



Multi-city comparative PM_{2.5} source apportionment for fifteen sites in Europe: The ICARUS project

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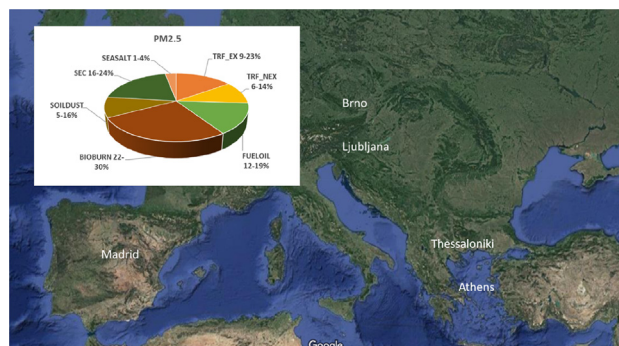
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HIGHLIGHTS

- Source apportionment was applied for 15 sites from 5 cities in Europe.
- PMF harmonized application was based on common sampling and analysis protocol.
- Traffic and biomass burning were the major control-demanding sources.
- The homogeneity of PM_{2.5} source chemical profiles was examined.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 May 2020

Received in revised form 1 August 2020

Accepted 19 August 2020

Available online 21 August 2020

Editor: Pavlos Kassomenos

Keywords:

Particulate matter
Chemical composition
Positive Matrix Factorization
Source apportionment
Multi-city study
Sources homogeneity

ABSTRACT

PM_{2.5} is an air pollution metric widely used to assess air quality, with the European Union having set targets for reduction in PM_{2.5} levels and population exposure. A major challenge for the scientific community is to identify, quantify and characterize the sources of atmospheric particles in the aspect of proposing effective control strategies. In the frame of ICARUS EU2020 project, a comprehensive database including PM_{2.5} concentration and chemical composition (ions, metals, organic/elemental carbon, Polycyclic Aromatic Hydrocarbons) from three sites (traffic, urban background, rural) of five European cities (Athens, Brno, Ljubljana, Madrid, Thessaloniki) was created. The common and synchronous sampling (two seasons involved) and analysis procedure offered the prospect of a harmonized Positive Matrix Factorization model approach, with the scope of identifying the similarities and differences of PM_{2.5} key-source chemical fingerprints across the sampling sites. The results indicated that the average contribution of traffic exhausts to PM_{2.5} concentration was 23.3% (traffic sites), 13.3% (urban background sites) and 8.8% (rural sites). The average contribution of traffic non-exhausts was 12.6% (traffic), 13.5% (urban background) and 6.1% (rural sites). The contribution of fuel oil combustion was 3.8% at traffic, 11.6% at urban background and 18.7% at rural sites. Biomass burning contribution was 22% at traffic sites, 30% at urban background sites and 28% at rural sites. Regarding soil dust, the average contribution was 5% and 8% at traffic and urban background sites respectively and 16% at rural sites. Sea salt contribution was low (1–4%) while secondary aerosols corresponded to the 16–34% of PM_{2.5}. The homogeneity of the chemical profiles as well as their

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relationship with prevailing meteorological parameters were investigated. The results showed that fuel oil combustion, traffic non-exhausts and soil dust profiles are considered as dissimilar while biomass burning, sea salt and traffic exhaust can be characterized as relatively homogenous among the sites.

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1. Introduction

Particulate matter (PM) air pollution deriving from traffic, industrial emissions, oil combustion, biomass burning and other anthropogenic activities as well as natural sources comprise one of the major global concerns. PM_{2.5} (particulate matter with aerodynamic diameter < 2.5 µm) is an air pollution metric widely used to assess air quality, with the EU having set targets for reduction in PM_{2.5} levels and population exposure. High levels of PM_{2.5} have been related to human health damage (WHO, 2016, EEA, 2018, Kampa and Castanas, 2008) and negative implications on ecosystem and climate on a global scale. Consequently, one of the major challenges for the scientific community is to identify, quantify and characterize, at the appropriate scale, the sources of atmospheric particles in order to propose effective control strategies to the public authorities.

In this direction, source apportionment (SA) is the practice of deriving information about pollution sources and the amount they contribute to ambient air pollution levels. A growing number of SA studies (Agarwal et al., 2020; Srishti et al., 2020) have indicated that atmospheric aerosol concentration and composition at a specific location is definitely affected by both local sources and regional background as well as a number of factors as the landscape, the climatic and meteorological conditions (Farao et al., 2014). The critical review and meta-analysis of PM source apportionment studies in Europe given by Belis et al., 2013 resulted in six major source categories for PM, that comprise almost all individual sources apportioned in Europe: atmospheric formation of secondary inorganic aerosol, traffic, re-suspension of crustal/mineral dust, biomass burning, (industrial) point sources, and sea/road salt. As also reported, from a total of 20 European countries, about 67% of the studies were conducted at urban background sites, out of which 7% located in suburban and residential areas. The remaining part was carried out at source-oriented sites (traffic, industrial, or harbor emissions) (18%), rural background sites (13%), and remote sites (4%). Although studies for source apportionment are rapidly spreading globally revealing both PM local and regional origin, the comparability of results among the different sampling sites is often hampered by different sampling frameworks, analytical procedures or modeling approaches.

Therefore, there is a need for harmonized SA outcomes from multi-city studies (different types of sites, regions and landscapes) which are still limited. Representatively, in the frame of APICE project, a PM_{2.5} chemical composition data base collected from five Mediterranean port cities was created (Salameh et al., 2015) and subsequently used by different receptor and source-oriented models, with the scope of distinguishing the main pollution sources affecting near-port areas (Pey et al., 2013; Bove et al., 2014; Pérez et al., 2016; Saraga et al., 2019). In the frame of the AIRUSE LIFE+ project (Amato et al., 2016), a harmonized source apportionment aimed to characterize the similarities and heterogeneities in PM sources and contributions across Southern Europe. Specifically for Athens and Thessaloniki, Greece, the long term evolution of sources has been documented (Diapouli et al., 2017). In Joaquin Project (Mooibroek et al., 2016), PM₁₀ sources were investigated, at four urban background sites and an industrial site in North West Europe using a harmonized approach for aerosol sampling, laboratory analyses and statistical data processing.

In the frame of ICARUS EU2020 project ('Integrated Climate forcing and Air pollution Reduction in Urban Systems'), a comprehensive database including PM_{2.5} concentration and chemical composition from three sites (traffic, urban background and rural) of five European cities

(Athens, Brno, Ljubljana, Madrid and Thessaloniki) during two seasons was created. The common and synchronous sampling and analysis procedure offered the prospect of a harmonized source apportionment approach, with the scope of identifying the similarities and differences of PM_{2.5} key-source chemical fingerprints across the cities and sampling sites. This paper presents an overview of Positive Matrix Factorization (PMFv.5) model results, focusing on dominant sources investigation while examining their statistical robustness and representativeness: traffic exhaust and traffic non-exhaust, biomass burning, fuel oil combustion, soil dust, sea-salt, secondary aerosol. In the majority of the cases, traffic, biomass burning, fuel oil combustion and sea salt sources revealed a clear dependence on the wind direction. The profiles similarity test indicated that fuel oil combustion, traffic non-exhausts and soil dust source profiles are considered as dissimilar while biomass burning, sea salt and traffic exhaust can be characterized as relatively homogeneous. Only secondary aerosol sources have been found to be characterized by similar profiles.

