and predicted concentrations, until a stable solution is achieved (Paatero, 1999):

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$$Q = \sum_{m=1}^v \sum_{n=1}^{\mu} \frac{E_{mn}^2}{s_{mn}^2} \quad (2)$$

where s_{mn} is the uncertainty of each species (n) in each sample (m).

Source apportionment was performed by the use of the EPA PMF 5.0 software. In order to address rotational ambiguity and achieve more realistic solutions, a combination of different species and model constraints was implemented depending on the specific site (Paatero and Hopke, 2008). The data below limit of detection (LOD) were replaced with $\frac{1}{2}$ of the LOD and their corresponding uncertainty values with $\frac{5}{6}$ of the LOD. The calculated expanded uncertainties for all concentration measurements, incorporating both sampling and analytical uncertainties, were included in the input database. The uncertainty estimates were based on the approaches by Manousakas et al. (2018), Paraskevopoulou et al. (2015), and Theodosi et al. (2018). Furthermore, an additional 5 to 7% uncertainty was introduced into the model to account for potential errors in the modeling process. Various variables were also identified as "weak" or "bad" and were determined by applying the signal-to-noise ratio (S/N) methodology explained by Paatero and Hopke (2003), while $PM_{2.5}$ was included as the total variable.

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Each dataset was run for a different number of sources. After an exploration of several possible solutions spanning from 4 to 10 sources, the final range of optimal solutions ranged between 6 and 7 factors for the different sites, which were identified by evaluating several key performance indicators, such as Q values, scaled residuals distributions, the goodness-of-fit of predicted PM concentrations, and an assessment of the physical plausibility and meaning of the resulting source profiles and contributions (Reff et al., 2007). To obtain the final solution for each dataset, 100 model runs were performed, and the uncertainty of each solution was assessed through the implementation of error estimation tools, including Bootstrapping (BS) and Displacement (DISP) given by EPA-PMF 5.0. BS results were generally good, revealing good reproducibility, above 80% for all factors. In addition, displacement showed no factor swaps for the solution, for all dQ levels.

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Rotational ambiguity is a common issue in PMF, particularly for datasets with a limited number of samples, such as the VOL-URB dataset (44 samples). To address rotational ambiguity and improve the stability and interpretability of the PMF solutions, multiple constraints were applied where appropriate across the different datasets, taking into account the



characteristics of each site and the corresponding source profiles (Manousakas et al., 2017). The specific species and constraints applied for each dataset are summarized in Section 3.3 (Table 3). The application of these constraints resulted in total %dQ changes of less than 2.5% relative to the corresponding unconstrained solutions. Bootstrapping showed successful factor mapping in more than 80% of the bootstrap runs for all factors, while DISP analysis showed no factor swaps across the tested dQ levels, indicating that the constrained solutions remained stable and reproducible.

2.4 Conditional Probability Function (CPF)

The conditional probability function (CPF) was utilized to examine the impact of various emission sources from different directions by combining source apportionment data with wind speed and direction information (Kim et al., 2003; Rai et al., 2016). Applying CPF is beneficial for pinpointing the sources of pollution, assuming these sources are located within a certain distance from the sampling site. For this analysis, the top 25% of the source contributions (75th percentile) were used. The mathematical formulation of CPF is expressed through the following equation:

$$CPF = m_{\Delta\theta} / n_{\Delta\theta} \quad (3)$$

In this context, $m_{\Delta\theta}$ represents the number of wind occurrences within sector $\Delta\theta$ that exceed a specified threshold, while $n_{\Delta\theta}$ indicates the total number of data points in that same wind sector. It is likely that the sources are located in the direction where the conditional probability values are relatively high.

2.5 Air mass back-trajectory analysis

Air mass backward trajectories were computed to investigate the origin of air parcels arriving at the monitoring sites during episodic events, using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT-4) model developed by the National Oceanic and Atmospheric Administration (NOAA) (Stein et al., 2015). Meteorological wind fields were obtained from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Reanalysis database. Five-day (120 h) kinematic back-trajectories were calculated for arrival heights of 500, 1000, and 1500 m above ground level (a.g.l.), representing transport within and immediately above the atmospheric boundary layer.

3 Results and discussion

3.1 PM_{2.5} and chemical composition

The overall campaign-average concentrations of PM_{2.5} and all determined chemical constituents are summarized in Table 2, while the corresponding seasonal breakdowns for the warm and cold periods are detailed in Table S5 (ATH.DEM-UB, ATH.THIS-UB, IOA-UB) and Table S6 (VOL-URB, PAT, XAN-RUR). Because measurements were collected during



seasonal campaigns rather than across a full calendar year, the campaign-average concentrations cannot be used to assess compliance with annual limit values. However, individual 24-h concentrations can be compared with the future 24-h limit value of $25 \mu\text{g m}^{-3}$ introduced in Directive (EU) 2024/2881 (to be attained by 2030). Across the 545 total sampling days, 108 samples (19.8%) exceeded $25 \mu\text{g m}^{-3}$. The highest frequency of daily exceedances occurred at IOA-UB (44 of 101 samples; 43.6%), followed by VOL-URB (18 of 44; 40.9%), ATH.THIS-UB (29 of 108; 26.9%), PAT (16 of 73; 21.9%), and ATH.DEM-UB (1 of 124; 0.8%), whereas XAN-RUR recorded no exceedances (maximum: $24.3 \mu\text{g m}^{-3}$). At IOA-UB, all 44 exceedances occurred during winter, driving a winter average of $58.4 \mu\text{g m}^{-3}$ and reaching a maximum daily concentration of $151.3 \mu\text{g m}^{-3}$. The highest campaign-average $\text{PM}_{2.5}$ concentration was observed at IOA-UB ($39.9 \pm 35.8 \mu\text{g m}^{-3}$), followed by VOL-URB ($29.8 \pm 15.4 \mu\text{g m}^{-3}$), ATH.THIS-UB ($20.7 \pm 15.3 \mu\text{g m}^{-3}$), PAT ($18.7 \pm 9.5 \mu\text{g m}^{-3}$), XAN-RUR ($12.9 \pm 5.3 \mu\text{g m}^{-3}$), and ATH.DEM-UB ($11.0 \pm 4.1 \mu\text{g m}^{-3}$).



Table 2. Average PM_{2.5} and component concentration levels for the six stations. PM_{2.5} is reported in $\mu\text{g m}^{-3}$, while all other chemical species are reported in ng m^{-3} . " NA indicates species that were not analyzed or were below the analytical limit of detection.

Species	ATH.DEM-UB	ATH.THIS-UB*	IOA-UB	VOL-URB	PAT-URB	XAN-RUR
PM _{2.5}	11.0	20.7	39.9	29.8	18.7	12.9
OC	2792	6465	16510	5941	6101	3341
EC	383	1344	1715	1200	787	300
Na ⁺	156	263	128	514	254	162
NH ₄ ⁺	629	1144	996	1386	878	865
K ⁺	136	245	853	366	389	203
Mg ²⁺	20	78	34	548	31	31
Ca ²⁺	137	521	714	84	272	137
Cl ⁻	72	406	378	285	138	243
NO ₃ ⁻	181	787	1996	1674	763	424
SO ₄ ²⁻	2452	3445	2964	6220	3049	1879
Na	106	NA	NA	NA	NA	NA
Mg	30	NA	NA	NA	NA	NA
Al	88	129	NA	NA	NA	NA
Si	172	501	NA	NA	NA	NA
S	784	NA	529	669	384	372
Cl	18	NA	56	26	33	1.9
K	150	NA	486	176	309	105
Ca	120	NA	528	624	92	80
Ti	6.5	4.2	6.3	10	7.7	4.8
V	1.1	NA	0.3	1.2	NA	NA
Cr	0.7	NA	0.4	1.9	2.8	0.6
Mn	1.5	7.3	2.8	22	6.5	1.1
Fe	110	181	119	416	54	59
Co	NA	NA	0.5	0.8	NA	NA
Ni	1.7	2	2.1	1.6	4.3	1.6
Cu	5.9	4.8	3.4	14	22	0.8
Zn	13.3	23.2	13	188	11	13
Br	2.2	NA	3	3.3	NA	2.4
Rb	NA	NA	1.5	NA	NA	NA
Sr	NA	NA	1.3	1.2	NA	NA
Cs	NA	NA	8.4	NA	NA	10
Ba	9.8	NA	NA	NA	NA	12
Pb	3.7	3.6	3.8	16	23	NA

*Sampling during the cold period at the ATH.THIS-UB station was conducted between 12/2018 and 03/2019, while the warm period was conducted between 07/2019 and 08/2019.



