

Chemical characterization and source apportionment of PM₁₀ in Belgrade, Serbia: influence of local and regional anthropogenic and natural sources

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Abstract

Substantial efforts and improvements in air quality across Europe lowered levels of air pollutants including particulate matter (PM) in the last decades. However, significant proportion of the European population still lives in areas exceeding WHO recommendations, especially in Northern Italy, Balkans and Eastern Europe, including Serbia. Targeted PM mitigation strategies require extensive air quality monitoring and modelling including source apportionment (SA) studies. In the past, numerous SA studies were conducted for Belgrade city, capital of Serbia. Nevertheless, comparisons across the results are difficult, as they encompass different datasets of pollutants contained in PM fractions such as elements and/or ions and/or PAHs. Here, the aim is to offer a broader insight on PM₁₀ sources at an urban background site in Belgrade by including 34 species as input variables for SA (carbonous aerosols, elements, ions and specific organic tracers). For SA, the USEPA PMF 5.0 software was applied. The factor that dominated PM₁₀ mass was biomass burning (21%), primarily during heating season, followed by ammonium sulphate (18%) and mineral dust (17%). A mixed traffic and industrial activity accounted for 15% of PM₁₀ mass while contribution of factors from biological origin, primary biological aerosol particles and biogenic secondary organic aerosols from isoprene, was 10% each. Mixed factor of long-range transport and road salt/local combustion contributed to the PM₁₀ mass 9%. This analysis provides more detailed perspective on the composition and sources of PM₁₀ in Belgrade, both from anthropogenic and natural, including biological origin. These findings are valuable for defining targeted PM₁₀ mitigation strategies.

Key words: air pollution, particulate matter, PM₁₀, source apportionment, chemical composition, organic tracers

1. Introduction

The World Health Organization (WHO) estimated that 4.2 million premature deaths at the global level are caused by exposure to outdoor air pollution (WHO, 2024). Among the air pollutants, particulate matter (PM) represents the biggest health concern. PM may originate from both anthropogenic and natural sources. These sources emit particles that vary in size, morphology, and chemical composition, and these differences influence how particles may be harmful for human health (Liu et al. 2025). Coarse particles (<10 µm and >2.5 µm) primarily deposit in the extra thoracic airways, whereas fine (<2.5 µm) and ultrafine particles (10-100 nm) (Ruuskanen et al. 2001) can penetrate deeper into the pulmonary region of respiratory tract (Khan et al. 2022, Zhai et al. 2024). Exposure to particles lower than 10 µm (PM₁₀)

is related to increased mortality and morbidity from cardiovascular and respiratory diseases (Polichetti et al. 2009; Newell et al. 2017). In 2016, the International Agency for Research on Cancer (IARC) classified outdoor air pollution, as well as PM, as carcinogenic to humans (group 1) based on sufficient evidence in both humans and experimental animals. According to IARC, exposure to PM contributes to the development of lung cancer (IARC, 2016).

Although substantial efforts and improvements in air quality across EU significantly lowered levels of air pollutants (especially SO₂, NO_x) in the period from 2000 to 2019 (Aas et al. 2024), there is still important proportion of the European population that lives in areas exceeding WHO recommendations (EEA, 2025a). The most severe situation is in low- and middle- income countries where is estimated that citizens are exposed to up to four times higher levels of ambient PM_{2.5} (Health Effects Institute, 2024). Cohen et al. (2017) demonstrated that even modest increases in PM concentrations can result in disproportionately large increases in health risks, underscoring the need for further mitigation. Moreover, substantially stronger evidence now indicates that air pollution may impact human health at lower exposure levels than previously recognized (Stafoggia et al. 2022). Therefore, the WHO established new guidance levels in 2021 where new set of annual and daily average levels of PM₁₀ and PM_{2.5} are lowered and may be used by policy makers who are responsible for air pollution control. WHO recommended average annual PM₁₀ and PM_{2.5} levels are 15 µg/m³ and 5 µg/m³ while average 24-hour target level is 45 µg/m³ and 15 µg/m³, respectively. Many studies demonstrated correlation between exposure to PM_{2.5} and cardiopulmonary and lung cancer mortality, making it the world's leading environmental risk factor (McDuffie et al. 2021, Burnett et al. 2018, Pope et al. 2002). However, some authors highlight that the health effects from coarse particulate matter should not be overlooked as the adverse health effects related to this fraction distinct beyond the attributable effects of PM_{2.5} alone. Therefore, the continuous monitoring of PM₁₀ is necessary as it includes both coarse and fine fraction (Tian et al. 2020, Choi et al. 2026).

Targeted airborne PM₁₀ mitigation strategies (< 10 µm) require extensive air quality monitoring and modelling including source apportionment studies. Therefore, new EU Air Quality Directive underlines the importance of monitoring at supersites novel pollutants such ultrafine particles, black carbon and elemental carbon, ammonia and oxidative potential (Directive (EU) 2024/2881). Directive emphasize that it is crucial to systematically monitor air quality in areas where pollutants concentrations are high, and measurements are scarce. Annual PM₁₀ levels in Serbia in 2023 and 2024 exceeded EU limit value (40 µg/m³) on several monitoring sites in Belgrade, Valjevo, Užice, Zaječar, Novi Pazar and Šabac. In 2023 and 2024, PM₁₀ was the pollutant with the highest number of exceedance days in the Republic of Serbia (SEPA, 2024, 2026). European Environment Agency reports show that Serbian PM₁₀ levels in 2023 were higher than European averages (EEA, 2025b) and Health Effects Institute report that air quality monitoring data is still scarce in this area (Health Effects Institute, 2022). Liu et al. 2025 emphasised that sources like secondary aerosols and road traffic, show consistent chemical profile, temporal variability, and contribution to PM₁₀ concentration in source apportionment studies conducted in twenty-four cities across Europe. However, emissions from industry, heavy oil combustion, and crustal sources vary considerably by location, making local source apportionment essential for effective pollution control.

Source apportionment studies using different approaches were also conducted in Belgrade Metropolitan area, collectively covering the sampling period from 2003 to 2015. The sources most commonly identified were coal and wood combustion, secondary aerosols, traffic (vehicle exhaust) and mineral matter (Mijić et al. 2012; Cvetković et al. 2015; Stojić et al. 2016; Todorović et al. 2020). The influence of marine aerosol, construction activities, fertilizer plant, oil combustion and industry were observed too (Rajšić et al. 2008; Đorđević et al. 2012) (Table S1, Figure S1). In these studies, source with the biggest contribution to PM concentration was coal and wood combustion which authors mainly attributed to the thermal power plants “Kolubara A” and “Nikola Tesla A and B”, located in 50 km and 25 km from the Belgrade Metropolitan area, tens of kilometers from the central zone, respectively, as well as the usage of coal and wood for district and household heating. (Đorđević et al. 2012) observed that the dominant ionic specie in 2008 in Belgrade

was formation of ammonium sulphate. Sulphate in the atmosphere mainly originates from the oxidation of SO₂ in urban areas and ammonium ion originates from biogenic NH₃ but also from fertilizer plant located in Pančevo, 15 km away from Belgrade (Đorđević et al. 2012). However, the fertilizer plant in Pančevo ~~was closed out of work during WeBaSOOP campaign today~~. In the period when the majority of the abovementioned studies were conducted, the consumption of natural gas for district heating was only 30% of the total gas consumption in Serbia (period 2001 - 2010) (Ivezić et al. 2016). Today, natural gas is the main fuel used for district heating in “Belgrade Power Plants” (<https://beoelektrane.co.rs/zastita-zivotne-sredine/>). Further, by 2020, around 1300 heating boilers within the “Belgrade Power Plants” system had been shut down and reoriented to operate on natural gas (<https://beoelektrane.co.rs/ona-nama/osnovni-podaci/>). In 2024, the flue gas desulphurisation plant at “Nikola Tesla A” started operating which resulted in reduction in SO₂ emissions (<https://www.eps.rs/eng/Pages/Istorija.aspx>). The international E-70 highway passes through Belgrade but today, it functions primarily for local transport since the new bypass road around Belgrade now serves as the main transit road (Ćirović et al. 2026).