In view of the fact that there is need of targeting on specific pollution sources, it is anticipated that this study significantly contributes to the literature, especially to the field of the receptor/PMF modeling as well as the key-source chemical fingerprints identification and quantification in different types of areas.

2. Methods and materials

2.1. Field sites description, PM sampling and chemical analysis

Intensive PM_{2.5} sampling campaigns were carried out at three sites (traffic, urban background, rural) of five European cities: Athens and Thessaloniki (Greece), Brno (Czech Republic), Ljubljana (Slovenia) and Madrid (Spain). The sampling sites selection was based on i) the features characterizing each surrounding area as traffic, urban background and rural and ii) the existing national air quality network stations. The sites' characteristics are shown in Table 1 and a map of the sites is given in Supplementary material.

Each PM_{2.5} sampling campaign was performed during two distinct time periods: during winter and summer 2017 whereas a total number of 60 samples were collected per site. For the needs of the campaign, a common protocol was developed for all cities defining the methodology for the sampling procedure (filter preparation/weighing/storage/transport), the calculation of the PM mass concentration as well as the filter preparation (cutting) for the chemical analysis. For PM_{2.5} sampling, 47 mm TissueQuartz 25000QAO PALL membrane filters (PALL) were used. This type of filters, used in both low (2.3 m³/h) and high (30 m³/h) volume samplers (Derenda, Leckel, Digitel), is appropriate for all the targeted chemical analysis (OC/EC, ions, PAHs and heavy metals). The determination of the PM mass was conducted in accordance to EN 12341:2014.

After PM mass concentration determination, a quarter (1/4) of the filter was used for OC/EC analysis, another quarter (1/4) for ions and half filter for elements and then for PAHs. In particular, PM_{2.5} samples were analyzed for 28 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123 cd)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene, retene, benzo(b)fluorene, benzo-naphtho-thiophene, benzo(ghi)fluoranthene, cyclopenta(cd)pyrene, triphenylene, benzo(j)fluoranthene, benzo(e)pyrene, perylene, dibenzo(ac)anthracene, anthanthrene, coronene), 24 trace elements (Mg, Si, Cl, K, Ca, Ti, V,

Table 1
Characteristics of the sampling sites.

City	Site (TRF: traffic; URBB: urban background; RUR: rural)	Coordinates	Traffic intensity at the in-front road	Distance from high traffic avenue/highway	Frequent transit of heavy road vehicles	Industrial activity	Vegetation	Agricultural activities	Domestic heating
Athens (ATH)	TRF Aristotelous	37° 59' 17" N 23° 43' 40" E	High	3 m	No	10 km	No	No	Diesel, gas, electric heaters, fireplaces
	URBB Aghia Paraskevi	37° 59' 43" N 23° 49' 09" E	Medium	400 m	No	>10 km	Yes	No	Diesel, gas, electric heaters, fireplaces
	RUR Aliartos	38° 22' 31" N 23° 06' 37" E	Low	500 m	Yes	0.5 km	Yes	Yes	Gas, electric heaters, fireplaces
Brno (BRNO)	TRF Brno-Kotlářská	49° 12' 19.627" N 16° 35' 49.990" E	High	3 m	No	3 km	Yes	No	Gas, electric heaters
	URBB Brno-Lány	49° 9' 54.937" N 16° 34' 50.925" E	Medium	520 m	Yes	1.7 km	Yes	Yes	Diesel, gas, electric heater, fireplaces
	RUR Košetice	49° 34' 24.221" N 15° 4' 49.002" E	Low	1000 m	No	No	Yes	Yes	Gas, electric heaters, fireplaces, coal
Ljubljana (LJUBL)	TRF MOL – Center	46°03'24.1"N 14°30'10.8"E	High	100 m	No	0.5 km	Yes	No	Diesel, gas, electric heaters, wood
	URBB SEA – Bežigrad	46°03'55.6"N 14°30'44.0"E	Medium	230 m	No	1 km	No	No	Diesel, gas, electric heaters, wood
	RUR Reactor Center Podgorica	46°05'37.7"N 14°35'51.1"E	Low	650 m	Yes	2 km	Yes	Yes	Diesel, gas, electric heaters, wood
Madrid (MAD)	TRF E. Aguirre	40°25'17.63"N 3°40'56.35"W	High	25 m	No	>10 km	Yes	No	Diesel, gas, electric heaters
	URBB Farolillo	40°23'41.20"N 3° 43'54.60"W	Low	1000 m	No	>10 km	Yes	No	Diesel, gas
	RUR Casa de Campo	40°25'09.68"N 3°44'50.44"W	Low	2500 m	No	>10 km	Yes	No	Diesel, gas, electric heaters
Thessaloniki (THESS)	TRF University	40°37'38.65"N 22°57'34.97"E	High	37 m	Yes	10 km	Yes	No	Diesel, gas
	URBB Stavroupoli	40°40'15.82"N 22°56'15.11"E	Medium	675 m	No	6 km	No	No	Diesel, gas, fireplaces
	RUR Neochorouda	40°44'23.32"N 22°52'33.83"E	Low	5000 m	No	5 km	Yes	Yes	Diesel, fireplaces

Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Br, Rb, Sr, Sb, Cs, Ba, Ce, Pb), anions (Cl^- , NO_3^- , SO_4^{2-}), cations (Mg^{2+} , Na^+ , NH_4^+), elemental and organic carbon (EC, OC).

OC/EC analysis was performed by the use of Thermo-Optical Transmittance technique according to EN 16909; 2017 Standard; water-soluble ions were analyzed using ion chromatography (Alltech 600 ion chromatography system with a Allsep Anion IC column for anions and a Universal Cation column for cations); elemental analysis was performed by the use of spectroscopy X-ray fluorescence non-destructive method; PAHs were analyzed by i) using a gas chromatograph (GC Agilent 5975C) coupled to a mass spectrometry detector (Agilent 7890A MS) or ii) the use of high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) (Agilent 7890A GC, coupled to AutoSpec Premier MS). The analytical procedures are described elsewhere (Saraga et al., 2017, Voutsas et al., 2014, Manousakas et al., 2018 and Degrendele et al., 2014).