Large seasonal variability in $\text{PM}_{2.5}$ concentrations was observed at most stations (**Figure 2**). Statistical significance of seasonal differences was evaluated using a two-tailed, two-sample t-test assuming unequal variances. The IOA-UB station recorded the most substantial seasonal contrast, rising from $13.8 \pm 3.8 \mu\text{g m}^{-3}$ in summer to $58.4 \pm 36.9 \mu\text{g m}^{-3}$ in winter ($p < 0.001$), representing a greater than fourfold increase driven by intense winter residential wood burning in the basin. At VOL-URB, average concentrations increased from $24.3 \pm 14.3 \mu\text{g m}^{-3}$ in summer to $41.6 \pm 10.5 \mu\text{g m}^{-3}$ in winter ($p < 0.001$). At ATH.THIS-UB, winter concentrations were nearly double those in summer ($26.1 \pm 17.6 \mu\text{g m}^{-3}$ vs. $14.5 \pm 5.9 \mu\text{g m}^{-3}$; $p < 0.001$). At PAT, average $\text{PM}_{2.5}$ concentrations increased from $12.6 \pm 3.9 \mu\text{g m}^{-3}$ in summer to $25.3 \pm 9.4 \mu\text{g m}^{-3}$ in winter. This increase reflects both seasonal emission variations and the relocation of the sampling setup between campaigns: summer measurements were conducted at the FORTH/ICE-HT campus (a rural environment), whereas winter measurements were performed at the University of Peloponnese -TEI campus- (an urban background site). In contrast, no statistically significant seasonal difference was observed at XAN-RUR ($13.2 \pm 4.4 \mu\text{g m}^{-3}$ in summer vs. $12.8 \pm 6.0 \mu\text{g m}^{-3}$ in winter; $p > 0.05$). Conversely, ATH.DEM-UB showed a significant decrease in $\text{PM}_{2.5}$ during winter, dropping from $12.4 \pm 3.6 \mu\text{g m}^{-3}$ in summer to $9.7 \pm 4.3 \mu\text{g m}^{-3}$ ($p < 0.001$). This pattern is largely explained by the strong seasonality of regional secondary sulfate, which peaked during the warm period and decreased from 3219 ng m^{-3} in summer to 1710 ng m^{-3} in winter (**Table 2**).

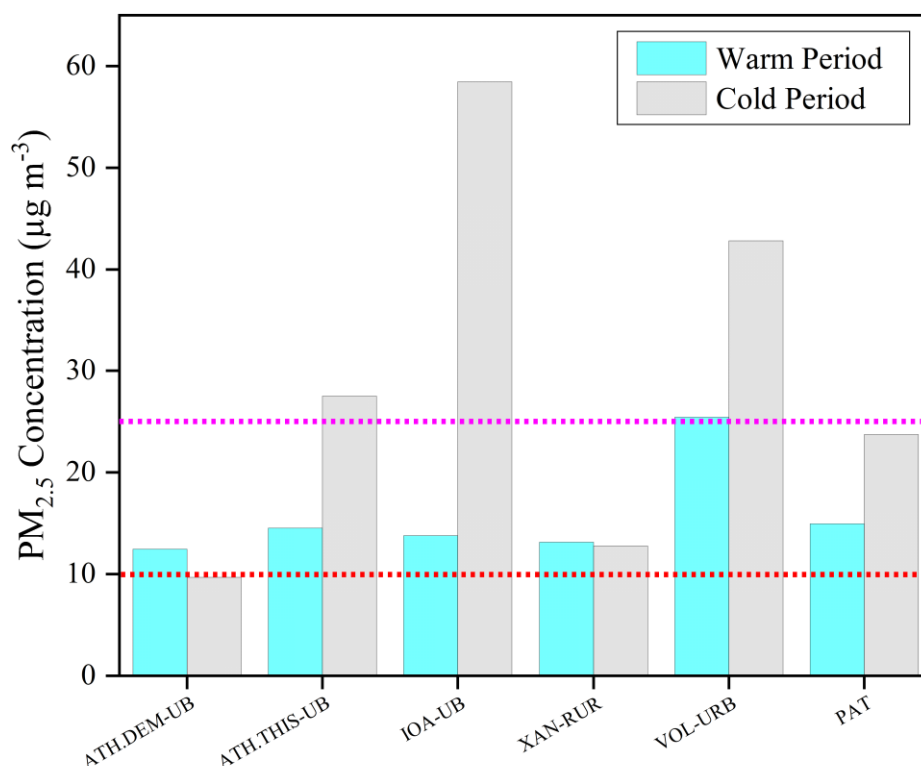


Figure 2: Seasonal concentrations of $\text{PM}_{2.5}$ for the six stations. The purple dotted line represents the current EU annual limit value ($25 \mu\text{g m}^{-3}$), while the red represents the new annual limit value to be attained by 2030.



Carbonaceous Species

Carbonaceous particles constituted the prevailing components of $PM_{2.5}$ across all monitoring sites. As detailed in **Table 2**, a
 310 consistent seasonal trend was observed across the network, with concentrations generally exhibiting marked increases during
 the cold period. For most urban sites, OC concentrations increased by a factor of 2 to 4 in winter compared to summer, with
 an extreme tenfold surge observed at the IOA-UB station (from 2.62 to 26.40 $\mu\text{g m}^{-3}$). EC concentrations followed a similar
 accumulation pattern, notably increasing by factors of 4 to over 8 at sites like ATH.THIS-UB, PAT, and IOA-UB during the
 winter months. The notable exception was the suburban ATH.DEM-UB site, which maintained relatively stable OC levels
 315 across both seasons. In contrast, all other sites including the rural XAN-RUR site, where OC increased by around 40% and EC
 by a factor of about 2.8 in winter, showed wintertime enhancements in carbonaceous aerosol. These enhancements are largely
 attributed to intensified primary emissions from residential biomass burning and reduced dilution within a shallower boundary
 layer.

Average seasonal OC/EC ratios were consistently elevated across the network, ranging from 2.9 to 18.5 during
 320 summer, and 4.1 to 10.0 during winter. These high ratios were expected as most of these urban background sites are situated
 away from direct, fresh traffic emissions. Furthermore, the exceptionally high winter OC/EC ratios at stations like IOA-UB
 (10.0) and VOL-URB (8.2) highlight a significant contribution from residential biomass burning, while the elevated summer
 ratios at XAN-RUR (18.5) and PAT (17.1) point toward strong secondary organic aerosol formation driven by biogenic
 emissions and photochemistry.

325

Major Inorganic Aerosols

The major secondary inorganic ions (SO_4^{2-} , NO_3^- , and NH_4^+) displayed distinct spatial differences and robust, opposing
 seasonal dynamics. Spatially, SO_4^{2-} exhibited the highest concentrations across the network, peaking at the coastal city of
 VOL-URB (averaging 6.79 $\mu\text{g m}^{-3}$ in summer and 5.00 $\mu\text{g m}^{-3}$ in winter), while the rural XAN-RUR site recorded the lowest
 330 and most stable levels ($\sim 1.9 \mu\text{g m}^{-3}$ across both seasons).

Examining their temporal variability, the data reveal significant seasonal variations across the monitoring network. SO_4^{2-}
 concentrations were systematically higher or remained stable during the summer months at almost all urban sites (**Table 2**).
 This behavior is driven by enhanced photochemical activity and higher solar radiation during summer, which accelerate the
 oxidation of SO_2 to SO_4^{2-} .

335 In contrast, particulate NO_3^- exhibited a massive enhancement during the winter period, increasing by factors ranging
 from 2.5 to nearly 30 compared to summer levels, with the most extreme accumulations observed at IOA-UB (3.34 $\mu\text{g m}^{-3}$)
 and VOL-URB (4.61 $\mu\text{g m}^{-3}$). Secondary nitrates (NO_3^-) are formed from the oxidation of NO_x emitted by different combustion
 sources, but their formation and stability strongly depend on temperature, humidity, ammonia availability, and aerosol
 composition (Fan et al., 2022). During winter, lower temperatures favor the partitioning of nitric acid (HNO_3) into particulate
 340 nitrate, while higher humidity enhances the uptake of ammonia (as NH_4^+) by acidic aerosols. Conversely, in the high
 temperatures and dry conditions of summer, the gaseous form (nitric acid) is favored, leading to lower particulate NO_3^- levels.



This is further supported by the highly acidic summer aerosol observed at Thisio and Ioannina (pH 1.35 and 1.75, respectively; [Neroladaki et al., 2025](#)), where the gas–particle partitioning of HNO_3 is shifted toward the gas phase, limiting the accumulation of particulate NO_3^- . Finally, NH_4^+ concentrations responded dynamically to these shifts, balancing the prevailing anions depending on the season, reaching its highest network concentration during the winter period at VOL-URB ($2.32 \mu\text{g m}^{-3}$).

Trace Elements and Natural Components

The concentration patterns of trace elements and ions of natural origin revealed distinct seasonal and site-specific drivers across the network. Tracers of mineral dust (Al, Si, Ca, and Ti) showed pronounced summer elevations at suburban sites such as ATH.DEM-UB (e.g., Al at $0.12 \mu\text{g m}^{-3}$ in summer vs. $0.06 \mu\text{g m}^{-3}$ in winter; Si at $0.22 \mu\text{g m}^{-3}$ vs. $0.13 \mu\text{g m}^{-3}$). This summer peak is indicative of enhanced local soil resuspension under dry Mediterranean conditions, combined with episodic long-range transport of Saharan dust. In contrast, urban and industrial sites like VOL-URB exhibited elevated crustal and metallic species (such as Fe at $0.47 \mu\text{g m}^{-3}$ and Ca at $0.70 \mu\text{g m}^{-3}$ during summer), pointing to localized anthropogenic dust resuspension from heavy traffic and port operations.