Abovementioned studies used different receptor modelling (Unmix, principal component analysis, positive matrix factorisation (PMF)), making it difficult to compare obtained results. ~~In addition, sampling sites where daily (24h) filter samples were collected, were in Belgrade city area, in triangle of 20 km² as it is presented at Figure S1. For one of SA study, Cvetković et al. (2015), one site was in the medium of triangle and another two sites were out of triangle nearby thermal power plants in Metropolitan area of Belgrade far away for several tens of kilometers from the city center. Only studies of Todorović et al. (2020) and Almeida et al. (2020) overlap with the period of sampling and sampling site as filter samples were collected at the urban background area at Zeleno Brdo (Figure S12). Furthermore, species that were used for in these SA studies were different (Table S1). Some studies were performed used only upon analyses of elements (Mijić et al., 2012, Rajšić et al., 2008, Almeida et al. 2020), ions (Đorđević et al., 2015) or PAHs (Cvetković et al., 2015) for source apportionment. Almeida et al. 2020 for SA study used data collected for 16 months and concentrations of elements while— Todorović et al. (2020) as input data set used one year of Almeida et al. (2020) data set and performed additional analyses of ions.~~ In light of this, the present study aimed to perform PM₁₀ source apportionment in Belgrade using PMF, a multivariate receptor model capable of ~~identifying factors without prior knowledge of locally relevant source profiles~~ resolving PM mass concentration into contributions of various source types (Paatero and Hopke, 2009) by utilizing error estimates of the ~~species -elements~~ from the data matrix and implements strict non-negativity constraints for the factors (Paatero and Tapper, 1994). ~~Input data set of one yearlong campaign consist of more than thirty species contained in PM₁₀ of atmospheric aerosols in Belgrade. That was for the first time that is perform SA upon data set that contain levels of both carbonaceous aerosols (OC, EC) -and organic tracers in the Republic of Serbia and even in wider Western Balkan area. (Hopke et al. 2020) and allows for the quantification of both the chemical composition of these factors and their contribution to PM concentrations (Weber et al. 2019). The objective of the study is to offer a broader perspective on PM₁₀ sources by incorporating ions and, elements, and for the first time number of tracers for biogenic aerosols as well as tracers for biomass burning together with OC and EC as input variables, and thereby quantify both natural, including biological, and anthropogenic sources at an urban background site in Belgrade.”~~

2. Material and methods

2.1. Sampling site

Our sampling campaign was performed at an urban background monitoring site Ada Marina (44.790166° N, 20.4169° E; 71 m above sea level) which is a part of the local air quality network in Belgrade Metropolitan, ~~operated by~~

120 ~~Public Health Institute of Belgrade~~ (Fig. 1) ~~where they have been measured~~ main air pollutants and meteorological
parameters (temperature, relative humidity, wind speed, wind direction and atmospheric pressure) have been measured.
Site is located at Ada Ciganlija, the largest recreational area in the central area of Belgrade city, along the Sava River.
Possible pollution sources include numerous restaurants in the vicinity of the site places around the lake, biomass burning
from the nearby residential area and a high traffic arterial road nearby. In addition, E-70 highway is located approximately
125 250 meters away from the sampling site. Other potential sources of aerosol pollution include a natural gas heating plants
for district heating, located about 1.5 km to the Northwest and Southeast. Airport “Nikola Tesla” is 10 km in the
Northwest. A municipal landfill at Vinča settlement is 10 km to the East. Another possible pollution source is road traffic
associated with 1.7 million citizens and the fact that passenger car fleet in Serbia primarily consist of imported, fossil-
fuelled second-hand cars (Mijailović et al. 2019). Furthermore, the coal-fired thermal power plant “Nikola Tesla” is
130 located around 25 km to the Southwest while power plant “Kolubara” is distanced 50 km to the South of the Ada Marina
site. Outside the city, there are the areas of agricultural activity as well as Smederevo ferrous smelter and “Kostolac”
thermal power plant, 30 km and 60km, respectively, to the East.

2.2 Aerosol filter samples

Three simultaneous ambient aerosol filter samples were collected from 6.6.2023 to 28.5.2024, each from three
135 co-located and identical low-volume samplers (LVS3, Leckel, $2.3 \text{ m}^3 \text{ h}^{-1}$) equipped with PM_{10} inlets. Daily filter samples
were collected for 24 hours. The field campaign lasted for one year, and for PMF analysis seven representative samples
for each month were used which yielded in 84 PM_{10} samples. The samplers were loaded with quartz fibre filters
(PALLFLEX Tissuequartz 2500QAT-UP, 47 mm in diameter), which were conditioned at $20 \pm 1 \text{ }^\circ\text{C}$ and $50 \pm 1 \text{ \% RH}$ for
48 h prior to sampling to enable gravimetric determination of PM_{10} mass. Filters from one sampler were designated for
140 the analysis of OC, EC, organic tracers, and oxidative potential. Filters from a second sampler were conditioned following
exposure for gravimetric analysis, then stored in polystyrene Petri slides at $-20 \text{ }^\circ\text{C}$ until elemental and ionic analyses were
performed. PM_{10} filter samples from a third sampler were retained as backups. All filters were stored at $4 \text{ }^\circ\text{C}$ prior to
exposure and at $-20 \text{ }^\circ\text{C}$ afterward. Field blank filters were collected to assess potential contamination during handling
and transport. OC, EC, ions, elements and organic tracers were analysed from 84 samples.

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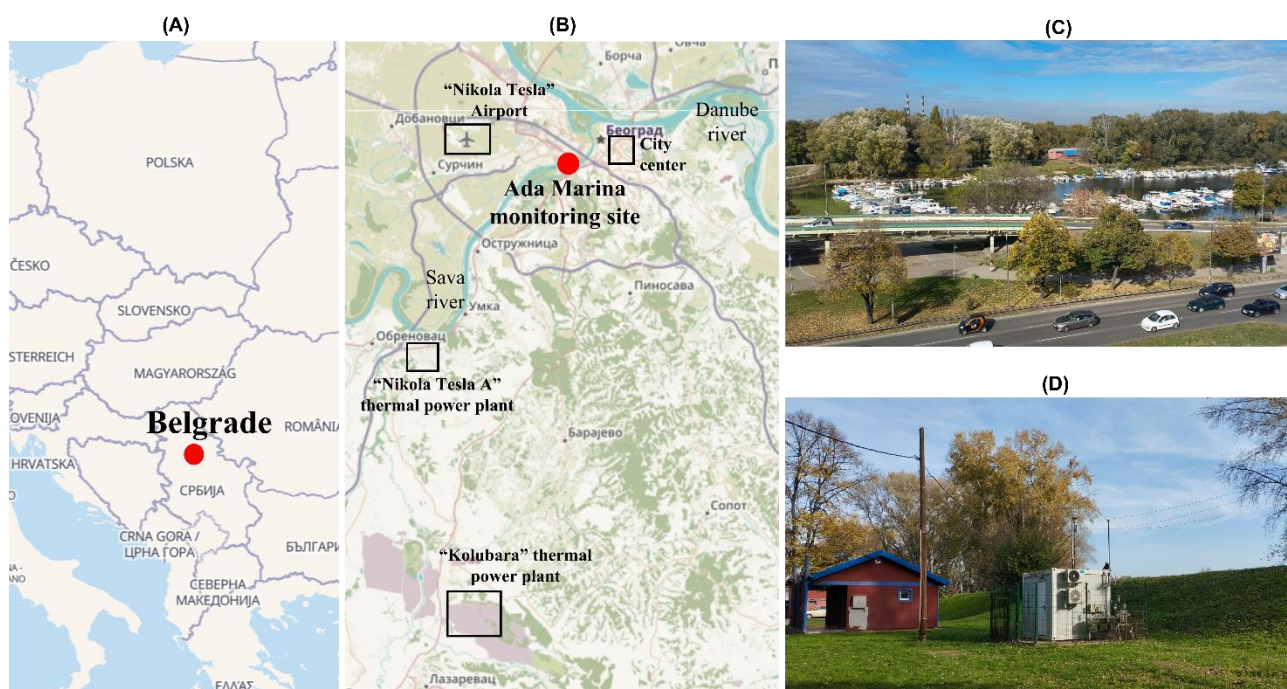


Figure 1. Location of the sampling site at Ada Marina, Belgrade, Serbia (Source: © OpenStreetMap contributors), (A) Map of Serbia with neighbouring countries, (B) wider region of the Belgrade area with points of interest, (C) and (D) the nearest surrounding of the monitoring site.

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2.3 Measurement of OC and EC

Organic carbon (OC) and elemental carbon (EC) were measured by thermal-optical analysis using a Sunset Laboratory OC/EC aerosol analyser. The instrument operated according to the EUSAAR-2 temperature protocol (Cavalli et al. 2009) using optical transmission correction for charring.

155 2.4. Measurement of the elements and ions

The elements (Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, Ba, Pb, P, Ti, Zr, Mo, Sb, Sn) were quantified utilizing inductively coupled plasma – mass spectrometry (Agilent model 7700), following the procedure described in (Querol et al. 2001). Ions (Cl^- , NO_3^- , SO_4^{2-} , NH_4^+) were analysed from the solid phase of suspended particles in the air using ion chromatography (IC). The analysis was performed on Thermo Scientific Dionex™ ICS-1600 ion chromatograph with suppressed conductometric detection.

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2.5. Measurements of organic tracers

Organic tracers (Table 1) were analysed using ultra-high-performance liquid chromatography (UHPLC; Vanquish UHPLC, Thermo Fisher Scientific) coupled with a Q Exactive™ Plus Orbitrap mass spectrometer (Thermo Fisher Scientific), following the method described by (Yttri et al. 2024).

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Table 1. Organic tracers analysed in this study and their source categories.

Organic tracers	Sources
Levoglucosan, mannosan galactosan	Biomass burning
Arabitol, mannitol, fructose, glucose, trehalose	Primary biological aerosol particles

2.6. Positive matrix factorization model

In the present study, the EPA PMF v.5.0 has been used. Our data matrix dimensions were 84×44 (sample number, number of species, respectively). As the input data we used concentration of species obtained from filter analysis and uncertainties calculated following procedure in (Norris et al. 2014). Uncertainties were calculated using Eq. (1) if the concentration of the species was higher than limit of detection (LOD) value.:

$$u = \sqrt{(\text{error fraction} \times \text{concentration})^2} + \sqrt{(0.05 \times \text{LOD})^2} \quad (1)$$

In the model, if the concentrations of the species were assigned as “below LOD”, a value equal to 1/2 of the LOD was entered. if the concentration data was below the LOD, it was replaced with half of the LOD and For those species below LOD, the uncertainties were set to calculated as 5/6 of the LOD (Polissar et al. 1998Glojek et al. 2024). Error fraction for all species was 20%.