To ensure the comparability of the results, all the elements, OC/EC and ions analyses were analyzed in the same laboratory. Only PAHs analysis was performed by three different laboratories (RECETOX Centre, Czech Republic; National Center for Scientific Research 'Demokritos', Greece and Aristotle University of Thessaloniki, Greece) but in this case, an inter-laboratory comparison test was conducted. The results were satisfactory (t -test, $p = 0.350$ – 0.998), suggesting that PAH concentrations obtained within the field campaigns by the different laboratories are comparable.

Finally, meteorological data were taken by either portable meteorological stations at the sampling sites or from the nearest station belonging to the national meteorological networks.

2.2. Source apportionment

Receptor models aim to re-construct the contribution of emissions from different sources of atmospheric pollutants (e.g. particulate matter), based on ambient measurement data (i.e. PM chemical composition) measured at monitoring sites. One of the most successfully applied receptor model (Belis et al., 2015) is Positive Matrix Factorization (PMF) (Paatero and Tappert, 1994). It introduces a weighting scheme taking into account errors of the data points, which are used as point-by-point weights. Adjustment of the corresponding error estimates also allows it to handle missing and below detection limit data. Moreover, non-negative constraints are implemented in order to obtain more physically meaningful factors. PMF analysis background is described in detail by Paatero (1997). In the present study, the latest PMF version available by USEPA (PMF v.5.0) has been used.

The selection of the specific model for this source apportionment study was based on its two main advantages: i) no need of a priori knowledge of the number and type of sources in an area, and ii) source chemical profiles is not a required input. These two features of the model assist to achieve the goals of the present study, which are both the investigation of the sources in the studied areas as well as the

comparison of these sources' chemical profiles (i.e. homogeneity of sources). The limitation of PMF is that in some cases, mixed factors can be produced from the model, which can be caused by several reasons such as the number of samples and species used in the analysis. In addition to the previous versions of the EPA PMF model, PMF v5.0 provides three advanced tools to evaluate the rotational ambiguity and investigate the uncertainty of the derived solution: bootstrap (BS) analysis, the displacement (DISP) method and a combination of DISP and BS (BS-DISP) as well as the possibility to apply constraints to the solution. Both of those additional features were used in the current study for the assessment and the improvement of the solution (see next paragraph).

2.3. Data pre-treatment, model runs and evaluation of PMF solutions

USEPA PMFv.5 model was run for each sampling site (dataset of $n = 60$ samples including both seasons). For the input to the model matrix, low molecular weight PAHs were excluded as these compounds are mainly present in the gaseous phase regardless of the ambient temperature (Degrendele et al., 2020). Therefore, the sum of the high molecular weight PAHs (i.e. benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene) was inserted as one specie, 'SPAHS'. For avoiding double mass counting of certain species, either the ion or the elemental form of them was included in the analysis (e.g. Ca and Ca^{2+}), depending on their uncertainty and impact on the model's solution. Especially for cases where biomass combustion was expected to be a possible source, K^+ was preferred (instead of K). Depending on the case, 'bad' species were excluded from the analysis due to the high percentage of missing values or very low signal/noise ratio (<0.2). On the other hand, depending on the case, some species were set as 'weak' due to their low signal/noise ratio ($0.2 < S/N < 2$) and/or bad scaled residuals (d-matrix). Finally, outliers were excluded from the analysis except for the cases that they corresponded to reported real events (e.g. fireworks, intense dust events), so useful information was derived for the sources identification. Concentration data below the detection limit (the maximum reported detection limit was used as a conservative limit for all samples) was substituted with one-half of the detection limit and missing concentration data were substituted with the median value (Polissar et al., 2001). The extra modeling uncertainty was adjusted to 8–12%.

A range of solutions were examined with different number of factors (3–10) in each case. Thirty runs were performed for each case, in order to obtain Q-value stability. The robustness and relevance of the selected solutions have been evaluated according to the recommendations of the European guide on air pollution source apportionment with receptor models (Mircea et al., 2020). Briefly, all runs converged and in each case, the Q-robust value was lower than 1.5 times the Q-true value, indicating that outliers are not significantly impacting the Q value. Another criterion which was confirmed was the normal-center distribution (between ± 3) of the weighted residuals for the selected variables (species).

Moreover, rotational ambiguity comprises a limitation of factor analysis because of the free rotation of matrices. PMFv.5 provides three advanced tools to evaluate rotational ambiguity of the derived PMF solution: bootstrap (BS) analysis, the displacement (DISP) method and a combination of DISP and BS (BS-DISP). BS estimates the effect that random errors on the matrix/dataset have on the solution, DISP explicitly explores the rotational ambiguity and BS-DISP is a combination of both. An extensive discussion on these tools has been given by Paatero et al., 2014. When the rotational ambiguity of the solution is high, the identity of the resolved factors may be swapped (exchanged) during DISP and BS-DISP runs. This is expressed in the diagnostic result as a number of factor swaps. Moreover, the number of cases used in BS-DISP expresses the number of accepted resamples. If all cases are accepted, this number is equal to 1 (base run) plus the number of bootstraps. Rotational ambiguity in PMF base runs can be reduced by

putting constraints on individual factor elements, either scores and/or loadings or prescribing values for ratios of certain key factor elements. In cases that constraints needed to be applied for a dataset, the limitation of dQ% being kept at the lowest value of 0.5% was retained. Keeping low maximum dQ% change ensures that significant perturbation of the model results are less probable. The constraints used for each data set are discussed in the Results section. Eventually, BS, DIS and BS-DIS runs were conducted for evaluating the model's solutions. In particular, 100 bootstrap runs were performed for each dataset (default value of minimum correlation $r^2 = 0.6$), and the results were regarded reliable as $>80\%$ of the factors were mapped. DIS runs resulted in the validity of the final PMF solutions as no factor swaps (i.e. exchanges) were observed for the smallest $dQ_{\max} = 4$ while the decrement of Q was $<1\%$. Through BS-DISP analysis, the final solution was considered to be valid according to Norris et al., 2014.

There was a good correlation between the model-predicted and the measured $\text{PM}_{2.5}$ mass concentration ($r^2 > 0.8$) in all cases. In the following, the results from PMF application for each site/city are presented. Abbreviations for the cities' names (ATH: Athens; BRN: Brno; LJUBL: Ljubljana; MAD: Madrid; THESS: Thessaloniki) and type of site (TRF: traffic; URBB: urban background; RUR: rural) have been used. Table S1 presents the constraints applied for each case (under the limitation of $dQ\% \leq 0.5$).