Marine aerosol indicators also displayed clear geographic and seasonal trends. Soluble Na^+ concentrations peaked during the warm season at the coastal VOL-URB site ($0.71 \mu\text{g m}^{-3}$ in summer vs. $0.10 \mu\text{g m}^{-3}$ in winter), driven by strong summer sea breezes and enhanced sea-spray generation. Meanwhile, Cl^- levels were systematically higher during winter across inland and northern stations (e.g., reaching $0.56 \mu\text{g m}^{-3}$ at IOA-UB and $0.38 \mu\text{g m}^{-3}$ at XAN-RUR), reflecting limited volatile HCl losses at lower temperatures, alongside potential contributions from residential biomass burning.

To further examine the origin and atmospheric processing of sea-salt aerosol, we calculated Cl^-/Na^+ mass ratios and compared them with the seawater ratio of 1.8 ([George et al., 2008](#)). This ratio is a widely used diagnostic: fresh sea salt has a Cl^-/Na^+ mass ratio of approximately 1.8, so values below this indicate chloride depletion, while values above it suggest additional non-sea-salt chloride sources. The calculated ratios showed seasonal and site-specific variability. During summer, Cl^-/Na^+ ratios were generally below the seawater reference value, particularly at VOL-URB (0.21), PAT (0.18), XAN-RUR (0.27), and ATH.DEM-UB (0.43), indicating substantial chloride depletion relative to Na^+ and/or contributions of Na^+ from non-marine sources. The summer ratio at ATH.THIS-UB (1.86) was close to the seawater value, suggesting a predominantly marine contribution with limited chloride modification at this site. In contrast, elevated winter ratios were observed at VOL-URB (5.82), XAN-RUR (4.86), and IOA-UB (3.34), substantially exceeding the seawater ratio and indicating an excess of Cl^- relative to that expected from sea-salt aerosol. These elevated winter ratios support the presence of additional non-marine chloride sources, consistent with the potential contribution of residential biomass burning, particularly at the inland IOA-UB and XAN-RUR sites.



3.2 Mass closure of PM_{2.5} components

"Chemical mass closure" is the process of reconstructing the measured weighed mass solely based on chemical composition. This involves comparing the combined masses of various chemical species to the gravimetric PM mass. In this process, the reconstructed PM_{2.5} mass comprises organic matter (OM), elemental carbon (EC), mineral dust (Min. Dust), sea salt (SS), secondary inorganic aerosol (SIA), and other trace elements excluding minerals (Chow et al., 2015). Crustal ratios from Mason (1966) were employed in order to estimate the concentration of missing crustal elements. Specifically, the crustal ratios of Na, Al and Si with respect to Ti were used.

For the calculation of the sea salt component, the main composition of sea spray (ss) was taken into account (Diapouli et al., 2017b) as:

$$\text{Sea Salt (SS)} = {}_{ss}[\text{Na}] + [\text{Cl}] + {}_{ss}[\text{Mg}] + {}_{ss}[\text{K}] + {}_{ss}[\text{Ca}] + {}_{ss}[\text{SO}_4^{2-}] \quad (4)$$

, where ${}_{ss}[\text{Na}] = [\text{Na}]_{\text{tot}} - {}_{nss}[\text{Na}]$, ${}_{nss}[\text{Na}] = 6.4 [\text{Ti}]$, ${}_{ss}[\text{Mg}] = 0.119 {}_{ss}[\text{Na}]$, ${}_{ss}[\text{K}] = 0.037 {}_{ss}[\text{Na}]$, ${}_{ss}[\text{Ca}] = 0.038 {}_{ss}[\text{Na}]$ and ${}_{ss}[\text{SO}_4^{2-}] = 0.253 {}_{ss}[\text{Na}]$. The highest sea salt concentrations were observed at the coastal ATH.THIS-UB site, reaching $1.63 \mu\text{g m}^{-3}$ during the warm period and $0.88 \mu\text{g m}^{-3}$ during the cold period (Figure 3 and Figure 4). At the coastal site, VOL-URB, sea salt was also higher in the warm period ($0.91 \mu\text{g m}^{-3}$) compared to the cold period ($0.17 \mu\text{g m}^{-3}$), consistent with enhanced sea-spray generation from summer sea breezes. In contrast, the inland IOA-UB site showed slightly higher sea salt during the cold period ($0.28 \mu\text{g m}^{-3}$) than in the warm period ($0.05 \mu\text{g m}^{-3}$). On average, sea salt accounted for 0.5% to 6.0% of PM_{2.5} contributions across sites.

Secondary inorganic aerosol (SIA) was calculated based on Seinfeld and Pandis, 1998 as:

$$\text{SIA} = {}_{nss}[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{NH}_4^+] \quad (5)$$

Here, ${}_{nss}[\text{SO}_4^{2-}]$ is the non-sea-salt $[\text{SO}_4^{2-}]$ concentration where ${}_{nss}[\text{SO}_4^{2-}] = [\text{SO}_4^{2-}]_{\text{total}} - {}_{ss}[\text{SO}_4^{2-}]$. The SIA concentrations varied geographically, with the highest levels observed at the VOL-URB station ($9.2 \mu\text{g m}^{-3}$), followed by the IOA-UB ($5.9 \mu\text{g m}^{-3}$), ATH.THIS-UB ($5.2 \mu\text{g m}^{-3}$), PAT ($4.6 \mu\text{g m}^{-3}$), ATH.DEM-UB ($3.2 \mu\text{g m}^{-3}$), and XAN-RUR ($3.1 \mu\text{g m}^{-3}$). The highest SIA concentrations were observed at VOL-URB, reaching $11.9 \mu\text{g m}^{-3}$ during the cold period and $7.9 \mu\text{g m}^{-3}$ during the warm period. The high SIA levels at VOL-URB could be attributed to cement industry activity, which utilizes high-sulfur limestone resulting in increased SO₂ emissions (Zhang et al., 2019), as well as shipping emissions in the harbor. At most other stations, SIA peaked during the warm period, notably at ATH.THIS-UB ($5.83 \mu\text{g m}^{-3}$ in summer vs. $4.64 \mu\text{g m}^{-3}$ in winter) and PAT ($5.46 \mu\text{g m}^{-3}$ vs. $3.56 \mu\text{g m}^{-3}$), driven by enhanced photochemical sulfate formation. In contrast, IOA-UB and XAN-RUR showed higher SIA during the cold period (6.9 and $3.3 \mu\text{g m}^{-3}$, respectively) than in the warm period (4.6 and $2.9 \mu\text{g m}^{-3}$),



reflecting increased nitrate formation under lower temperatures. On average, SIA accounted for 14.9% to 30.8% of PM_{2.5} mass.

405 Mineral dust was calculated based on [Nava et al. \(2012\)](#) from the contributions of crustal, non-sea salt (nss) components as:

$$\begin{aligned} \text{Min. Dust} = & 1.35_{\text{nss}}[\text{Na}] + 1.66_{\text{nss}}[\text{Mg}] + 1.89[\text{Al}] + 2.14[\text{Si}] + 1.21_{\text{nss}}[\text{K}] + 1.95_{\text{nss}}[\text{Ca}] \\ & + 1.67[\text{Ti}] + 1.43[\text{Fe}] \end{aligned} \quad (6)$$

, where $_{\text{nss}}[\text{Mg}] = [\text{Mg}^{2+}]_{\text{tot}} -_{\text{ss}}[\text{Mg}]$, $[\text{Al}] = 18.5[\text{Ti}]$, $[\text{Si}] = 63.0[\text{Ti}]$, $_{\text{nss}}[\text{K}] = [\text{K}]_{\text{tot}} -_{\text{ss}}[\text{K}]$ and $_{\text{nss}}[\text{Ca}] = [\text{Ca}]_{\text{tot}} -_{\text{ss}}[\text{Ca}]$. The highest mineral dust concentrations were observed at VOL-URB, reaching $4.2 \mu\text{g m}^{-3}$ during the warm period and $2.3 \mu\text{g m}^{-3}$ during the cold period. At ATH.DEM-UB, mineral dust was also higher in the warm period ($1.4 \mu\text{g m}^{-3}$) than in the cold period ($1.0 \mu\text{g m}^{-3}$). In contrast, IOA-UB and ATH.THIS-UB showed higher mineral dust during the cold period (3.2 and $3.1 \mu\text{g m}^{-3}$, respectively) than in the warm period (2.2 and $1.8 \mu\text{g m}^{-3}$). On average, mineral dust accounted for 3.6% to 12.2% of PM_{2.5} mass across the sites.