In this study, signal-to-noise ratio (S/N) and percentage of the samples below LOD (50%) were used to classify species as “strong”, “weak” and “bad”. Species selected for PMF are reported in Table S4Fig. S1. The species that had $S/N < 1$ and samples below LOD $> 50\%$ were considered as “bad” (in our study Se, Ga, Co, Zr), while species that had $S/N < 1$ and samples below LOD $< 50\%$ and vice versa ($S/N > 1$, below LOD $> 50\%$) were considered as “weak” (Cl⁻, Cu, As, Cd, Ti, Sn). Species with S/N ratio > 1 and samples below LOD $< 50\%$ were considered “strong” (OC, EC, NO₃⁻, SO₄²⁻, NH₄⁺, Na, Mg, Al, K, Ca, V, Mn, Fe, Rb, Sr, Pb, Sb, galactosan, mannosan, levoglucosan, 2-methylerythritol, 2-methylthreitol, glucose, fructose, mannitol, arabitol, trehalose). Few species, although having a satisfactory S/N and percentage of above LOD, were excluded from the model due to the contamination of the blanks (Cr, Ni, Mo, Ba) or higher analytical uncertainty of the results (Inositol, Erythritol, Zn, P).

To determine the optimal number of factors, solutions with a total number of factors from 3 to 9 with random seed number and no applied factor constraints were examined. The final solution was derived from 100 base runs, with robustness evaluated according to the recommendations of the European guide on air pollution source apportionment with receptor models (Belis et al. 2019a): (1) all factors’ chemical profile and temporal variability could have been interpreted, (2) $Q_{\text{true}}/Q_{\text{exp}}$ ratio, (3) normal distribution of modelled species with more than 95% uncertainty-scaled residuals was within ± 3 , and (4) on displacement (DISP) and bootstrap (BS) analysis which confirmed the stability of the model.

The input data included sets of chemical tracers that allowed identification of chemical profile and temporal variability connected to certain sources based on previously conducted studies. Therefore, levoglucosan, mannosan, galactosan, K, Rb, OC and EC were tracers for biomass burning (Yttri et al. 2011, Weber et al. 2019), sugars and sugar alcohols for primary biological aerosol particles (Bozzetti et al. 2016) and 2-methyl tetrols for biogenic secondary organic aerosol from isoprene (Srivastava et al. 2018) (Table 1). As mineral dust tracers were considered Al, Ti, Sr, Ca, Mg (Moreno et al. 2006, Tursun et al. 2025), As, Cd, Ni indicated industrial emission (Querol et al. 2007) and EC, Sb, Sn, Fe, Pb for exhaust and non-exhaust emissions (Amato et al. 2009, Srivastava et al. 2018). Q_{true} was 1574.62 and Q_{robust} 1574.66 which resulted in $Q_{\text{true}}/Q_{\text{exp}}$ ratio of 1.03 which is less than 1.5 meaning the effect of outliers on the results was negligible (Belis et al. 2019a). In case of DISP test, no factor swaps were reported and the change in Q value remained minimal (-0.013). BS analysis based on 100 runs is showed in Table 2). All factors had > 70 out of 100 mapped factors which is considered as appropriate solution (Belis et al. 2019aGlojek et al.2024). The extra model uncertainty was 7%.

205 The correlation between observed and modelled PM₁₀ concentrations was 0.92 indicating good reconstruction of PM₁₀ mass concentration.

Table 2. Bootstrap values of the base run.

Factors	BS mapped factors
Biomass burning	100
NaCl/COMB	92
Mineral dust	100
PBAP	100
BSOA _{Isoprene}	100
Ammonium sulfate	88
TRA/IND	92

210 NaCl/COMB – long-range transport and road-salt/local combustion; PBAP – primary biological aerosol particles; BSOA_{Isoprene} – biological secondary organic aerosol from isoprene; TRA/IND – traffic/industry factor.

2.7. Air mass transport modelling

215 To examine and support the physical plausibility of the resolved PMF factors that they represent realistic local and transported sources influencing the monitoring site, backward trajectories and polar plots analysis were performed. To understand air mass transport to the Ada Marina station, the standard ATMO-ACCESS Research Infrastructure (<https://flexpart-request.nilu.no/data-access>) set-up was used for dust. Specifically, the Lagrangian particle dispersion model FLEXPART version 10.4 (Pisso et al. 2019) ran in the classic retroplume mode for 30 days backward in time for 3-hourly timesteps. The model was driven by ECMWF ERA5 reanalysis (Hersbach et al. 2019) with 0.5° spatial and hourly temporal resolution over 137 vertical levels. The resulting footprint emission sensitivity expresses the probability of potential emissions to arrive at Ada Marina, showing air mass origin, and can be converted to atmospheric concentrations at the receptor (Ada Marina) if combined with an emission dataset. For dust, emissions were first calculated using the FLEXDUST module (Groot Zwaafink et al. 2016). FLEXDUST uses input parameters, such as soil type, vegetation/snow cover, threshold friction velocity, particle-size classes combined with surface and meteorological conditions from ECMWF ERA5 data (0.25° resolution, hourly) to calculate gridded emission fluxes for 10 size-classes of dust particles from 0.2 to 20 µm.

225 Beside FLEXPART, air mass transport modelling was performed also by Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model developed by the National Oceanic and Atmospheric Administration (NOAA). The 24h back-trajectories used GFS Meteorological Data and vertical velocity model and were calculated at 100 m, 200 m and 500 m above ground level.

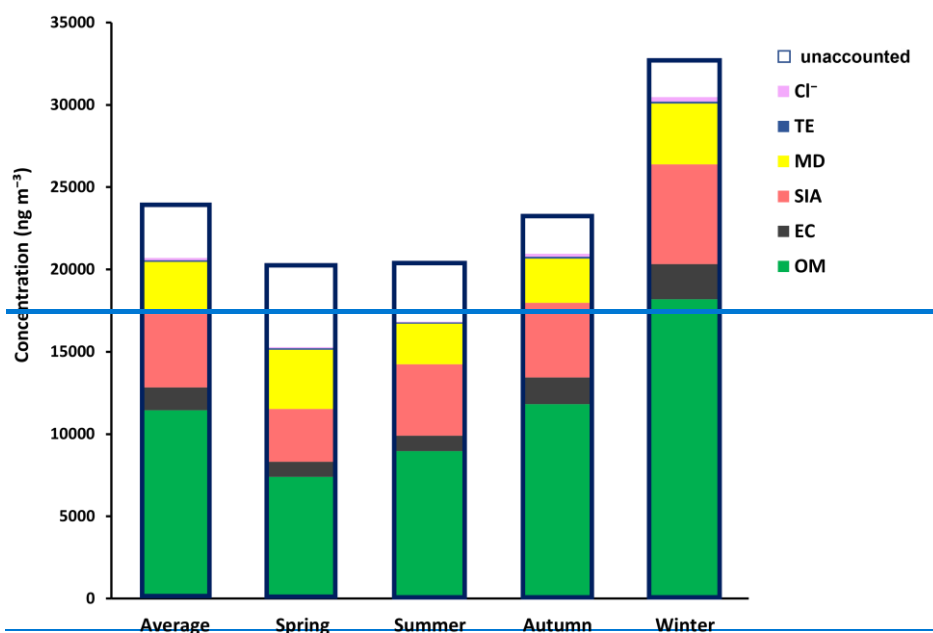
230 The directional dependence and temporal behaviour of each factor was examined using polarPlot function from the openair (version 2.18-2), R package (version 4.4.2) (Carslaw, 2012).