3. Results & discussion

3.1. Identified sources by PMF

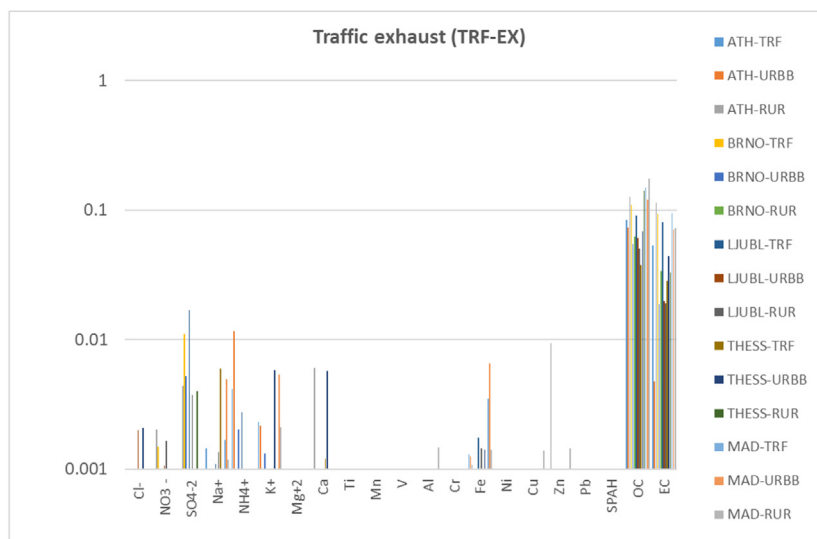
The number of factors identified by PMF model at each ICARUS site varied between five and eight. The resolved sources were qualitatively identified by the trace markers shown in the mass profiles (Fig. 1a-h). A well-known weakness of PMF is that it cannot always efficiently distinguish the sources, especially in cases that the sources share common tracers, while no primary emission sources such as secondary formation can be identified as separate factors. In cases of concurrent emissions from different sources, the analysis can be rather complicated as the obtained factors represent combined sources or atmospheric processes rather than single emission sources (Pérez et al., 2016). Except for the emission sources, the intense photochemical activity and large/mesoscale/local meteorological processes can play a crucial role on the aerosol levels over the studied areas. The similarity among the resolved profiles of the same source at the different sites is examined in a subsequent paragraph.

In brief, traffic exhaust (TRAF-EX) and traffic non-exhaust (TRAF-NEX) sources were commonly identified at all sites. Fuel oil combustion (FUELOIL) source was found at all cities, including industrial emissions in most cases while biomass burning (BIOBURN) source was found at all sites except for Madrid sites. Soil dust source (SOILDUST) was traced at all sites, with the exception of LJUBL-URBB, where it was combined with road dust factor. Sea-salt (SEASALT) was identified in two or three sites of all cities, except for Brno city where it was absent. Secondary aerosol source appeared in all cases, either as secondary sulfate (SEC-SULF) or as mixed secondary nitrate and sulfate (SEC). The unaccounted fraction of $\text{PM}_{2.5}$ (ranging from <1 to 9.88%) could be attributed to non-identified sources such as non-fossil OC and the formation of enhanced biogenic secondary organic aerosol due to lack of specific organic tracers' analysis. A discussion for each source category follows. The % contribution of each source to $\text{PM}_{2.5}$ concentration for every site is presented in Fig. 2a-c.

3.1.1. Traffic-related sources (TRAF-NEX, TRAF-EX)

Two traffic-related sources were distinguished in all sites: the traffic-exhaust source (TRAF-EX) and the traffic non-exhaust source (TRAF-NEX). Vehicular exhausts (TRAF-EX) source is mainly characterized by carbonaceous species, i.e. OC and EC (sum of their contribution to mass: 83% - 97%), and particularly their ratio (OC/EC). An OC/EC

a)



b)

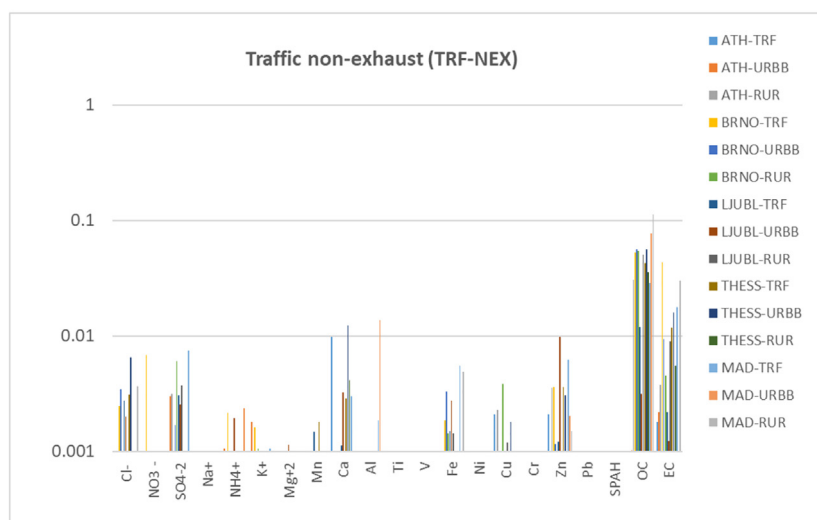
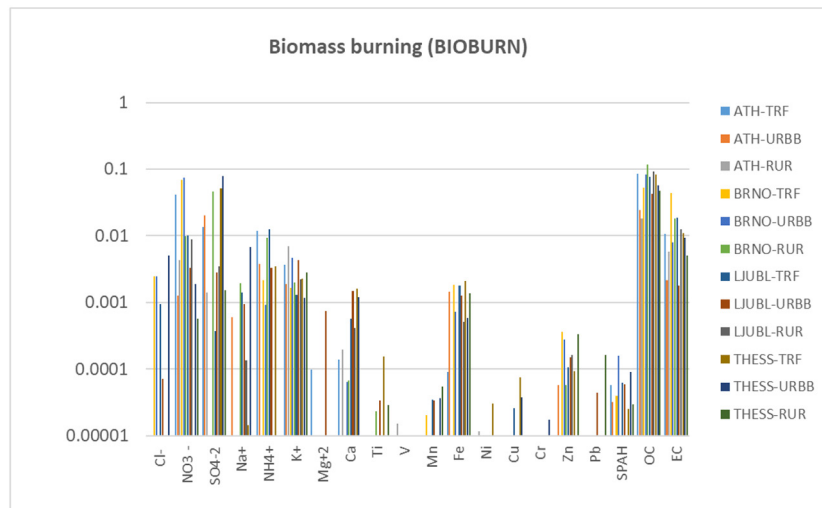


Fig. 1. a-h. PMF factor profiles ($\mu\text{g}/\mu\text{g}$).