As for organic matter (OM), it was calculated by multiplying OC by a factor (or multiplier) that transforms OC into OM ([Chow et al., 2015](#)):

$$\text{OM} = f \times \text{OC} \quad (7)$$

The magnitude of the factor multiplier was set to 1.6 which is consistent with the recommended value for urban aerosols ([Turpin and Lim, 2001](#)) and falls within the range of 1.4 to 1.8 typically reported in mass closure studies ([Chow et al., 2015](#)). The concentration level of organic matter varied among the studied cities, with the highest average concentration level observed at the IOA-UB station ($26.4 \mu\text{g m}^{-3}$), reaching up to $42.2 \mu\text{g m}^{-3}$ during the winter period, due to residential biomass burning ([Papanikolaou et al., 2022](#); [Tsiodra et al., 2025](#)). The same situation seems to prevail at the VOL-URB, PAT and ATH.THIS-UB stations as well. Similar cold-period enhancements were observed at VOL-URB ($19.1 \mu\text{g m}^{-3}$ vs. $5.0 \mu\text{g m}^{-3}$), PAT ($14.1 \mu\text{g m}^{-3}$ vs. $6.6 \mu\text{g m}^{-3}$), ATH.THIS-UB ($13.9 \mu\text{g m}^{-3}$ vs. $3.4 \mu\text{g m}^{-3}$), and XAN-RUR ($6.0 \mu\text{g m}^{-3}$ vs. $4.5 \mu\text{g m}^{-3}$). In contrast, ATH.DEM-UB showed relatively stable OM levels across seasons ($4.4 \mu\text{g m}^{-3}$ in the cold period vs. $4.6 \mu\text{g m}^{-3}$ in the warm period). Overall, OM accounted for 31.9% to 66.3% of the PM_{2.5} contributions, with the highest contributions at IOA-UB and the lowest at ATH.DEM-UB and XAN-RUR.

Regarding EC, levels ranged from 0.2 to $2.7 \mu\text{g m}^{-3}$ across all sites and seasons, with the highest values observed during the cold period at IOA-UB ($2.7 \mu\text{g m}^{-3}$), ATH.THIS-UB ($2.1 \mu\text{g m}^{-3}$), and VOL-URB ($1.5 \mu\text{g m}^{-3}$). Trace elements accounted for minor contributions, ranging between 0.01 and $0.26 \mu\text{g m}^{-3}$. The remaining unaccounted mass averaged between 1.50 and $5.40 \mu\text{g m}^{-3}$ across sites (representing 7.0% to 22.3% of PM_{2.5} mass). The unaccounted mass can be attributed to various factors, including the samples' water content, which is not accounted for in chemical analyses, missing PM components



from the chemical mass balance and/or measurement errors. **Figure 3** and **Figure 4** show the mass closure contributions for the six sites during the warm and cold periods, respectively.

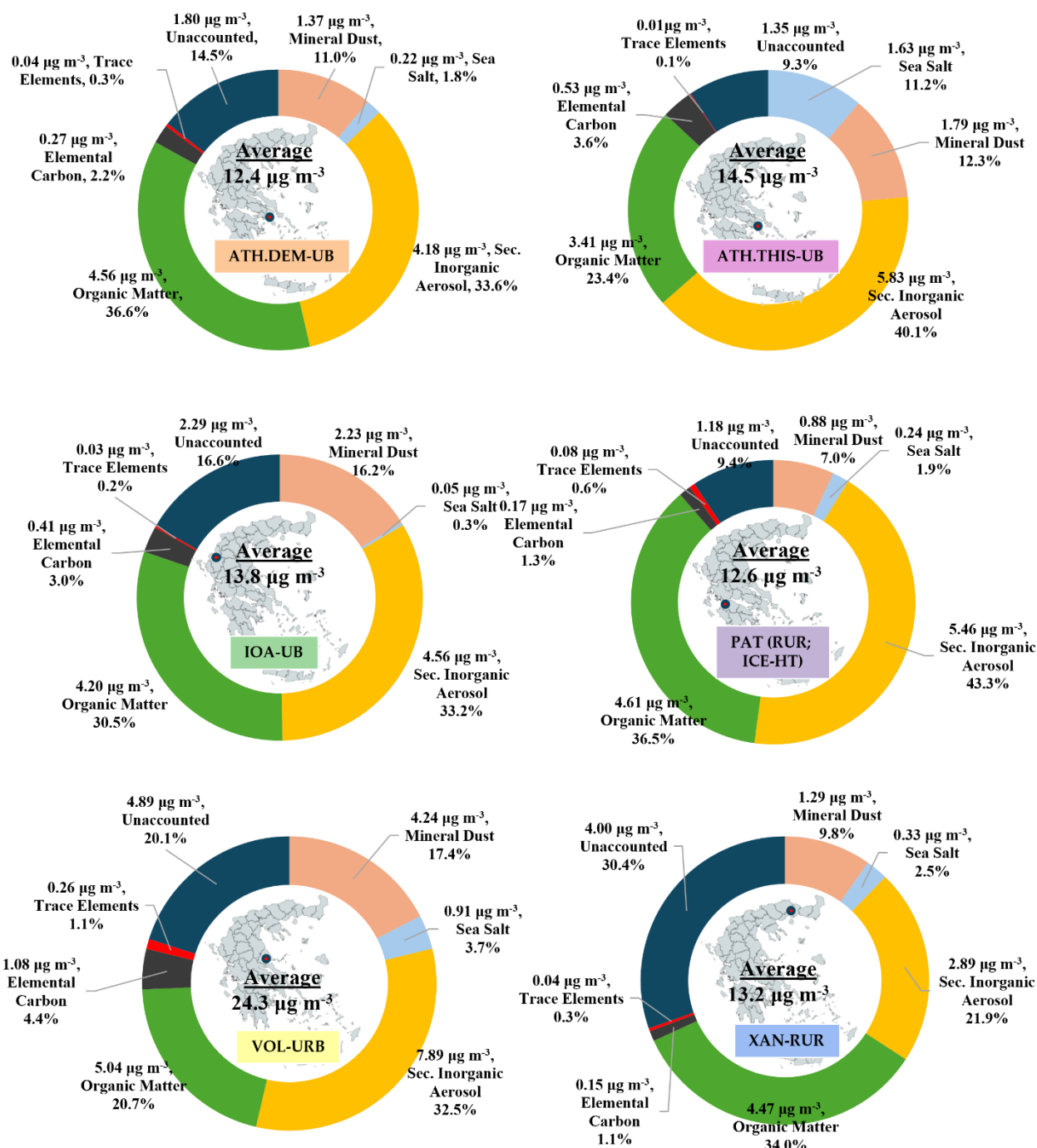


Figure 3: Mass closure contributions for the warm period for the six sites.