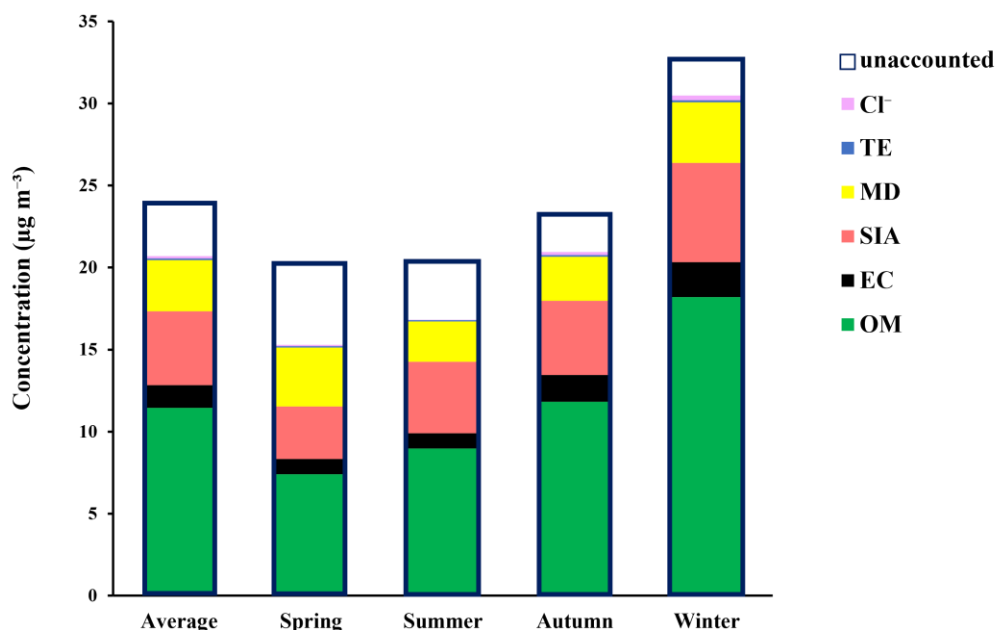
3. Results and discussion

3.1 PM₁₀ mass concentration and chemical composition

The average annual level of PM₁₀ during WeBaSOOP campaign ($23.9 \mu\text{g m}^{-3}$) (Table S32), was below threshold value of $40 \mu\text{g m}^{-3}$ (Government of the Republic of Serbia, 2013). Regulation on conditions for monitoring and requirements for air quality is based on Serbian Law on Air protection (Government of the Republic of Serbia, 2025) which is in accordance with Directive from 2008 (Directive (EU) 2008/50/EC). However, average annual level measured in Belgrade exceed the latest limit value in new EU Directive 2024/2881, that will be in force from 2030, ($20 \mu\text{g m}^{-3}$) as well as WHO's guidelines from 2021 ($15 \mu\text{g m}^{-3}$). PM₁₀ concentrations showed seasonal pattern with higher levels during heating ($28 \mu\text{g m}^{-3}$) (15th October to 15th April) than during non-heating season ($19 \mu\text{g m}^{-3}$). Daily limit value ($50 \mu\text{g m}^{-3}$) was exceeded four times and WHO recommended value ($45 \mu\text{g m}^{-3}$) seven times during campaign, in heating season, with the highest daily concentration recorded on December 19th ($92 \mu\text{g m}^{-3}$).

Carbonaceous fraction (OM + EC) was the major contributor to PM₁₀ mass concentration with the highest contribution in winter (62%, $20 \mu\text{g m}^{-3}$), then in autumn (58%, $13.5 \mu\text{g m}^{-3}$), summer (49%, $9.9 \mu\text{g m}^{-3}$) and spring (41%, $8.3 \mu\text{g m}^{-3}$) (Fig. 2, Table S3). Organic matter was calculated as $\text{OC} \times 1.4$ for all seasons (Turpin and Lim 2001). The second major contributor to PM₁₀ mass concentration was secondary inorganic aerosol (SIA) with 19% on average. Sulphate and ammonium ions didn't show seasonal variability, while nitrate was higher in winter ($2.7 \mu\text{g m}^{-3}$) and autumn ($1.6 \mu\text{g m}^{-3}$) season, compared to summer ($0.4 \mu\text{g m}^{-3}$) and spring ($0.6 \mu\text{g m}^{-3}$). Semivolatile character of nitrate is responsible for its lower levels during warmer seasons due to increased temperatures and photochemical activity while sulphate is more stable under the same conditions (Waked et al. 2014). Mineral dust (MD) content was estimated following methodology described in (In't Veld et al. 2021; Querol et al. 2001). MD contributed to PM₁₀ mass with 13% on annual average, without pronounced seasonality. Negligible contribution of trace elements (0.5%, $0.12 \mu\text{g m}^{-3}$) and Cl⁻ (0.6%, $0.135 \mu\text{g m}^{-3}$) was observed (Fig. 2). The unaccounted PM₁₀ mass concentration on average was $3.2 \mu\text{g m}^{-3}$ which is around 16%. During spring, the unaccounted PM₁₀ mass was the highest, $4.8 \mu\text{g m}^{-3}$ while during winter was two times lower ($2.0 \mu\text{g m}^{-3}$). The higher fraction of unaccounted mass might be attributed to the PARTICLE-BOUND particle-bound water content of PM₁₀, and/or conversion factors adopted for OM and mineral dust which represent simplified calculations and may lead to uncertainties (Terzi et al. 2010).





260 Figure 2. Major composition of PM₁₀ in Belgrade on annual level and during different seasons. Every bar represents total PM₁₀ on annual and seasonal average concentration. Major PM₁₀ reconstructed components were: OM – organic matter, EC – elemental carbon, SIA – secondary organic aerosol, MD – mineral dust, TE – trace elements.

3.2 Identification of the factors

265 Using the PMF model, seven factors were identified based on their chemical profiles and the tracer species characteristic of specific emission sources (Fig. 3): Biomass burning (BB); Long range transport and local combustion (NaCl/COMB); Mineral dust (MD); Primary biological aerosol particles (PBAP); Biogenic secondary organic aerosol from isoprene (BSOA_{Isoprene}); Ammonium sulphate; Traffic/ Industry (TRA/IND). Factor fingerprints and relative contribution of the identified factors to PM₁₀ are presented in Fig. S12 and S23 and in Table S4. Factor chemical profiles for each factor are presented in Fig. 3, whereas time evolution of daily contributions and wind polar plots are depicted in 270 Fig. 4.

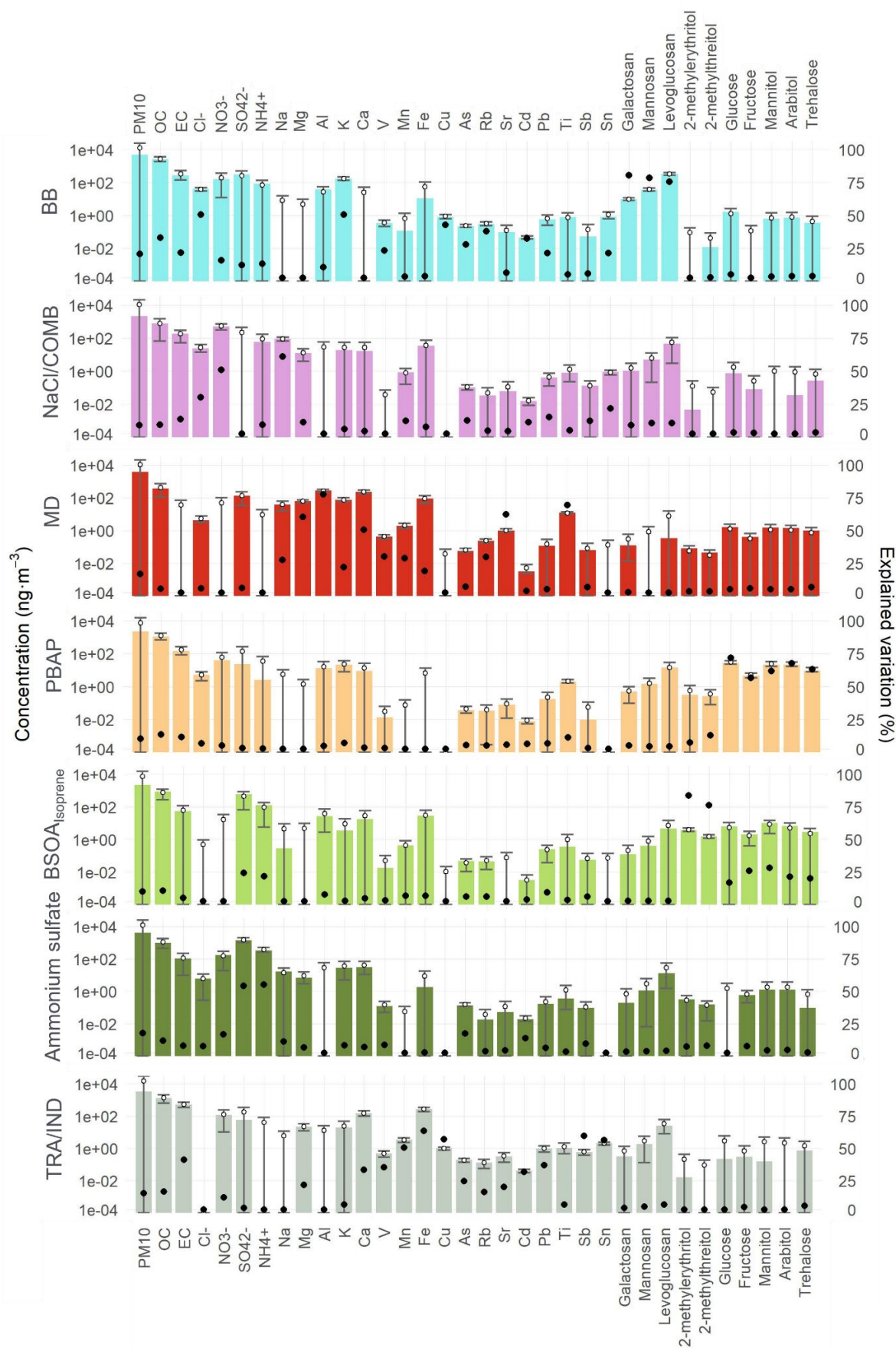
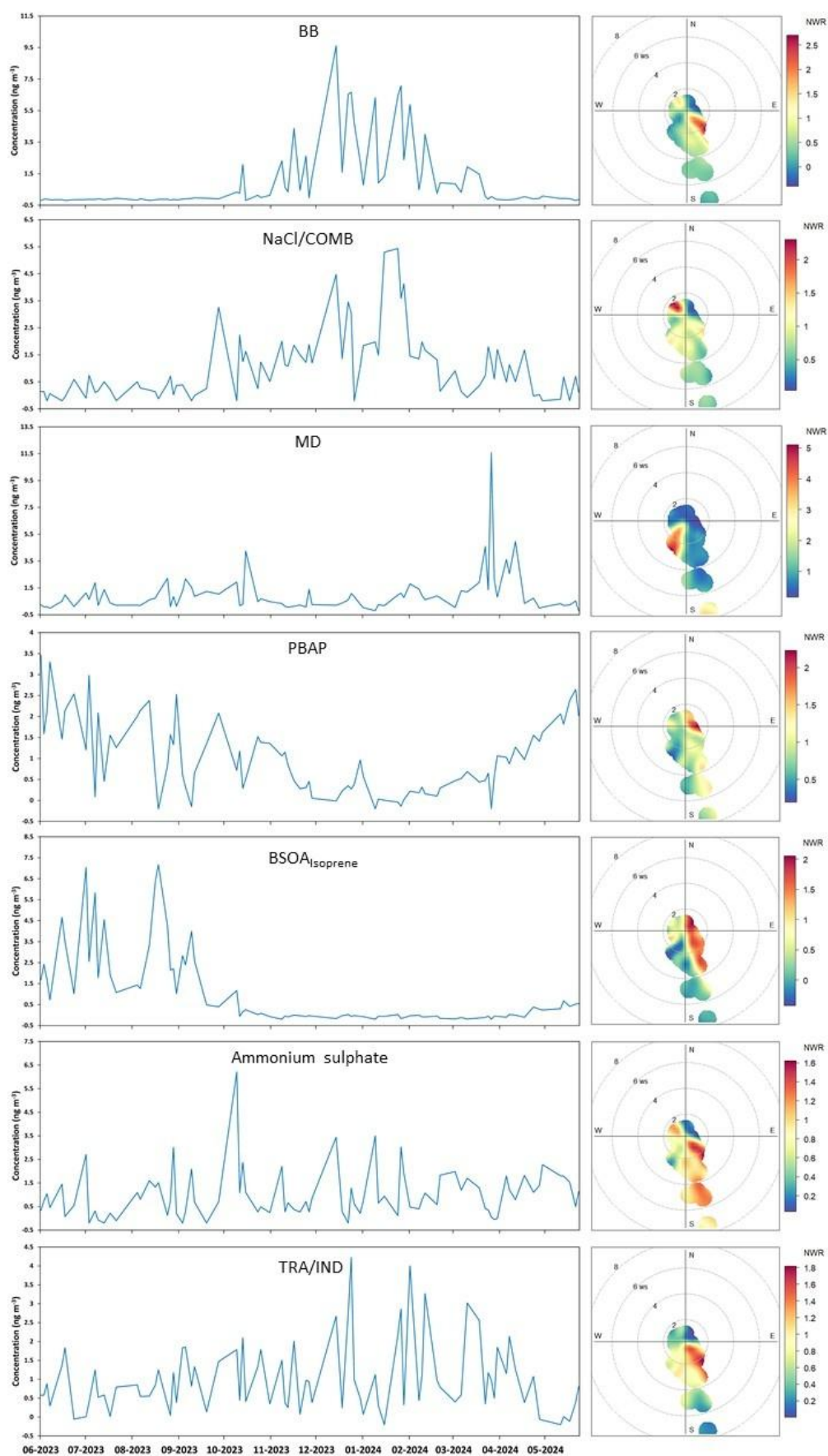