ratio value close to unity implies traffic exhausts, without excluding lower or higher values indicating predominance of diesel or gasoline catalytic car emissions, respectively (Argyropoulos et al., 2017; Salameh et al., 2015; Waked et al., 2014; El Haddad et al., 2009). In ICARUS cities, this ratio ranged between 1.1 and 15.3. The lowest values were observed for TRAF-EX sources at traffic sites (min: 1.1, LJUBL-TRF; max: 1.6, ATH-TRF) due to the proximity of the sampling points to the vehicle circulation and therefore the traffic exhausts (Table 1). At urban background sites, OC/EC ratio ranged between higher values: 1.5 (THESS-URBB) and 3.1 (LJUBL-URBB), due to the longer distance from the traffic source (Table 1) and the consequent higher fraction of secondary OC (Samara et al., 2014). The only exception was an extremely higher OC/EC value (15.3) in Athens urban background site, quite close to that reported by Amato et al., 2016, for the same site. This value was then attributed to the reduced share of diesel vehicles in the local fleet; however, it could be also linked to a possible influence of biomass burning source (fireplace use), which is intense at the

specific site during the winter sampling period (Saraga et al., 2015). This is also supported by the presence of K^+ in the source profile. At rural sites, OC/EC ratio ranged between 1.1 (ATH-RUR) and 4.28 (THESS-RUR). The low value in Athens rural site is possibly attributed to the frequent diesel-engine trucks circulation close to (200 m) the sampling site. Nevertheless, as an average, OC/EC ratio was very similar between urban background (2.3) and rural (2.5) sites, compared to the lower average at all traffic sites (1.4). In general, the variation of OC/EC ratio values among the resolved TRAF-EX profiles in the present study is consistent with Querol et al., 2013 findings, where OC/EC ratio values were compared among 78 remote and urban monitoring stations in Spain. Finally, a significantly lower contribution to PM mass is found for other species (Fe , Zn , SO_4^{2-}), which have been associated in literature with engine oil additives or antifreeze inhibitors (Amato et al., 2009). The contribution of TRAF-EX source to $\text{PM}_{2.5}$ concentration was on average 23.3% at traffic sites, 13.3% at urban background sites and 8.8% at rural sites (excluding ATH-RUR site, where it was 21.2% due to frequent

c)



d)

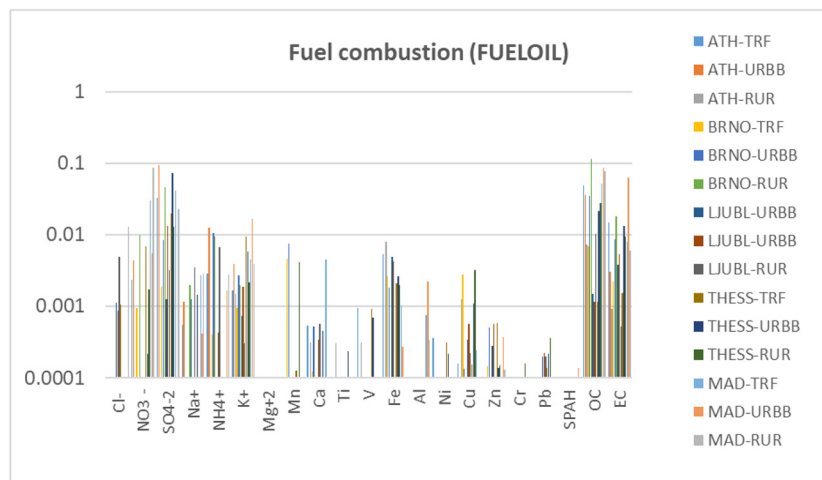


Fig. 1 (continued).

heavy vehicles circulation). The highest contribution of this source is observed at LJUBL-TRF site (37.8%) while the lowest (5.6%) at BRNO-RUR and THESS-RUR sites.

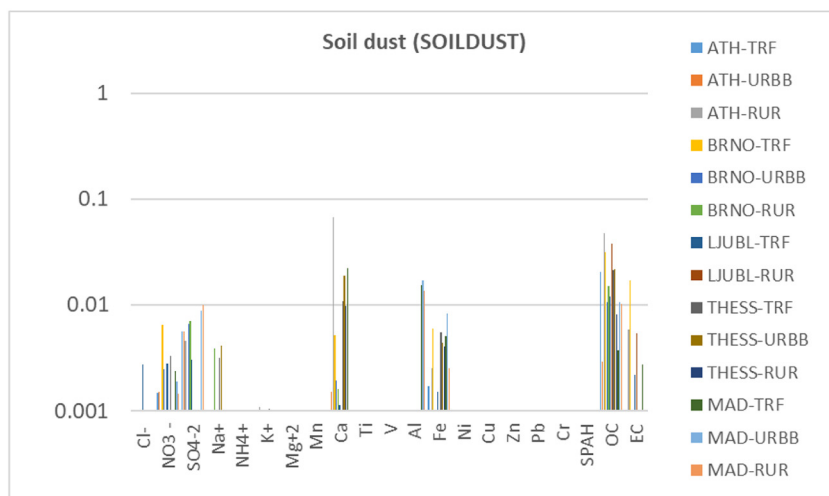
Traffic non-exhaust source (TRAF-NEX) represents anthropogenic dust sources such as inorganic materials (probably metals or their oxides) emitted from vehicles brake pads, tires and mechanical parts and comprises the mineral-road dust source (Waked et al., 2014; Hassan et al., 2020). It is characterized by significant shares of elemental and organic fractions (10–35% of total OC or EC) which is an indication of mixing of soil dust and organic matter during aging or by entrainment of organic materials from the soils (Kuhn, 2007). TRAF-NEX is also traced by crustal species (3–63% of total Ca, 6–68% of total Fe; 9–31% of total Al only in Madrid sites) and trace elements as Zn (9–66%), Cu (18–89%) and Mn (7–78%). It should be noted that especially at rural sites, the prevalence of organic material (OC higher than EC shares) combined with elevated contribution of natural soil tracers (Ca, Fe) implied that this source is probably mixed with soil dust or dust from unpaved roads. Finally, sulfate ion is also present in most TRAF-NEX profiles, with a rather low contribution on $PM_{2.5}$ mass (<10%), except for the case of ATH-URBB (30% of PM mass). The average contribution of TRAF-NEX to $PM_{2.5}$

concentration laid on similar levels at traffic (12.6%) and urban background (13.5%) sites while being lower (6.1%) at rural sites.

3.1.2. Fuel oil combustion and industry (FUELOIL)

Particles originating from fuel oil combustion are traced by high shares of OC, EC, SO_4^{2-} , K or K^+ , and in few cases (ATH-TRF, THESS-TRF, THESS-URBB) also by Ni and V. In the majority of the cases, FUELOIL source includes the refinery activities/industrial emissions, being present in both seasons (e.g. Fig. S1a, b) and traced also by Fe, Cu, Zn and Pb, revealing emissions from metallurgical, chemical and pharmaceutical, food, paper industry as well as power plants (Pey et al., 2013; Taiwo et al., 2014). Indeed, the highest contributions of these elements to PM mass has been reported in sites located at a distance of less than 5 km from an industrial zone (ATH-RUR, BRNO-TRF, BRNO-URBB, LJUBL-TRF, LJUBL-URBB, LJUBL-RUR and THESS-RUR). It should be mentioned that in the cases of THESS-TRF, THESS-URBB sites, this factor possibly includes also shipping emissions (the port is at a distance of 5 < km from both sites) traced by a V:Ni ratio close to 3 (Saraga et al., 2019; Tolis et al., 2015). The average contribution of FUELOIL to $PM_{2.5}$ concentration did not reveal a clear predominance in

e)



f)