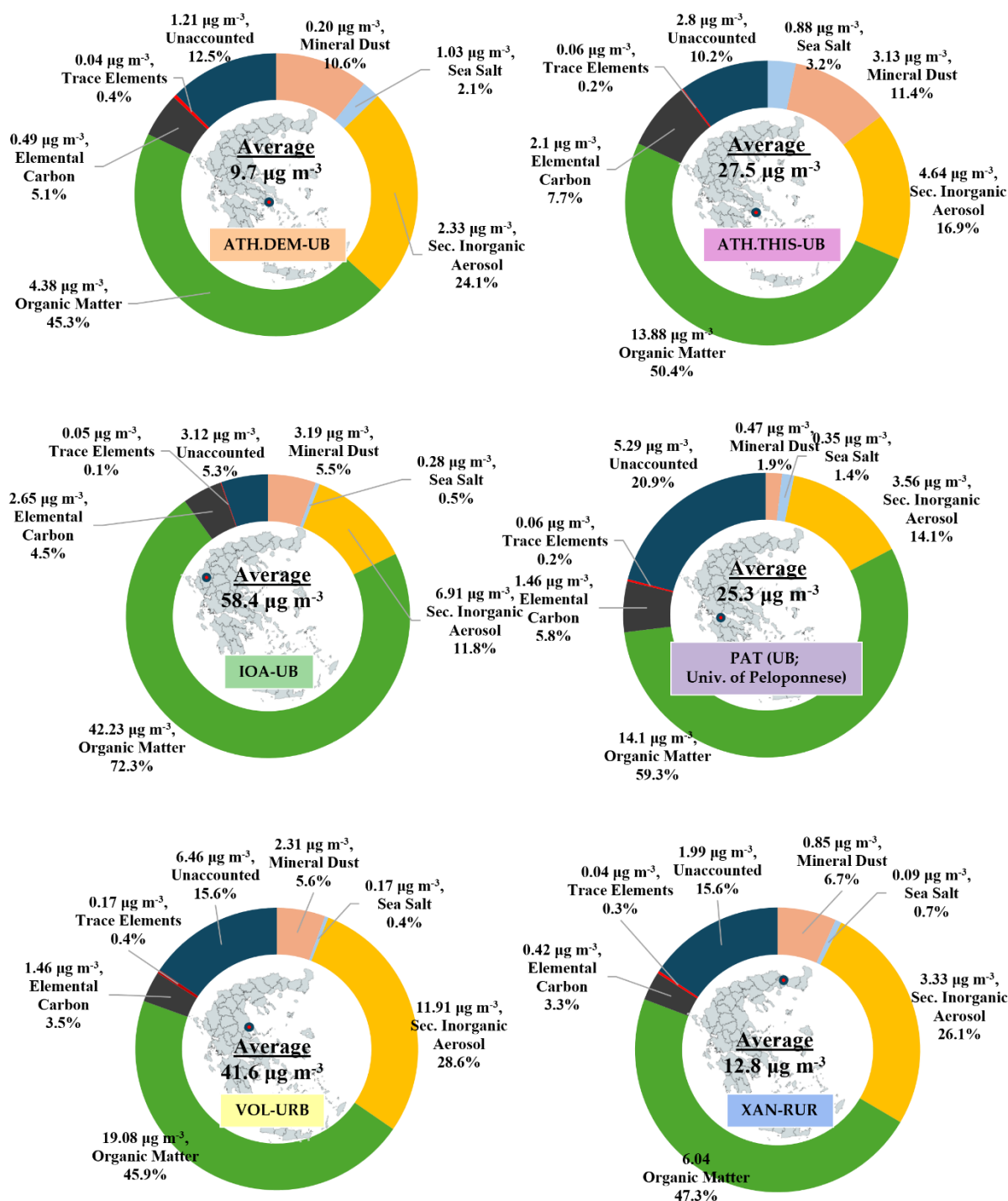


Figure 4: Mass closure contributions for the cold period for the six sites.



3.3 PM_{2.5} Source Apportionment

The EPA PMF 5.0 was applied separately for each site to identify the major PM_{2.5} sources and quantify their contribution to the observed concentration levels. **Table 3** summarizes the input species, number of samples, identified sources, and the specific constraints applied to the PMF model for all six stations.

The factors obtained through PMF were grouped into seven PM_{2.5} source categories, namely: Biomass burning, Heavy oil combustion, Industrial emissions, Mineral dust, Sea Salt, Secondary sulphates & Organics, and Vehicular traffic. There were five shared factors among all sites including: Biomass burning, Secondary sulphates & Organics, Vehicular Traffic, Mineral dust and Sea salt. Industrial sources were found at XAN-RUR and VOL-URB stations, while the Heavy oil combustion was detected at ATH.DEM-UB, ATH.THIS-UB, IOA-UB and VOL-URB. Additionally, the Vehicular Traffic factors showed some variation among the cities. In ATH.DEM-UB, IOA-UB and PAT, Vehicular Traffic was split into two components: Vehicular Exhaust and Vehicular Non-Exhaust, while in ATH.THIS-UB, XAN-RUR and VOL-URB, Vehicular Traffic was identified as a single factor, due to the inability of the PMF model to resolve the distinct contributions of exhaust and non-exhaust emissions. Lastly, a specific industrial source (Cement industrial factor) was identified at VOL-URB, separating it from the other, generic industrial source at XAN-RUR. **Figures S1 to S6** (Supplementary Material) illustrate the PMF factor profiles for each station. The daily time series of reconstructed source contributions, showing the temporal variability and seasonality across stations, are shown in **Figures S7 - S12**. **Figure 5** presents the average source contributions to PM_{2.5} for the different sites.



Table 3. Summary table of input species, number of samples, identified sources and constraints applied to the PMF model.

Station	Input Species	No. of samples	Sources/Factors	Constraints
ATH.DEM-UB	PM _{2.5} , OC, EC, Na ⁺ , NH ₄ ⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Al, Si, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br, Pb	124	Sec. Sulphates & Organics, Oil Combustion, Vehicular Exhaust, Vehicular Non-Exhaust, Mineral Dust, Sea Salt and Biomass Burning.	-Vehicular Non-Exhaust, Zn Pulled Up Maximally -Vehicular Exhaust, EC Pulled Up Maximally - Oil Combustion, V and Ni pulled up maximally, - Secondary Sulphates, EC set to Zero -Biomass Burning, OC Pulled Up Maximally, EC pulled down maximally
ATH.THIS-UB	PM _{2.5} , OC, EC, Na ⁺ , NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Al, Ti, V, Mn, Fe, Ni, Cu, Zn, Pb	108	Sec. Sulphates & Organics, Oil Combustion, Vehicular Traffic, Mineral Dust, Sea Salt, Biomass Burning	-Sec. Sulphates, EC set top Zero, Cl ⁻ Pulled Down Maximally -Oil Combustion, OC and EC Pulled Up Maximally - Mineral Dust, EC set to Zero
IOA-UB	PM _{2.5} , OC, EC, Na ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb	101	Sea Salt, Biomass Burning, Mineral Dust, Vehicular Non-Exhaust, Vehicular Exhaust, Oil Combustion and Sec. Sulphates.	- Vehicular Exhaust, K pulled down maximally.
PAT	PM _{2.5} , OC, EC, Na ⁺ , NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Ca, Ti, Fe, Ni, Cu, Zn, Pb	73	Biomass Burning, Vehicular Exhaust, Vehicular Non-Exhaust, Mineral Dust, Sea Salt, and Sec. Sulphates & Organics.	- Vehicular Exhaust, Fe pulled up maximally.
VOL-URB	PM _{2.5} , OC, EC, Na ⁺ , NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Pb	44	Oil Combustion, Secondary Sulphates & Organics, Biomass Burning, Mineral Dust, Cement Industry, Sea Salt, and Vehicular Traffic.	- Vehicular Traffic, EC & OC pulled up maximally. - Secondary Sulphates, EC set to zero. - Mineral Dust, EC and V set to Zero.
XAN-RUR	PM _{2.5} , OC, EC, NH ₄ ⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Cs, Ba	95	Sea Salt, Secondary Sulphates & Organics, Industry, Vehicular Traffic, Mineral Dust and Biomass Burning.	- Vehicular Traffic, Zn pulled up maximally.





480 Biomass Burning

Biomass Burning (BB) was identified in all six stations as one of the most dominant contributors to $PM_{2.5}$. BB is mainly traced by the high levels of OC, EC and K ([Viana et al., 2008](#)). The OC/EC ratio can help to distinguish between biomass burning and other sources of carbonaceous aerosols since biomass burning typically produces aerosols with a higher OC/EC ratio than other combustion sources because the burning process is not as complete, resulting in more organic matter being emitted along with elemental carbon ([Zhang et al., 2013](#)). This ratio varied between sites: 4.1 in ATH.THIS-UB, 5.7 in ATH.DEM-UB, 6.0 in PAT, 6.2 in XAN-RUR, 10.2 in VOL-URB and 12.3 in IOA-UB. This variability may be attributed to the distinct character of each site, resulting in different types of wood fuel, combustion conditions and ageing, all impacting the obtained source profiles. Cl, Zn, Br, Rb and Pb were also observed in some cases, which are typically tracers of waste burning activities ([Moffet et al., 2008](#)).

490 Nitrate (NO_3^-) was found to contribute significantly to the BB factor profile in most stations. Secondary nitrate may be formed by the oxidation of NO_x emitted by biomass burning. Moreover, BB produces organic aerosols that can act as seeds for nitrate condensation ([Kodros et al., 2022](#)).

The average contributions for BB varied from $1.8 \mu g m^{-3}$ (16.2% of $PM_{2.5}$) at XAN-RUR to $16.3 \mu g m^{-3}$ (50.9% of $PM_{2.5}$) at IOA-UB. Biomass burning emissions showed a strong impact during the winter months for almost all sites, due to the use of wood burning for residential heating (**Figure S7 to S12**). This temporal variability was particularly dominant at IOA-UB, PAT, VOL-URB and ATH.THIS-UB with BB contributions of $28.2 \mu g m^{-3}$ (62.2% of $PM_{2.5}$), $14.2 \mu g m^{-3}$ (58.1% of $PM_{2.5}$), $25.2 \mu g m^{-3}$ (61.2% of $PM_{2.5}$) and $10.4 \mu g m^{-3}$ (50.9% of $PM_{2.5}$) respectively. Regarding the ATH.DEM-UB and XAN-RUR stations, the increase in BB contribution was moderate, with winter-time levels reaching at $4.2 \mu g m^{-3}$ (44.4% of $PM_{2.5}$) and $3.2 \mu g m^{-3}$ (28.0% of $PM_{2.5}$) respectively.

500 Significant contributions from BB during cold season at Ioannina was documented by [Kaskaoutis et al. \(2022\)](#), who reported exceptionally high average Black Carbon from BC_{wb} and $PM_{2.5}$ concentrations of $4.5 \mu g m^{-3}$ and $57.5 \mu g m^{-3}$, respectively. Additionally, they observed very high levoglucosan concentrations, averaging $6.0 \mu g m^{-3}$ and peaking at $15.9 \mu g m^{-3}$. The BB-emitted fine aerosols in Ioannina pose significant risks to public health, due to their content in carcinogenic polycyclic organic compounds ([Tsiodra et al., 2025](#)).