Figure 3. Chemical profiles of the PMF factors in Belgrade Ada Marina. The names of the species are shown on x-axis, on y-axis are shown chemical concentrations of the species in ng m⁻³, with mean DISP values (white dots) and DISP confidence intervals (error bars). and, on the secondary y-axis are shown relative contributions of the species apportioned by the factor (black dots). Biomass burning (BB); Long range transport and local combustion (NaCl/COMB); Mineral dust (MD); Primary biological aerosol (PBAP); Biogenic secondary organic (BSOA_{isoprene}); Traffic/ Industry (TRA/IND).



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Figure 4. Daily factor contribution to PM_{10} mass concentration during one-year campaign (left) and wind polar plots with normalized concentration of the apportioned PMF factors (right). Biomass burning (BB); Long range transport and local

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3.2.1 Biomass burning

Biomass burning (BB) factor contributed the most to the total PM₁₀ concentration (21%, Fig. S2). It was characterized by the presence of galactosan (80% of total galactosan), 79% mannosan, 76% levoglucosan, 51% of K and Cl⁻, 38% of Rb and 33% of OC (Fig. 3), typical indicators of BB. This factor also contains relatively high contribution of the As (28%), Cd (32%), Pb (21%). Unlike the species that are produced during incomplete combustion (like polycyclic aromatic hydrocarbons or black carbon), heavy metals emissions from BB are related to the biomass characteristic itself (e.g., natural metal accumulation from soil) (Yao et al. 2023). Metals may also originate from surface contamination from soil and dust or activities like wood treating (e.g., with arsenic-contained preservatives) (Stojić et al. 2016). Further examination of this factor included deriving OC/EC (9.4), OC/levoglucosan (8.3) and EC/levoglucosan ratios (0.88) which were in accordance with the values found in the literature (Table 32). Higher contribution of BB factor was observed during heating season in many European cities due to increased heating demand and stable atmospheric conditions in colder seasons (Liu et al. 2025). During cold seasons, as a result of near-surface cooling effect, temperature inversions occur, and stable boundary layer is formed which results in accumulation of the pollutants and prevention of their vertical mixing (Glojek et al. 2022). In our study, contribution of BB factor to total PM₁₀ concentration during heating season was 34% and temporal variability with peak during heating season (from October till April) further confirmed this factor (Fig. 4). In urban areas, BB factor is associated with domestic heating (Belis et al. 2013). In Belgrade, it is estimated that around 300 000 households are not connected to district heating, and they mostly rely on wood as heating fuel (Belgrade's air quality action plan, 2021). This indicates that residential wood burning substantially influence local air quality.

Biomass burning was a commonly identified source in Belgrade, and Balkan region as well. In the study of Stojić et al. 2016, the contribution of solid fuel burning was almost 30% of PM₁₀ in 2010-2011 in Belgrade. However, comparison with this study is difficult since sampling was conducted 13 years before our campaign and not all tracers needed for the complete PMF were included. The source apportionment of PM₁₀ in Sofia, Bulgaria resolved biomass burning factor with contribution of 23% (Hristova et al. 2020) while source apportionment study in urban area of Skopje, Macedonia, resulted in much higher contribution of BB (around 70%) (Mirakovski et al. 2020). In case of PM_{2.5}, contribution of BB factor was 24% of total PM_{2.5} in Budapest, Hungary and 28% in Zagreb, Croatia (Perrone et al. 2018).

Table 32. OC/levoglucosan, EC/levoglucosan and OC/EC ratios from PMF BB factor, dataset and other European studies.

	BB factor (PMF)	Gilardoni et al. (2011) ¹⁾	Zotter et al. (2014) ²⁾
OC/EC	9.4	6.54 ± 0.25	8.6 ± 2.9
OC/ Levoglucosan	8.3	5.62 ± 0.3	7.8 ± 2.7
EC/ Levoglucosan	0.88	0.89 ± 0.06	0.87 ± 0.27

1) Po Valley; 2) South of the Alps;

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According to (Rowell et al. 2012), wood biomass is grouped into two groups: softwood and hardwood. Levoglucosan to mannosan (L/M) ratio may be used to apportion biomass burning emissions to burning from hardwood (14-15) or softwood (<4) (Schmidl et al. 2008). The L/M ratio derived from our PMF factor was 8.9, indicating probably a mixed contribution from both soft and hardwood burning, which is further confirmed with spruce (softwood) percentage of 53%. As shown in Fig. S34, the L/M ratios were different between summer (18.9) and winter (8.0) season suggesting possible

origin of levoglucosan from other sources rather than burning of biomass for heating only. Ratios in spring and fall were consistent, 12.7 and 12.3, respectively. On the 2nd of October, increases in levoglucosan, mannosan and galactosan concentrations were observed. The heating season in Belgrade officially begins on October 15th and if unusually low temperatures occur earlier, the season may start sooner. However, on 2nd of October, the ambient temperature was 15°C which indicates another possible source of anhydrosugars beside burning of biomass for heating. (Gajović and Todorović, 2013) observed open fire phenomena in Serbia every year in October in the period from 2000 to 2013. The authors attributed this phenomenon to burning of agricultural waste in the autumn. During WeBaSOOP campaign, on the October 2nd, satellite data showed fire occurrence in Vojvodina (Fig. S45), a common region where agricultural fires were distributed (Gajović and Todorović, 2013). The same sudden increase in biomass burning tracers' concentrations was observed in Belgrade in 2008 in study of (Zangrando et al. 2016), which was also attributed to burning of agricultural waste. In their study, L/M ratio in October was in range from 2.5 – 16.7, which agrees with our L/M average ratio in October (14.9). Beside agricultural waste burning, the high L/M ratio in summer may also be explained by wood combustion (e.g. charcoal) in restaurants located in the Ada Ciganlija recreational area in the vicinity of Ada Marina monitoring site. The wind polar plots indicate strongest influence of air masses coming from the West in non-heating season, which coincides with direction of recreational area. Northeast, East, and Southeast wind direction may be observed during heating season, indicating influence from residential area (Fig. S56), thus supporting this interpretation.