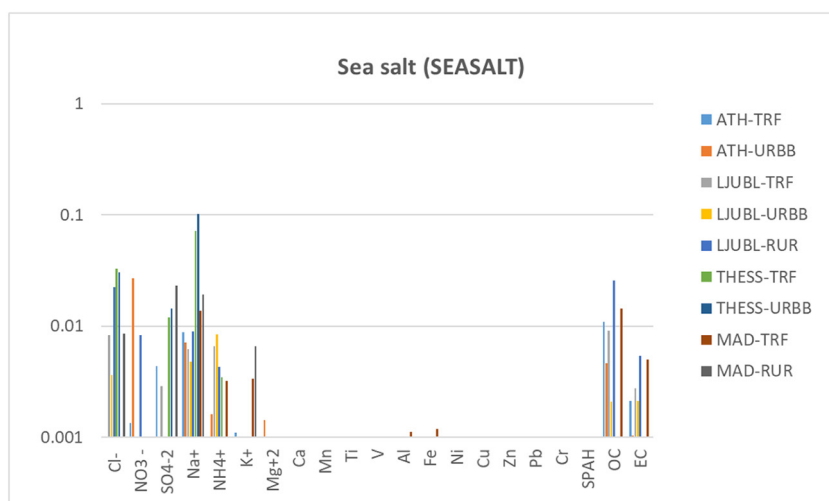


Fig. 1 (continued).

a specific type of areas (13.8% at traffic, 11.6% at urban background and 18.7% at rural sites).

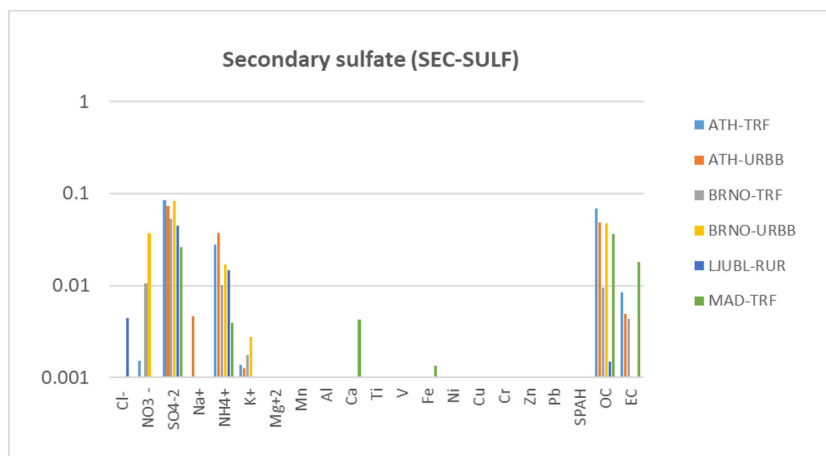
3.1.3. Biomass burning (BIOBURN)

Biomass burning (BIOBURN) source was present at all sampling sites, except for Madrid sites. Major tracers of this source are both carbonaceous fractions (OC:30–78%; EC:3–15% of $PM_{2.5}$ mass), K^+ (2–19%), SO_4^{2-} (3–33%), NH_4^+ (<10%) without neglecting PAHs which although corresponding to a very small part of PM mass (<1%), they prevail in BIOBURN factor (53–74% of measured PAHs contribute to BIOBURN factor). In some cases, specific elements (Cu, Zn, Fe) appear in the factor profile (<3% of PM mass) possibly because of inappropriate kinds of flammable material (treated wood, old furniture or combustible wastes) burning (Sarigiannis et al., 2014) or mixing with traffic emissions. While carbonaceous fractions are major components in combustion-related sources (Popovicheva et al., 2016), the OC/EC ratio is considered as a robust diagnostic of biomass burning. Indeed, this ratio ranged between 2.5 (BRN-TRF) and 11.2 (ATH-URBB), being in line with previous studies (Salameh et al., 2015 and references within) highlighting the occurrence of wood burning emissions. Especially for LJUBL-URBB, a significantly higher ratio value was observed (24.3),

possibly attributed to a higher proportion of secondary organic aerosol. Finally, a noteworthy contribution of sulfate ion is observed for BIOBURN factor in the cases of ATH-URBB, THES-TRF and THESS-URBB (32–33%), BRNO-RUR (23%), while the percentages at the other sites were < 8%. The presence of sulfate ion in biomass burning factor was also observed by Diapouli et al., 2017 (especially for the city of Thessaloniki) and Popovicheva et al., 2014, where it was implied that formation of secondary inorganic compounds is enhanced during biomass burning events. Especially for the case of BRNO-RUR, the elevated fraction of sulfate ion can be also attributed to coal burning during the measurement campaign which was reported for that area.

BIOBURN factor time variation indicates the prevalence of the source during winter (fireplaces or wood stoves burning), without excluding biomass combustion emissions from agricultural activities (in cases of Athens, Ljubljana and Thessaloniki rural sites). Wood burning for domestic heating in Greece (Athens and Thessaloniki) has been considerably increased during the last decade due to the economic crisis and the high price of diesel. In Brno, wood combustion is the second most frequent type of domestic heating in residential buildings (after natural gas). Although fireplaces use is not common in Ljubljana, wood combustion in stoves is frequent. On the contrary, in Madrid sites, no domestic

g)



h)

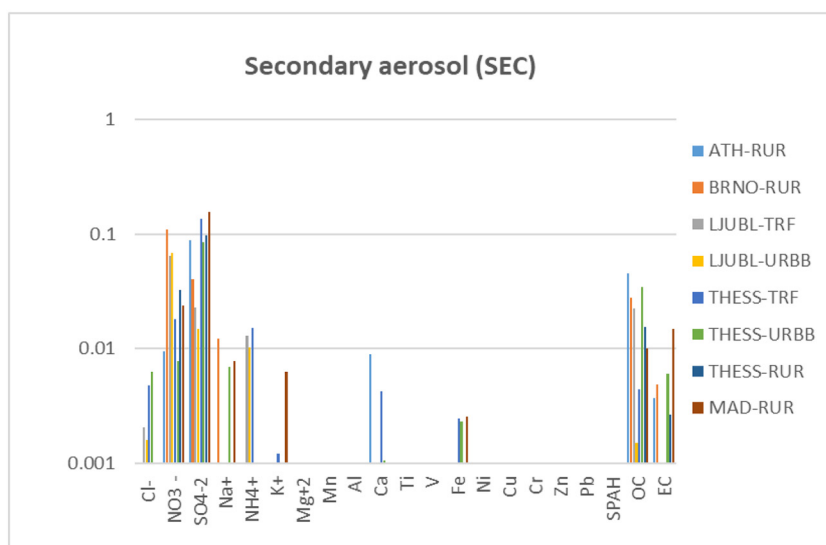


Fig. 1 (continued).