505 In the Athens Metropolitan Area, our winter BB contribution at ATH.THIS-UB ($10.4 \mu g m^{-3}$, 50.9% of $PM_{2.5}$) aligns with the winter range observed by [Theodosi et al. \(2018\)](#) at the same site, where the wintertime BB factor averaged $7.3 \mu g m^{-3}$ (31% of $PM_{2.5}$), reaching $11.3 \mu g m^{-3}$ (39%) during nocturnal hours. On a campaign-average basis, the BB contribution at ATH.DEM-UB ($2.95 \mu g m^{-3}$, 27.5% of $PM_{2.5}$) agrees with the long-term mean of $2.6 \mu g m^{-3}$ (23% of $PM_{2.5}$) reported for the station by [Diapouli et al. \(2017 a\)](#). The contrast between ATH.THIS-UB and ATH.DEM-UB, evident in both campaign averages (6.32 vs. $2.95 \mu g m^{-3}$) and cold periods (10.40 vs. $4.20 \mu g m^{-3}$) may be attributed to the higher residential density in the city center, where ATH.THIS-UB station is located. Additionally, the variation may also be influenced by differences in the time periods during which the sampling was conducted.



Heavy Oil Combustion

515 A Heavy Oil Combustion (HOC) factor was resolved at ATH.DEM-UB, ATH.THIS-UB, IOA-UB, and VOL-URB, characterized by high loadings of V and Ni alongside EC and OC ([Viana et al., 2008](#)). Heavy fuel oils are primarily used in industrial activities, refineries and in ship diesel engines.

Campaign-average contributions of the HOC factor ranged from $0.41 \mu\text{g m}^{-3}$ (2.5% of $\text{PM}_{2.5}$) at ATH.THIS-UB to $2.44 \mu\text{g m}^{-3}$ (8.2% of $\text{PM}_{2.5}$) at VOL-URB. Marked seasonal differences were observed across the network. At VOL-URB, HOC concentrations were four times higher during the warm period than in the cold period (3.20 vs. $0.80 \mu\text{g m}^{-3}$; 14.8% vs. 2.0% of $\text{PM}_{2.5}$), consistent with peak summer passenger and commercial shipping in the harbor. At IOA-UB, higher absolute concentrations were recorded during the cold period than in the warm period (3.00 vs. $1.53 \mu\text{g m}^{-3}$). However, this increase was accompanied by a reduction in relative contribution (falling from 12.6% in summer to 6.6% in winter).

At ATH.THIS-UB, HOC remained consistently low across both seasons ($0.43 \mu\text{g m}^{-3}$ in summer vs. $0.39 \mu\text{g m}^{-3}$ in winter). These levels are consistent with cold-period online observations at Thissio ($0.7 \mu\text{g m}^{-3}$) by [Grivas et al., 2026](#). They also reflect the long-term reduction in shipping-related fine aerosol over central Athens compared to the 2013–2016 period ($1.5 \mu\text{g m}^{-3}$, representing 7% of $\text{PM}_{2.5}$; [Theodosi et al., 2018](#); [Grivas et al., 2026](#)). Conversely, higher HOC contribution was observed at ATH.DEM-UB ($1.62 \mu\text{g m}^{-3}$); the elevated suburban setting of Demokritos (270 m a.s.l.) remains exposed to unhindered maritime advection across the Saronic gulf and Aegean Sea.

530 The CPF plots for the HOC factor are presented in (**Figure 6**). CPF plots for all identified sources are provided in **Figures S13 to S18**. At ATH.DEM-UB, CPF analysis suggested that the HOC factor related to shipping emissions from Piraeus harbor, the Saronic gulf and the Aegean Sea. Moreover, high conditional probabilities from the west pointed to industrial emissions from the Elefsina refineries, in accordance with previous studies ([Diapouli et al., 2017a](#); [Manousakas et al., 2021](#)). At ATH.THIS-UB, high conditional probabilities were concentrated within the south-to-southwest sector, pointing directly toward Piraeus harbor and the Saronic shipping lanes. Previous receptor modeling studies at the site demonstrated that the HOC factor mainly relates to maritime traffic in the port of Piraeus and navigation routes in the Saronic Gulf to the south-southwest, rather than from industrial sources in the Thriassion plain ([Grivas et al., 2018](#); [Theodosi et al., 2018](#); [Grivas et al., 2026](#)). At VOL-URB, the CPF analysis showed high probabilities from the southeast and east, corresponding to the harbor basin and the industrial cement complex. For IOA-UB, peak probabilities coincided with elevated wind speeds from the west and southwest, confirming long-range advection from maritime shipping lanes in the Ionian and Adriatic Seas ([Tsiodra et al., 2025](#)). Additionally, the industrial area of Ioannina (located at the NW outside the city) also contains various industries that utilize HOC (metallurgy, pellet production, etc.).

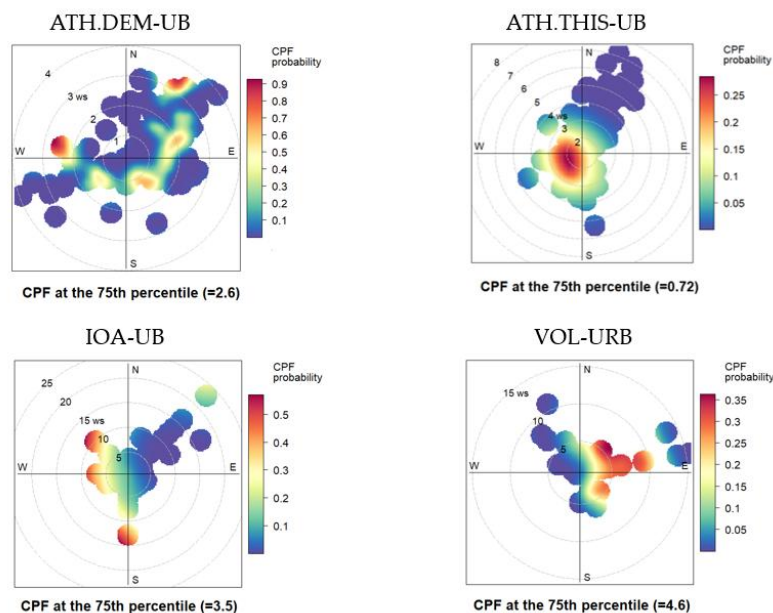


Figure 6: CPF analysis for HOC emissions at the ATH.DEM-UB, ATH.THIS-UB, IOA-UB and VOL-URB stations (an independent HOC factor was not resolved by PMF at PAT and XAN-RUR). Wind speed (ws) is expressed in m s^{-1} .

Industrial Emissions

The presence of Industrial Emissions (IE) has been detected in two cities, Volos and Xanthi. The average contributions of IE varied between $4.2 \mu\text{g m}^{-3}$ (14.4% of $\text{PM}_{2.5}$) at VOL-URB and $0.4 \mu\text{g m}^{-3}$ (3.3% of $\text{PM}_{2.5}$) at XAN-RUR. No typical seasonal variability was observed for any site.

Specifically, in Volos, the presence of certain elements including OC, EC, Ca, Mg, Ti, Fe, V, and Ni were identified as indicators of cement industrial emissions due to the prevalence of cement dust (which contains crustal elements like Ca) and combustion emissions (Papagiannis et al., 2024). Increased concentrations of Ca, Mg and Fe in PM_{10} was also identified in a previous study in the vicinity of the HERACLIS III Lafarge Group cement plant in Greece and was attributed to cement plant emissions (Kourtidis et al., 2014). The cement industrial profile was also compared with published cement and industrial oil profiles from the SPECIEUROPE (EC-JRC) repository (Pernigotti et al., 2016). SPECIEUROPE contains particulate chemical profiles, including organic and inorganic species, derived from both measurements of emission sources and source apportionment studies carried out in Europe. The cement industrial factor identified at VOL-URB showed very good agreement with the profile from Yatkin and Bayram (2008) (Cement Kiln) for the crustal elements but also for elements associated with combustion processes like Ni, V and Zn. One of the largest cement factories in Greece, AGET HERACLIS, is located about 5 km east of the VOL-URB station. Additionally, two industrial areas lie to the west of the station at distances of approximately 5 km and 10 km.



In Xanthi, industrial emissions were detected based on the presence of Ni, Zn, Fe, OC, and Ba, which are typically associated with industrial activities ([Sharma and Mandal, 2023](#)). The industrial area of Xanthi features a number of different applications such as the production and processing of aluminum, batteries and plastic products. Sunlight Group produces high-performance industrial batteries 17 km SW of the sampling site, while Thrace Polyfilms S.A (7 km to the SW), Plastics Pack S.A. and Nonwovens and Geosynthetics S.A. (7 km to the S) produce plastics. Besides OC and Fe, the presence of Ni and Zn indicate metallurgy and combustion activities. 7 km SW of the sampling site SMIRDEX S.A. produces coated abrasives. In the same SW direction there are also other plants with metallurgical activities. Ba also finds extensive use in various industrial applications ([Peana et al., 2021](#)). Its compounds, including nitrate and sulfate, are utilized in the production of a wide range of materials, such as plastics, ceramics, and various adhesives. The high concentration of NH_4^+ in the XAN-RUR PMF profile (**Figure S6**) may bear a contribution from the synthetic fertilizer plant 37 km to the SW. We also note that in the vicinity of the area there are large regions, from Skopje to Sarajevo to the NW that have $\text{PM}_{2.5}$ and PM_{10} concentrations well in excess of EU limit values ([Banja et al., 2020](#)), as well as one of the largest European lignite-fired power plants in Bulgaria (Maritsa Iztok complex). A contribution from these sources to the industrial emissions detected may be possible, since the CPF industry plot for Xanthi (**Figure S11**) shows high probabilities from the NW direction. However, what is the extent of the contribution of transboundary emissions cannot be resolved at this stage, as diurnal changes in wind direction from S-SW during daytime to NW during nighttime are frequent, hence recirculation of emissions from sources in the vicinity may also contribute to the high CPF probabilities from NW.