In the previous SA studies performed for Belgrade region and Metropolitan, biomass and/or wood burning were identified as separate or mix factor. In the study of Đorđević et al. (2012) this factor was identified as separate factor based on the dominant presence of K⁺ as dominant (8%) while; Cvetković et al (2015) verified it by PAHs such as there are Nap, Acy and Ace (10.4%). and In the studies of Todorović et al. (2020) and Almeida et al. (2020) biomass burning was identified with Cl, K, Zn, Pb and S- with contribution of about (about 15% in the both studies). In this study where biomass burning was 21% of PM₁₀ mass concentration, that is factor proved and was identified based on with OC, EC, organic tracers (levoglucosan, mannosan and galactosan) and Rbu, -methal that is, beside K, one of the alternative tracers for this factor (Massimi et al. 2020, Pereira et al. 2025).

3.2.2 Long-range transport and road-salt/local combustion

The next factor was a mix of NaCl from long-range transport and local emission from road salting with contribution of local combustion. It accounts for 9% of PM₁₀. The factor is dominated by Na (61% of total Na), NO₃⁻ (51%), and Cl⁻ (30%). As NaCl travels toward the Balkans, it is likely reacting with HNO₃, forming NaNO₃ and releasing HCl that is a typical aging process for sea salt aerosol (Pandolfi et al. 2020). Although Na-Cl high Pearson correlation coefficient (0.75) (Table S35) and Mg/Na (0.14) ratio (Seinfeld and Pandis, 2016) confirm marine origin, K/Na (0.22) and Ca/Na (0.18) ratios (Ooki et al. 2002) from PMF output do not comply with ratios typical for marine aerosol and thus indicate mixing with other salt sources. Extensive road salting on 20th of January contributed to the pronounced peak on that day (<https://nsuzivo.rs/srbija/na-auto-putevima-celu-noc-99-kamiona-prosuto-100-tona-soli-vesic-na-terenu-cak-200-radnika-veceras-cisti-saobracajnice/>).

A slight seasonality and peaks during the heating season (Fig. 4) point to local sources of salt from road mixed with fossil fuel and biomass combustion. This factor accounts for 13% of EC, 11% of levoglucosan, and 9% of OC. Wind rose data (Fig. 4) show the dominant influence of air masses from the Northwest, aligning with the location of the “Novi Beograd” heating plant. Belgrade's district heating system covers 360,000 households and 4.4 million m² of commercial space, with 90% of its thermal energy derived from natural gas (<https://beoelektrane.co.rs/zastita-zivotne-sredine/>). Although natural gas emits less particulate matter than other fuels, it remains a potential source of PM. The influence of nearby plants is supported by wind patterns corresponding to the positions of the Novi Beograd (Northwest) and, to a

lesser extent, “Banovo Brdo” (Southeast) heating plants (Fig S7). Additional fuels used by Belgrade Power Plants include CNG, light heating oil, low- and medium-sulphur heating oil, coal, and pellets which may also contribute to elevated PM₁₀ levels during the heating season.

Flexpart footprint analysis (Fig. S68) for the two peaks in the time series of this factor shows air masses from the Atlantic and Northern Sea (Fig. S86-1) but also local influence of combustion on the 19th December which is the day with the highest concentration in the whole WeBaSOOP campaign (Fig. S86-2). The NaCl/COMB factor contributed the least to PM₁₀ mass concentration, 9%. Similar findings were found in an urban background site in Northwest Germany, located 250 km from the coast. The aged sea salt factor in this study was explained mainly by Na, NO₃⁻, Mg and OM and contributed to the PM₁₀ mass same as our factor, 9% (Beuck et al. 2011). Although located around 300 km away from closest sea, other source apportionment studies in Belgrade observed the influence of marine aerosol also. In the study of (Đorđević et al. 2012), marine aerosol (14.9%) was confirmed by the presence of Na and Cl in the coarse mode of measured particles.

3.2.3 Mineral dust

The mineral dust (MD) factor accounts for 17% of PM₁₀ and is characterized by high contributions from crustal elements: Al (78% of total Al), Ti (69%), Sr (62%), Mg (60%), and Ca (51%), which are typical markers of soil and mineral matter. Moderate enrichments of V (30%), Mn (29%), and Fe (20%) are also observed, although less pronounced than in the TRA/IND factor. Diagnostic ratio of K/Fe (0.8) complies with typical ratio in dust (Liu et al. 2022). Wind polar plots confirm the strongest influence of air masses coming from the Southwest (Fig. 4). Moreover, on 31st March 2024, high PM₁₀ concentration (48.5 µg/m³), partially attributed to a Saharan dust outbreak, as confirmed by characteristic Na/Al (0.14) and K/Al (0.27) ratios, closely matching values reported for Saharan dust (Na/Al = 0.12; K/Al = 0.31) by (Moreno et al. 2006). (Nicolas et al. 2008) observed that Saharan outbreaks are marked by a more pronounced increase in Ti relative to Si and Ca. Therefore, Ti/Ca ratio is good marker for Saharan dust episodes. In our study, Ti/Ca (0.05) and Ti/Fe (0.14) ratios were both consistent with the values from the literature (Ti/Ca = 0.02; Ti/Fe = 0.10) (Nicolas et al. 2008) and aligned with ratios obtained in Debrecen, Hungary (Ti/Ca = 0.07; Ti/Fe = 0.09) (Borbely-Kiss et al. 2004). Although these observations were made during the March to April 2024 transition, no clear seasonal pattern was evident (Fig. 4).

Beside the long-range transported dust, the influence of local dust was also observed. The WeBaSOOP campaign coincided with preparatory work for the starting station of Belgrade metro. Sand and crushed stone were applied around the future depot site in Makiš, roughly 7 km Southwest of the Ada Marina site. This proximity is reflected in the mineral dust polar plot, which shows a joint influence of construction activity and natural mineral dust (Fig. S98).

The MD factor accounts for 17% of PM₁₀, but only 5% to OC was attributed to MD, indicating no mixing of dust and organic matter by aging and thus making it the lowest contributor to OC among all identified factors. In the study of (Mijić et al. 2012), mineral matter contributed to PM₁₀ with 19%, with the most dominant southwest wind, which agrees with our results and indicates mineral dust constant influence in Belgrade. However, factor soil, in this study titled mineral dust, was identified in the studies of Almeida et al. 2020 and Todorović et al. 2020 in this study titled mineral dust, was identified in the study of Almeida et al (2020) and Todorovic et al (2020) that contributed to PM₁₀ mass concentration with 8% and 5% respectively. Our results complied with other European cities where contribution of MD factor accounted for 10% in Milan, Italy to 25% in Athens, Greece (Amato et al. 2016).

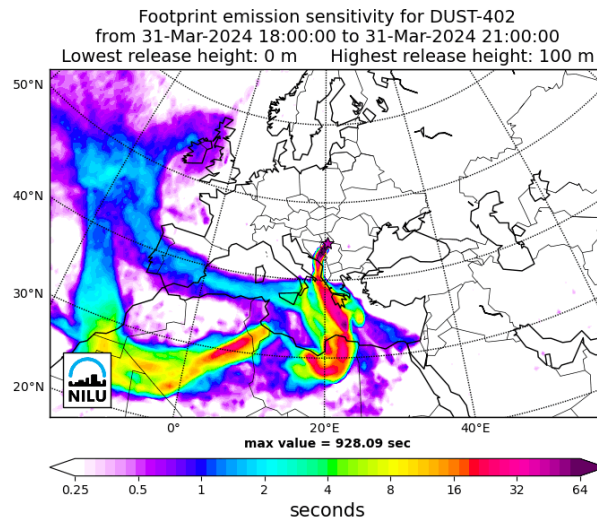


Figure 5. FLEXPART Footprint analysis for 3 hour time set on 31st of March confirming influence of Saharan dust on that day.

Qualitatively in support of our analysis.