biomass burning is reported as buildings' heating is sufficiently supplied by natural gas. BIOBURN contribution to $PM_{2.5}$ was on average 22% at traffic sites, 30% at urban background sites and 28% at rural sites. The highest percentage of BIOBURN contribution was found in THESS-URBB (45%), while the lowest in LJUBL-TRF (12%). There is a moderate difference between traffic and urban background sites, as the latter are characterized by more intense wood burning (residential buildings). However, BIOBURN contribution percentage is strongly dependent on the type of fuel and combustion device used for heating in each area. In terms of temporal variation, a clear predominance of BIOBURN source during the cold season (fireplaces burning period) is observed for the majority of the cases. An exception is noticed for ATH-RUR, LUBL-RUR and THES-RUR, where the source is present also during the warm season campaign as there is contribution from reported agricultural activities or potential long-range transport of aerosols emitted by grassland and/or forest fires during summer. Typical examples of the two cases are given in Fig. S2a,b.

3.1.4. Soil dust (SOILDUST)

Soil dust (SOILDUST) was identified in all cases except for LJUBL-TRF and LJUBL-URBB sites, where it was combined with TRAF-NEX factor.

This source is associated with elements from the earth's crust and presented different profile among the sites, even in the same city. In general, the dominant elements of this source are Ca (28–90%), Al (40–77%) and Fe (10–60%). It is worth mentioning that this factor also includes a fraction of OC mass (20–68% of PM mass), which is an indication of mixing of dust and organic matter during aging or by entrainment of organic materials (Kuhn, 2007). Indeed, in most of the cases, OC/Ca ratio was found to be significantly higher than the stoichiometric ratio of carbonate carbon to calcium (CC/Ca) in calcite (0.3), revealing additional organic carbon sources, such as biogenic OC or road dust. ATH-RUR and THESS-RUR sites were an exception (0.7 and 0.8, respectively), confirming the prevalence of mineral dust profile of the source. SOILDUST contribution to $PM_{2.5}$ concentration ranged between 5% and 25%. A remarkable difference between traffic/urban background and rural sites is noticed, as SOILDUST average contribution was twofold in the latter (5% and 8% at TRF and URBB sites; 16% at rural sites). Finally, SOILDUST factor does not present a seasonal trend but it is often characterized by sharp peaks corresponding to dust transportation events. In three cases (Athens, Thessaloniki and Madrid), these peaks are noticed simultaneously in the source's temporal contribution of two different sites (4-6/2/2017 for ATH-TRF and ATH-URBB; 21-24/2/2017 for

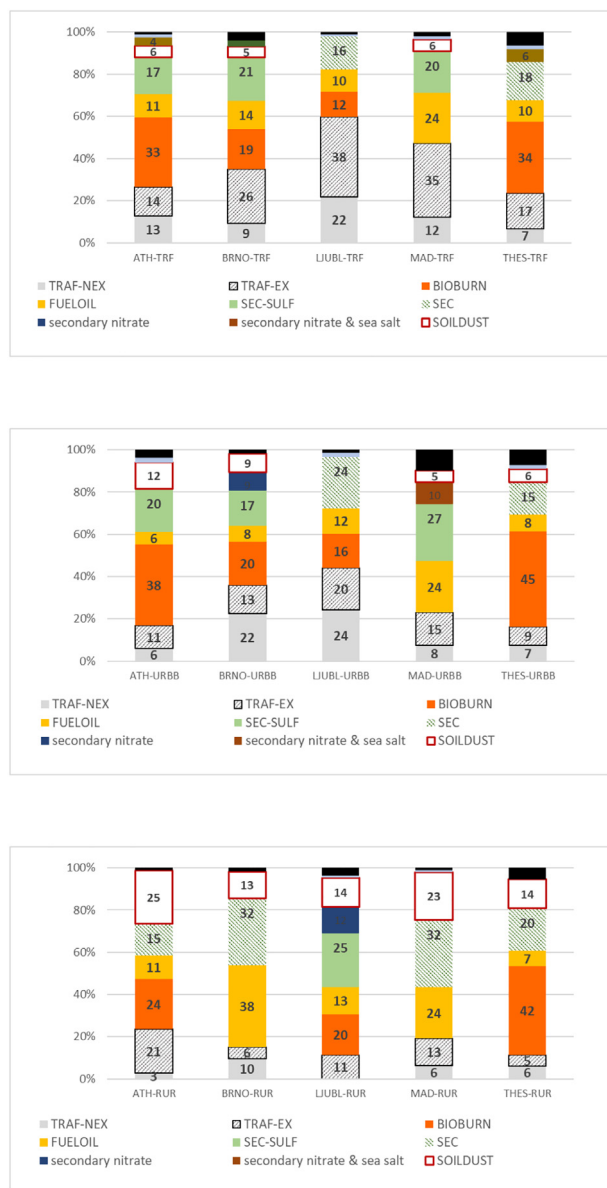


Fig. 2. a-c. The contribution (in %) of each source to PM_{2.5} concentration at a) traffic b) urban background and c) rural sites.

MAD-TRF and MAD-URBB; 29/6-1/7/2017 for THESS-URBB and THESS-RUR) of the city revealing a dust transportation event occurring in the broader area (Fig. S3a-f). Indeed, the application of the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005) applied on these specific samples (Fig. S4a-c), confirmed that a Saharan dust event transport occurred between 3 and 5/2/2017, affecting both Athenian sites and another one between 29/6-1/7/2017 affecting Thessaloniki and Athens (ATH TRF, Fig. S3a).

3.1.5. Sea salt (SEASALT)

Sea salt (SEASALT) source was identified in Athens, Ljubljana, Madrid and Thessaloniki and was mainly traced by Cl^- , Na^+ , Mg^{+2} ions. Chloride to sodium ratio values were all lower than the expected value of 1.81 in the sea water (McInnes et al., 1994). This means that the marine contribution is rather aged and presents chlorine depletion due to chemical reactions involving NaCl and HNO_3 or H_2SO_4 , which led to the formation of NaNO_3 or Na_2SO_4 and gaseous HCl (Pio et al., 1996). Sea salt has been identified in Madrid and Ljubljana, despite

the long distance from the sea. Moreno et al., 2013 had also identified the marine aerosol in Madrid while for Ljubljana sites, SEASALT can possibly originate from street salting (technical salt NaCl or solution of CaCl_2) during winter. SEASALT contribution was in lower than the other sources' levels (1–4%).

3.1.6. Secondary aerosol (SEC)

Secondary particles source has been identified either as secondary sulfate and organics (SEC-SULF) or as sulfate and nitrate-rich (SEC).