Mineral Dust

Mineral Dust (MD) is predominantly composed of crustal particles originating from both natural windblown soil erosion and anthropogenic fugitive sources, such as construction activities, agricultural practices, and traffic-induced road dust resuspension. Natural dust occurs when wind traverses over land surfaces, causing the formation or re-suspension of particles characterized by a notable presence of naturally occurring elements found in the Earth's crust, such as Al, Si, Ca, Fe, Ti, Mn and Fe ([Vasilatou et al., 2017 b](#)). MD was identified at all six stations with relative contributions ranging from 4.8% of $\text{PM}_{2.5}$ at PAT to 16.4% at XAN-RUR. The high relative contribution of MD in XAN-RUR reflects the background character of the site. The highest contributions are associated with S and SW directions (**Figure S18**), hence pointing to a contribution from the agricultural fields in the plain extending S of Xanthi.

Beyond local suspension, long-range transport from North Africa contributed substantially to episodic fine crustal concentrations across the network. Intense African dust outbreaks were recorded simultaneously at multiple stations (notably ATH.DEM-UB, IOA-UB, and XAN-RUR), as confirmed by HYSPLIT back-trajectory analysis (**Figure 7**). A major winter dust intrusion occurred between 20 and 22 December 2019, causing daily MD concentrations to surge to $14.3 \mu\text{g m}^{-3}$ at XAN-RUR, $16.8 \mu\text{g m}^{-3}$ at ATH.DEM-UB, and $28.7 \mu\text{g m}^{-3}$ at IOA-UB.

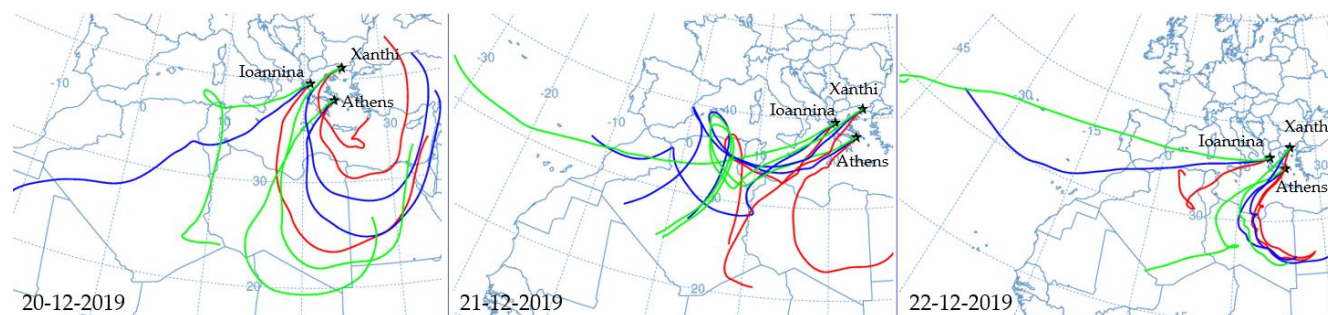


Figure 7: Backward trajectories using Hysplit from NOAA: end at 20, 21 and 22 December 2019 (left to right) at ATH.DEM-UB, IOA-UB and XAN-RUR, indicating the long-range transport of MD from the Sahara Desert. The Green, blue and red lines refer to starting height equal to 1500 m, 1000 m and 500 m, respectively.

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Sea Salt

Sea salt (SS) was identified in all studied locations, and it is mainly traced by the high contributions of Na, Cl and Mg ([Viana et al., 2008](#)). It has to be noted that the Na^+ ion was excluded from Xanthi's database since the S/N ratio was 0.2 ([Paatero and Hopke, 2008](#)) and the profile was traced by the high contribution of Mg^{2+} , Cl^- , SO_4^{2-} , and Br. A noteworthy characteristic of aged sea salt was consistently observed in all cases, which can be traced by the Cl depletion and high NO_3^- contribution in the obtained profiles. The extent of chloride depletion in sea salt can be estimated by calculating the mass concentration ratio of Cl/Na, which in seawater has been reported to be typically around 1.81 ([Bowen, 1979](#)). The Cl/Na ratio ranged from 0.2 to 0.9 for all cities, except for XAN-RUR, where Na^+ data were excluded from the input database. Significant proportions of Bromine (Br) were observed in SS emissions at both IOA-UB (29.8%) and XAN-RUR (23.9%), in addition to the major species typically associated with these emissions. The Cl/Br ratio, a key indicator of the SS profile in Xanthi, generally ranges between 288 and 292 ([Davis et al., 1998](#)). Notably, the measured Cl/Br ratio for Xanthi's profile was 299, which closely aligns with this expected range.

The contributions of SS ranged between 1.6% of $\text{PM}_{2.5}$ at IOA-UB and 11.7% at ATH.THIS-UB. A notable seasonal variability was observed across the network, characterized by distinctly higher SS contributions during the cold period at most locations. The most pronounced winter increase occurred at XAN-RUR, PAT, and both Athens sites (ATH.DEM-UB and ATH.THIS-UB), where cold-season mass concentrations were two to four times higher than those recorded in the warm season. For example, the relative SS contribution at XAN-RUR surged from 2.6% ($0.3 \mu\text{g m}^{-3}$) in the warm period to 10.5% ($1.2 \mu\text{g m}^{-3}$) in the cold period. We note that the sea is to the south of the XAN-RUR station and mean daily wind direction vectors at XAN-RUR are from SW to NW directions during summer and from SE to SW directions during winter, so the site receives more air of marine origin during the latter season. Conversely, the absolute SS concentrations at VOL-URB and IOA-UB remained relatively stable year-round, lacking significant seasonal fluctuations.

620



Secondary Sulphates & Organics

625 Secondary aerosols are not directly emitted into the atmosphere from a single identifiable source. Instead, they form through chemical transformations of gaseous precursors originating mainly from combustion processes and biogenic emissions during summer. These transformations lead to the conversion of these precursors into PM over varying time scales, also involving heterogeneous processes. As a result, secondary aerosols may contain marker species that are also found in anthropogenic emissions (Viana et al., 2008). Secondary sulphates, specifically, are associated with long-range transport events and are
630 commonly found in "aged air masses" due to the gradual oxidation of sulfur dioxide (SO_2) to sulfate (SO_4^{2-}) (Manousakas et al., 2017).

The Secondary Sulphates & Organics (SSO) factor was resolved across all six sites; it was identified as Secondary Sulphates & Organics (SSO) at five stations, whereas in Ioannina it was resolved predominantly as inorganic Secondary Sulphates with a negligible OC contribution (**Figure S3**). The dominant components of the Secondary sulphate & organics
635 profile were found to be SO_4^{2-} , NH_4^+ , and OC. This outcome arises from the secondary formation of aerosols in the atmosphere through the photochemical oxidation of released gaseous sulfur oxides and volatile organic compounds (VOCs). Similar SSO profiles were also identified by Amato et al. (2016), Diapouli et al. (2017a), and Paraskevopoulou et al. (2015) containing both $(\text{NH}_4)_2\text{SO}_4$ and OC at urban background and suburban sites in Europe. Additionally, the presence of EC in the ATH.DEM-UB profile (10.9%) may suggest mixing with other primary sources.

640 The lowest SSO relative contribution was found at IOA-UB (7.1%), followed by ATH.THIS-UB (19.8%), while all other sites displayed similar contributions ranging from 26.7 – 33%. A noticeable seasonal pattern emerged, with higher SSO concentrations observed during the warmer months. This temporal trend is attributed to enhanced photochemical oxidation during periods of higher solar radiation and temperature, coupled with increased biogenic VOC emissions from surrounding vegetation, which promote secondary organic aerosol formation at sites with extensive forested cover such as XAN-RUR.

645

Vehicular Traffic

The identified Vehicular Traffic (VT) factors varied across the studied locations. At ATH.DEM-UB, IOA-UB, and PAT, the VT factor was further subdivided into two distinct components: Vehicular Exhaust (VEX) and Vehicular Non-Exhaust (NEX). However, at ATH.THIS-UB, XAN-RUR, and VOL-URB, the PMF model was not able to differentiate between exhaust and
650 non-exhaust emissions.