3.2.4 Primary biological aerosol particles

Primary biological aerosol particles (PBAP) factor contributes to 10% of PM_{10} and it was traced by sugars (Glucose, Fructose, Trehalose) and sugar alcohols (Mannitol and Arabitol). It accounted for 72% of total glucose, 68% arabitol, 63% trehalose, 62% mannitol, and 57% fructose. The remaining sugars and sugar alcohols were apportioned by PMF in the BSOA_{Isoprene} factor. This factor shows a clear seasonal variation with higher levels during warmer seasons (Fig. 4) due to increased solar radiation and higher surface temperatures (Waked et al. 2014). PBAP factor is indicator of a highly heterogenic source of particles coming from bacterial and fungal cells or spores, their fragments (e.g. endotoxins, mycotoxins), viruses, pollen grains, and fragments of plants and insects (Barbaro et al. 2024; Samake et al. 2019). PBAP are found mainly in the coarse fraction of PM, with a maximum in a range from 5.6 to 10 μm which can contribute to the PM mass concentration to up to 5 $\mu g/m^3$ in the summer period (Marcovecchio and Perrino, 2021). As this factor gathers the particles released into the atmosphere from living organisms, they are usually referred as bioaerosols (Fröhlich-Nowoisky et al. 2016). Dispersed in the air, bioaerosols may interact with PM which then serves as a carrier for bioaerosols. As a result, allergic sensitization and respiratory infections may occur and the incidence of these diseases is higher in areas with higher air pollution (Huang et al. 2024). Mannitol and arabitol are established tracers of fungal spores while glucose is being used as tracer for plant material like pollen and fragments of plant material (Tonon et al. 2017, Samake et al. 2019). In our study, fungal spores were estimated using mannitol to arabitol ratio (M/A) (Bauer et al. 2008). The M/A ratio (1.0) derived from the PBAP factor and dataset, aligns closely with values reported for fungal spores (Bauer et al., 2008) and for aerosol filter samples collected across Europe (Yttri et al., 2011, 2024; Samake et al., 2019) (Table 3). Additionally, by applying specific OC to mannitol ratio of 5.2 and 10.8 to our dataset (Bauer et al. 2008), we estimated that 21-44% of OC_{PBAP} comes from fungal spores' source (Platt et al. In preparation). Further resolving this heterogeneous group and estimating its contribution to the total PBAP factor remains challenging, as a broader range of primary biological organic tracers has yet to be examined (Samake et al. 2019). The polar wind diagram shows a Northeasterly influence, likely related to the vegetation zones of the Ada Ciganlija recreational area near Ada Marina. A slight Southeasterly influence is also observed, where the Košutnjak forest is located, 3 km away and covering an area of

300 ha (Fig. S109). Borlaza et al. 2021 indicated that the influence of this source is more local than large-scale impact, complying with our conclusion that biggest influence of this factor is from vegetation at Ada Ciganlija.

The PBAP factor accounts for 10% of PM₁₀, 14% to OC and 11% to EC which was less expected result. However, in the study of Waked in Lens, France, contribution of EC to PBAP factor was 16% on average annual level. Such results were obtained due to possible atmospheric mixing process, limitations in PMF modelling or OC/EC analysis artifacts. Possible explanation for this may be that some types of PBAP, char and evolve as a modern carbon EC during OC/EC analysis (Yttri et al. 2020). Similarly to our study, PBAP contributions at two urban sites in France were 9% Lens (Waked et al. 2014) and 11% in Grenoble, (Srivastava et al. 2018). Slightly higher contributions (16%) were measured in a peri-urban area 25km away from Rome, Italy (Marcovecchio and Perrino, 2021).

Table 43. Mannitol to arabitol ratios for PBAP factor from both PMF and dataset compared with other studies in Europe.

	PBAP factor (PMF)	Ratio from Belgrade dataset	Bauer et al. (2008) ¹⁾	Yttri et al. (2011) ²⁾	Yttri et al. (2024) ³⁾	Samake et al. (2019) ⁴⁾
Mannitol/Arabitol	1.0	1.0 ± 0.3	1.5 ± 0.5	1.4 ± 0.3; 1.1 ± 0.3	1.1 ± 0.5; 1.0 ± 0.0	1.15 ± 0.59

1) Vienna, Austria; 2) Oslo, Norway, summer and winter season, respectively; 3) Zeppelin Observatory, Birkenes Observatory, respectively; 4) France

3.2.5 Biogenic secondary organic aerosol from isoprene

This factor represents biogenic secondary organic aerosol formed from isoprene oxidation (BSOA_{Isoprene}), a major volatile organic compound emitted from land vegetation (Van Drooge and Grimalt, 2015). It accounts for 10% of PM₁₀ (Fig. 3) and is characterized by the presence of 2-methylerythritol (84% of total 2-methylerythritol) and 2-methylthreitol (76%), both known isoprene oxidation products (Claeys et al., 2004). A modest contribution from PBAP tracers (17–28% of their total content) likely reflects co-varying biological activity, as these two factors exhibit similar temporal patterns (Fig. 4), although these species do not define this factor. Liu et al. (2025) emphasised that including secondary biogenic organic aerosol tracers, such as 2-methyltetrols or pinic acid and 3-MBTCA (markers for α -pinene oxidation), in PMF analysis led to the separation of a substantial OC fraction in the form of biogenic secondary organic aerosol from a sulphate-rich factor. A similar split was observed in our study. This is supported by the co-occurrence of SO₄²⁻ (24%) and NH₄⁺ (22%), present as NH₄HSO₄ and/or (NH₄)₂SO₄, suggesting that 2-methyltetrols are formed via acid-catalysed aqueous-phase reactions, confirming the secondary origin of this factor. Wind polar plot shows influence from East, and both North and Southeast, indicating influence from the nearby vegetational sources as well as influence from Košutnjak forest, even higher than for PBAP factor (Fig. 4). The BSOA_{Isoprene} factor appears exclusively in the growing season, peaking in summer. It serves as a clear proxy for isoprene-derived SOA formed under conditions of high photochemical activity and enhanced biogenic emissions. It contributes 10% to the PM₁₀ mass concentration and 11% to OC. Similarly to our result, average annual contribution to PM₁₀ of biogenic secondary organic aerosol was in range from 8 % - 11 % in the study of (Borlaza et al. 2021) in Grenoble, France. The similar contribution to OC of 10 % was observed in Norway (Yttri et al. 2020). To date, to our knowledge, no source apportionment study including tracers for secondary biogenic aerosol particles has been conducted in Belgrade, except to other WeBaSOOP campaign papers.

3.2.6 Ammonium sulphate

This ammonium sulphate is a secondary factor accounting for 18% of PM₁₀ and represents the long-range transport of aged air masses and secondary aerosol formation. It is dominated by NH₄⁺ (55% of total NH₄⁺) and SO₄²⁻

(54%), with the coexistence of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ indicating only partial neutralization of H_2SO_4 . An elevated NO_3^- fraction (17%) further supports its secondary origin. Trace contributions from As (18%), Cd (14%), and levoglucosan (5%) point to minor influences from industrial and combustion sources, likely associated with long-range transport. A high OC/EC ratio (9.1) corroborates the secondary and aged nature of this factor.

The occurrence of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ in both, this and in the $\text{BSOA}_{\text{Isoprene}}$ factor likely reflects a common regional background that persists year-round but co-varies with distinct seasonal processes. In summer, partially neutralized sulfuric acid acts as an acid seed facilitating IEPOX (Isoprene Epoxydiol) uptake and subsequent 2-methyltetrol formation. During other seasons, it primarily represents regional SIA. The $(\text{NH}_4)_2\text{SO}_4$ factor accounts for 18% of PM_{10} and 12% of OC, making it the second largest contributor to PM_{10} after the BB factor. The contribution of this factor is similar to the ones previously reported for various urban sites in Europe (Beuck et al. 2011; Borlaza et al. 2021) as well as in Belgrade. (Đorđević et al. 2012) found that the formation of $(\text{NH}_4)_2\text{SO}_4$ has the dominant influence on the contents of aerosol ionic species in Belgrade in 2008. (Belis et al. 2019b) indicated that secondary sulphate in the Danube and Western Balkan region is mostly associated with coal combustion since its precursor is gas SO_2 . [In the study of Todorović et al. \(2020\), factors secondary sulphate from regional combustion sources \(S, \$\text{NH}_4^+\$ \) \(28.8%\) and local combustion sources and ammonium nitrate \(V, Ni, \$\text{NO}_3^-\$, \$\text{NH}_4^+\$ \) \(29.7%\) accounted for around 2/3 of \$\text{PM}_{10}\$ total mass concentration. For the same sampling site, Almeida et al. \(2020\) identified sulphate factor with contribution of 3%, which was separated from oil fuel combustion \(38%\). Comparing their results to ammonium sulphate contribution in our study \(18%\), differences may be explained by nonidentical PM fraction, SA with \$\text{PM}_{10}\$ identified factors that are not only from combustion sources, -the chemicals analysed and used as input data in PMF, -time period when studies were conducted as well as long-term trends that indicate airborne PM decrease \(de Hoogh et al. 2025\). Almeida et al. \(2020\) analysed 19 elements \(Table S1\) while Todorović et al 2020 analysed ions beside the 19 elements \(Table S1\). Furthermore, Todorović et al. \(2020\) as well as Almeida et al. \(2020\) had sampling campaign in the period from 2014-2015. Their studies represent the last SA studies in Belgrade until WeBaSOOP sampling campaign. In the time span of eight years, the sources in Belgrade changed due to: substantial changes in traffic routes in Belgrade central zone, industrial activities, observed reductions in \$\text{PM}_{10}\$ concentrations during the 2010s. The \$\text{PM}_{10}\$ decrease likely reflect the combined effects of the long-term replacement of coal- and oil-fired boiler houses with district heating supplied predominantly by natural gas, together with the gradual phase-out of small local boiler plants and other emission control measures \(\[https://beoelektrane.co.rs/saopstenja/veliki-doprinos-beogradskih-elektrana-u-borbi-za-cistiji-vazduh-i-smanje-zagadenja-u-glavnom-gradu/?utm_source=chatgpt.com\]\(https://beoelektrane.co.rs/saopstenja/veliki-doprinos-beogradskih-elektrana-u-borbi-za-cistiji-vazduh-i-smanje-zagadenja-u-glavnom-gradu/?utm_source=chatgpt.com\)\). Finally, Almeida et al. \(2020\) emphasised that in their study contributions of some tracers were not well defined which led to overestimation of oil combustion and underestimation of other factors.](#)

Wind polar plots showed highest influence from the Southeast and South (Fig. 4). The "Kolubara" thermal power plant is located around 50 km South of Belgrade, and "Kostolac" is approximately 60 km East. Peak on 14th October showed HYSPLIT backward trajectories from the Southwest and influence on that day may be attributed to operation of "Nikola Tesla A" thermal power plant, located around 25 km way from Belgrade (Fig. S11). Our results complied with results obtained previously in Belgrade. In the study of (Stojić et al. 2016), secondary aerosol contributed to PM_{10} 19.5%, while contribution of 16% was obtained in Sofia, Bulgaria (Hristova et al. 2020). Our results are within the European range too, 15% to 26% (Liu et al. 2025).