The traffic-related profiles associated with NEX were primarily traced by species originating from crustal sources, such as Fe, Mn, and Ti, representing road dust (Jandacka et al., 2023), as well as trace elements like Cu and Pb, indicative of brake and asphalt wear, respectively (Huang et al., 2018; Thorpe and Harrison 2008; Jeong et al., 2022).

655 NEX relative contribution was generally low, ranging on average from 2% at ATH.DEM-UB to 7.8% at PAT. The difference in concentration values can be attributed to the varying proximities of the sampling stations to busy traffic arteries.

The VEX sources were primarily composed of carbonaceous compounds (OC and EC). The highest OC/EC value was found at ATH.DEM-UB (12.9), which may be related to a reduced share of diesel vehicles in the local fleet, aligning well



with the findings of [Amato et al. \(2016\)](#). A lower OC/EC ratio was observed at IOA-UB (5.3) and PAT (5.7), suggesting a potentially higher contribution from diesel cars to the VEX profiles in those regions. In addition to OC and EC, other trace elements such as Ca, Zn, Ni, Fe, and Mn, related to lubricating oils and engine wear, were also detected, which could be emitted from vehicle tailpipes, as noted in the study by [Wang et al. \(2021\)](#). The concentrations of VEX emissions ranged from $0.8 \mu\text{g m}^{-3}$ (7.7% of $\text{PM}_{2.5}$) at ATH.DEM-UB, to $7.2 \mu\text{g m}^{-3}$ (22.6% of $\text{PM}_{2.5}$) at IOA-UB.

At IOA-UB, combined traffic emissions (VEX and NEX) accounted for 27.6% of $\text{PM}_{2.5}$ ($8.8 \mu\text{g m}^{-3}$), compared to the 16% total traffic share reported by [Tsiodra et al. \(2025\)](#), where only a single combined factor was resolved. Regarding wind directions, [Tsiodra et al. \(2025\)](#) linked peak traffic contributions to the entrance of the southern highway into the basin. Our CPF plots showcase that non-exhaust probabilities are highest from this southern road axis, while exhaust emissions also point toward the east-north-east, reflecting traffic from the main urban avenues and the commercial center (**Figure S15**). At PAT, where sampling moved from a rural site in summer (ICE-HT) to an urban background site in winter (University of Peloponnese), the elevated traffic levels were driven by the cold period. During winter, proximity to urban traffic arteries combined with lower boundary layer heights led to a sharp increase in VEX ($6.2 \mu\text{g m}^{-3}$; 25.4% of $\text{PM}_{2.5}$), compared to only $0.9 \mu\text{g m}^{-3}$ (7.5%) at the rural summer location. In contrast, the ATH.DEM-UB station is situated further from the city center, and is characteristic of the suburban areas of Athens, where direct primary emissions undergo a certain degree of ageing. This likely explains the high OC/EC ratio in the VEX profile (indicative also of aged VEX emissions) and the lower contributions observed at ATH.DEM-UB.

Combined vehicular traffic (VT) profiles (including both exhaust and non-exhaust emissions) were observed at ATH.THIS-UB, VOL-URB and XAN-RUR. These profiles comprised carbonaceous species (OC and EC) along with substances associated with brake, tire, and road wear, as well as dust resuspension, such as Cu, Zn, Pb, Ba, Ca, Fe, Mn and Cs ([Viana et al., 2008](#); [Khan et al., 2017](#)). In contrast to ATH.DEM-UB, the ATH.THIS-UB station exhibited a significantly lower OC/EC ratio of 4.4, suggesting more fresh exhaust emissions and/or increased share of diesel vehicles (such as taxis). This difference can be expected due to the ATH.THIS-UB station's closer proximity to the Athens city center. The highest OC/EC ratio was observed in the XAN-RUR VT profile, pointing to aged exhaust emissions in this background site. In total, traffic emissions contributed around 10% to 12% at ATH.DEM-UB ($1.0 \mu\text{g m}^{-3}$), VOL-URB ($3.3 \mu\text{g m}^{-3}$), and ATH.THIS-UB ($2.0 \mu\text{g m}^{-3}$), and between 27% and 28% at PAT ($4.9 \mu\text{g m}^{-3}$) and IOA-UB ($8.8 \mu\text{g m}^{-3}$), while Xanthi stood at 24.1%.



4 Conclusions

In the current study, we conducted source apportionment analyses for PM_{2.5} in five Greek cities—Athens, Ioannina, Xanthi, Volos, and Patras, covering both summer (June-August) and winter (December-February) of 2019-2020. A supplementary campaign at the Athens "Thissio" station from December 2018 to March 2019 and July to August 2019, provided insight into the variability of PM_{2.5} levels and sources within the Greater Athens Area.

The observed average PM_{2.5} concentrations varied substantially across the studied locations, with Ioannina showing the highest levels ($39.9 \pm 35.8 \mu\text{g m}^{-3}$), followed by Volos ($29.8 \pm 15.4 \mu\text{g m}^{-3}$), Athens "Thissio" in the city centre ($20.7 \pm 15.3 \mu\text{g m}^{-3}$), Patras ($18.7 \pm 9.5 \mu\text{g m}^{-3}$), Xanthi ($12.9 \pm 5.3 \mu\text{g m}^{-3}$), and Athens "Demokritos" in the suburbs ($11.0 \pm 4.1 \mu\text{g m}^{-3}$). Notably, campaign averages in Ioannina and Volos exceeded $25 \mu\text{g m}^{-3}$, pointing to a substantial air pollution burden and high risk of non-compliance with European standards, whereas concentrations at the remaining stations were lower.

Seven source categories were identified: biomass burning, heavy oil combustion, industrial emissions, mineral dust, sea salt, secondary sulphates, and vehicular traffic. Five of these sources: biomass burning, secondary sulphates, traffic, mineral dust, and sea salt were consistently present across all sites, highlighting their widespread regional impact on PM_{2.5} pollution in Greece.

Biomass burning was identified as a dominant source of PM_{2.5} across all stations, with significant contributions, particularly during the winter, due to the continuous use on wood for residential heating, even in recent years. This issue was especially pronounced in Ioannina and Volos, where winter BB contributions reached $28.2 \mu\text{g m}^{-3}$ (62.2% of PM_{2.5}) and $25.2 \mu\text{g m}^{-3}$ (61.2% of PM_{2.5}), respectively, highlighting the severity of the problem in these areas. The average contributions of BB ranged from 27.5 to 50.9%.

Secondary Sulphates & Organics (SSO) was also identified as a major source of PM_{2.5}, with relative contribution ranging from around 20 to 33%, at all cities, except for Ioannina. In Ioannina this source related mainly to Secondary Sulphates and had a much lower contribution (7%). SSO displayed significant seasonal variability with increased contributions during the warmer months due to enhanced photochemical activity.

Heavy oil combustion was identified in Athens, Ioannina and Volos and was primarily associated with industrial activities and shipping emissions. Across the stations, HOC contributions to PM_{2.5} averaged between 2.5% and 15.1%. Industrial emissions (IE) were prevalent mainly in Volos ($4.2 \mu\text{g m}^{-3}$ - 14.4% of PM_{2.5}), while a small contribution was also found in Xanthi. The contribution from IE showed no significant seasonal variation, indicating a consistent year-round impact.

Vehicular traffic contributed substantially across all environments, accounting for 10% to 28% of PM_{2.5}. The contribution of VEX was always larger than the NEX; NEX are expected to be found mostly in the coarse fraction and are, thus, not fully captured by PM_{2.5} measurement. In total, traffic emissions contributed significantly to the observed PM_{2.5} concentration levels, even at rural background sites, such as is the case in Xanthi.

Mineral Dust was detected across all cities, with contributions from both local sources and long-range transport events from northern Africa. Sea Salt was also identified through sodium (Na), chloride (Cl), and magnesium (Mg). The Cl/Na ratio



ranged from 0.2 to 0.9, indicating significant chloride depletion, which points towards aged sea salt mixed with anthropogenic pollution. These two natural sources contributed on average between 6.8% and 26.2%.

Overall, this study provides the first harmonized overview of PM_{2.5} sources across multiple Greek urban environments, establishing a robust reference dataset for future air-quality assessments and supporting the development of evidence-based mitigation strategies under increasingly stringent European air-quality standards.

Code and data availability

The datasets generated and analyzed during this study are deposited in the Zenodo repository at <https://doi.org/10.5281/zenodo.22794818> (Papagiannis et al., 2026).

Supplement link

The link to the supplement will be included by Copernicus.

Author contributions

KE, NM, and ED contributed to the conceptualization of the study. ED, NM, KE, and SP provided the methodology. All authors performed the investigation and data curation. SP conducted the formal analysis. ED performed the validation. SP and LD were responsible for visualization. KE, NM, KK, and CK handled the project administration. KK also performed filter handling at the XAN-RUR site. SP and ED prepared the original draft. All authors contributed to reviewing and editing the manuscript.

Competing interests

At least one of the (co-)authors is a member of the editorial board of *Aerosol Research*. The authors have no other competing interests to declare.

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750 Review statement

The review statement will be added by Copernicus Publications listing the handling editor as well as all contributing referees according to their status anonymous or identified.

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