3.2.7 Traffic/industry

This Traffic/Industry factor (TRA/IND) is likely a mixture of tail pipe and non-tail pipe emissions with influence of industrial activity based on presence of As, Cd, Pb and V. It accounts for 15% of PM_{10} and it is characterized by EC

(41% of total EC) and a broad suite range of trace metals, notably Fe (64%), Sb (60%), Cu (57%), Sn (57%), Mn (51%), Pb (37%), V (35%), Cd (32%), and As (25%). Fe, Sb, Sn and Cu are typical non-exhaust tracers (e.g., from brake wear), V relates to heavy oil combustion and As, Cd and Pb are associated with coal combustion and metallurgic activities (Yttri et al. 2020; Pandolfi et al. 2016). The enrichment of Ca (34%) and Mg (22%) suggests road dust resuspension and influence of construction activity. Therefore, this factor is considered as a mix of traffic exhaust and non-exhaust emissions and industrial sources. Low contributions from levoglucosan (6 %), 2-methyltetrols (< 0.5 %), and sugars and sugar alcohols (< 5%) confirm a minor to negligible influence by biomass burning, biogenic SOA, and PBAP. SIA species are moderate for NO_3^- (12%), minor for SO_4^{2-} (2%) and absent for NH_4^+ , consistent with limited regional influence. This factor does not change throughout a year. The TRA/IND factor contributed 15 % of PM_{10} and 17% of OC, making it the second largest contributor to OC. The OC/EC ratio of 2.5 is higher than the typical OC/EC traffic ratio (1.4) found in literature (Pio et al. 2011), which indicates the contribution of other combustion sources to this factor (probably SOA mixed with primary emissions). Since the PMF model results are based on internal correlations among species that have similar time series, it is difficult to differentiate sources that do not vary independently. The limitation of 24h sampling methodology is that it couldn't capture the diurnal variations of traffic source, therefore, some primary and secondary sources are not separated (Waked et al. 2014).

Traffic with metal industry influence was also observed in Rijeka, Croatia and accounted for 11 % of total PM_{10} mass concentration (Mifka et al. 2021). In other countries of the Balkan region, traffic contributed 9% in Sofia, Bulgaria, and 18.9% in Istanbul, Turkey, with slight seasonality observed in winter (Hristova et al. 2020; Kocak et al. 2011). Our results also complied with range observed in other European urban background sites (5-25%) (Srivastava et al. 2018).

4. Conclusion

This study presents the chemical composition and source apportionment of PM_{10} mass concentrations during the WeBaSOOP campaign (June 2023 to May 2024). Although average PM_{10} concentration complied with current EU and national legislation, $23.9 \mu\text{g m}^{-3}$, it exceeded the limit value proposed by the new EU 2024/2881 AQ Directive on ambient air quality and cleaner air for Europe, to be in force from 2030, and the WHO AQ Guidelines updated in 2021. By the application of mass reconstruction model₂, it was estimated that carbonaceous fraction (OM + EC) constituted the dominant PM component (54% on annual average), followed by secondary inorganic aerosol (19%) and mineral dust (13%). Source apportionment using USEPA PMF 5.0 resolved seven factors contributing to PM_{10} as follows: biomass burning (21%), ammonium sulphate (18%), mineral dust (17%), traffic/industry (15%), primary biological aerosol particles (10%), biogenic secondary organic aerosol from isoprene (10%), and long-range transport and road salt/local combustion (9%).

Eight SA studies were conducted in the past in Belgrade urban and Metropolitan area upon data sets collected in the period from 2003 and 2015 and WeBaSOOP year-long campaign in 2023-2024. Although WeBaSOOP study was conducted upon data set collected eight years after the last study and having different, broader range of, species used for SA, factors traffic, industry, different combustion sources, mineral/soil dust and secondary inorganic aerosol were identified in all studies in the past and ours. This indicates a continuity of these factors throughout the years on air quality in Belgrade. One study performed on data sets collected 15 years ago identified marine aerosol also but with higher contribution than in our, WeBaSOOP, study. However, in contrast to other studies, this was the first one that identified factors from biological origin (PBAP and BSOA_{Isoprene}).

Evaluation of ratios of PM elements and species, back trajectory analysis and wind polar plots verified the local and regional sources contributing to PM_{10} in Belgrade. Compatibility of the two approaches, mass reconstruction and SA,

indicated that more than 40% of PM₁₀ mass was related to different combustion sources, between 30%-35% may be devoted to mineral dusts and inorganic aerosols of anthropogenic and natural sources, while specific organic tracers proved that about 20% of PM₁₀ mass originated from biological sources. Seasonal patterns varied among factors. Biomass burning and the long-range transport and road salt/local combustion factors exhibited elevated levels during heating season. The biomass burning driven primarily by residential wood burning and the long-range transport and road salt/local combustion reflecting contributions from local sources during winter period of road salt events and local combustion. In contrast, primary biological aerosol particles and biogenic secondary organic aerosol from isoprene peaked during the non-heating season, coinciding with increased biological activity. Mineral dust, ammonium sulphate, and traffic/industry showed no clear seasonal variability. Ammonium sulphate was resolved as a distinct factor, but its influence was also evident in the BSOA_{Isoprene} factor, supporting the secondary origin of this aerosol and its likely role in facilitating isoprene oxidation. Traffic factor has more enhanced diurnal variation than seasonal which cannot be observed with resolution of 24 hours sampling. Therefore, time series of traffic and industry tracers were not different enough to separate them which is a limitation of this 24h sampling resolution.

Incorporation of specific organic tracers in PMF enabled the identification of biogenic activity-related factors and provided deeper insight into the composition and sources of PM₁₀ in the Belgrade Metropolitan area. Our results showed influence of both, local (biomass burning, traffic, biogenic aerosols) and regional sources (mineral dust, salt from long-range transport) on PM₁₀ concentration in this area. Continuous measurements and source apportionment are needed in data-scarce areas of Europe to better understand source impacts on air quality. Therefore, such findings may offer a scientific basis for air quality management and support policy makers in identifying priority sectors and targeted measures to mitigate PM₁₀ pollution. However, further work for better understanding of PM₁₀ regional and local sources in Belgrade is needed by performing SA study at least for two fractions of airborne PM represent by fine and coarse fraction as well as to be, included in combination of offline and online PMF analysis and long-term measurements.

Mineral dust events, marine aerosol and biogenic aerosols contribute to the background concentration of PM₁₀ and PM_{2.5} and are largely beyond the scope of emission control measures. Although sea salt was not extracted as a separate factor in WeBaSOOP study, its contribution to PM₁₀ mass may be accounted as 1-2 µg/m³, but in case of mineral dust, contribution is estimated to be around 4 µg/m³. In WeBaSOOP study, mineral dust represents mix of both natural and anthropogenic sources from local and long-range transport, while 1/5 of PM₁₀ mass (around 5 µg/m³) was attributed to primary and secondary airborne particulate matter of biogenic sources. As emissions from these sources are beyond controllable measures compliance with ambient air quality limit values consequently requires sufficient reductions in controllable anthropogenic emissions to offset the irreducible natural background. Where legislation permits, documented contributions from specific natural sources, such Sahara dust events and sea salt, may be excluded from compliance assessment. However, routine exclusion of biogenic aerosol contributions is generally not possible to be applied without measurements such WeBaSOOP study enabled.

Data availability

All data on OC, EC, ions, elements and organic tracers are available at EBAS (<https://ebas.nilu.no/>).

Supplement link

585 **Author contributions**

Conceptualization: MJS, AA, KEY. Data curation: BP, BR, RK, MD. Formal analysis: BP, AA, KEY, AB, MJS, DS, MP. Funding acquisition: MJS. Investigation: BP, MJ, BR, RK, DS, MD, MJS. Project administration: MJS. Supervision: MJS, AB, AA. Validation: AA, KEY, MJS, MP, SMP. Visualization: BP. Writing (original draft preparation): BP. Writing (review and editing): BP, MJS, AA, MP, DS, SMP.

590 **Competing interests**

The authors declare that they have no conflict of interest.

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