The main tracers of SEC-SULF source are SO_4^{2-} , NH_4^+ and OC. SO_4^{2-} comprised the 42–70% of PM mass while OC share was between 3% and 40%. This source is usually characterized by constant composition revealing mainly regional origin (Almeida-Silva et al., 2016; Viana et al., 2008). Particularly, it is typically associated with long-range transport events, as it is considered as an ingredient of aged air masses, because the oxidation of SO_2 to SO_4^{2-} is slow and thus this aerosol component is more related to transported rather than local pollution (Manousakas et al., 2017). The stoichiometric $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio for $(\text{NH}_4)_2\text{SO}_4$ is 2.7. In the present study, in the cases where SEC-SULF sources was separately identified, the $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio was found to be close to the stoichiometric: ATH-TRF (3.1), ATH-URBB (2.0), BRN-TRF(2.8), BRN-URB (3.1), LJUBL-RUR (3.0).

In all other cases, secondary aerosol was represented by a both sulfate and nitrate-rich chemical profile. Specifically, the share of NO_3^- to PM mass ranged between 10 and 70%, SO_4^{2-} between 9% and 65% and OC between 2% and 29%. A separate secondary nitrate factor has been identified only in LJUBL-RUR site (NO_3^- : 81%, NH_4^+ : 19%). In that case, the ratio $\text{NO}_3^-/\text{NH}_4^+$ was found to be 4.2, close enough to 3.4, which is the stoichiometric ratio calculated for NH_4NO_3 . In the other cases, the ratio was much higher, indicating that a major part of nitrate may have been associated with other species as K^+ and OC.

No clear seasonal trend for secondary aerosol source is observed for the majority of the cases, possibly due to the balanced prevalence of sulfate during summer and nitrate during winter. Only in BRN-TRF, BRN-RUR and THESS-RUR, a vague seasonal trend with slightly higher percentages during summer is noticed, which can be attributed to the enhanced photochemical activity. Regarding secondary aerosol factor contribution, SEC-SULF accounted for the 20–27% of PM_{2.5} concentrations while SEC contributed for the 16–34% of PM_{2.5} concentrations. No significant variation in the source contribution is observed among the type of the sampling areas, although higher percentages are expected in urban areas (Grivas et al., 2018). In case of LJUBL-RUR, the secondary nitrate source contribution was 11%, which could be attributed to vicinity of industrial and especially agricultural emissions to water/air matrixes.

It should be taken under consideration that the road-transport sector (gaseous traffic emissions and their secondary processing into particulate matter) may in the end account for a much more significant contribution to secondary particles, at a regional scale. Specifically, Waked et al., 2014 related, partly, the nitrate-rich factor to NO_x emissions originating from traffic sector, especially during the spring season when nitrates and dust markers were at their highest levels. On the other hand, the presence of OC in the source profile, associates the factor with secondary organic particles, too. It is evident that vehicle emissions of volatile organic compounds may also account for a significant fraction of secondary organic aerosols (Bahreini et al., 2012). Therefore, it can be concluded that this secondary-particle factor may represent not only the formation of secondary aerosol over relatively long distances, but also a part of traffic-related pollution.

3.1.7. Other sources

In the case of ATH TRF, a separate factor of high shares of calcium was revealed, without significant seasonal variation and with a total contribution to PM_{2.5} concentrations of 6%. This factor was attributed to resuspended dust from constructions in the surrounding area (Samara et al., 2003). The source of fireworks burning has been

identified for BRNO TRF site, being characterized by K, Cu, EC (tracers of fireworks materials, Scerri et al., 2018) and a characteristic sharp peak on 14/6/2017 when a firework competition took place in the city. The low but non-zero contribution of this factor during the other days, can be attributed to the model's limitation to distinguish the source.

3.2. PMF outcomes relationship with PM_{2.5} exceedances and meteorological parameters

Source contributions were also averaged separately for days of PM_{2.5} limit (WHO daily limit: 25 µg/m³) exceedance. The limit value was exceeded in 50% of the sampling days at ATH-TRF, 51% at ATH-URBB and ATH-RUR, 28% at BRNO-TRF, 25% at BRNO-RUR, 10% at BRNO-RUR, 28% at THES-TRF, 37% at THES-URBB, 8% at THES-RUR. It is remarkable that the majority (>70%) of the exceedances were recorded during the winter period. The exceedances at Madrid sites were less than 7% of the sampling period.

It is mainly the biomass burning and traffic-related sources contribution that present a noticeable –positive– change during the days of PM_{2.5} limit exceedance. In detail, the highest increase in BIOBURN contribution was noticed in ATH-TRF (from 26% to 33%), ATH-URBB (from 32% to 38%), THES-TRF (from 29% to 34%), THES-URBB (from 40% to 45%), THES-RUR (from 38% to 42%), highlighting the strength of this source due to the elevated use of biomass combustion for domestic heating. A quite lower (<2%) increase was also revealed for Brno and Ljubljana sites. Further, TRAF-EX contribution exhibited an increase during days of PM_{2.5} exceedances, which in most of the cases was lower than 2% except for the cases of BRNO-TRF (from 23% to 26%), BRNO-URBB (from 10% to 13%), LJUBL-TRF (from 32% to 38%), MAD-TRF (from 32% to 35%), THES-TRF (from 14% to 17%). Correspondingly, for TRAF-NEX contribution, a negligible or low (<2%) increase was reported during the exceedances except for LJUBL-TRF (from 17% to 22%) and MAD-TRF (from 8% to 12%). It should also be mentioned that a non-negligible increase is noticed for SOILDUST contribution for the exceedances period at ATH-TRF (from 3% to 6%), ATH-URBB (from 10% to 12%), THES-TRF (from 4% to 6%), THES-URBB (from 4% to 6%) and THES-RUR (from 10% to 14%). For all the other sources, the contribution either remains almost stable or decreases, as a relative suppression of the above discussed source contributions.

Pearson correlation was examined (by the use of IBM-SPSSv.32) for the identification of potential positive or negative correlation among the factors/source temporal variation and temperature, relative humidity and wind velocity. Statistically significant –negative– correlation (at 0.05 level) was recorded for most of the cases between BIOBURN and temperature. Particularly, the specific *r* ranged between –0.52 and –0.74 at traffic sites and between –0.48 and –0.78 at urban background sites. At rural sites, significant anti-correlation was observed only at ATH-RUR and THES-RUR, with *r* equal to –0.68 and –0.61 respectively. The inverse trend of biomass combustion contribution increasing while temperature decreases, confirms the source's prevalence during cold months (i.e. intense domestic wood burning). A moderate correlation is observed between SEC contribution and temperature at BRN-RUR (*r* = 0.78, *p* < 0.05) and THES-RUR (*r* = 0.54, *p* < 0.05) and between SEC-SULF and temperature at BRN-TRF (*r* = 0.57, *p* < 0.05), possibly due to the enhancement of secondary particles' formation during warm and sunny days (Lee et al., 2014). In the other cases, the absence of this correlation may imply the fact that this source can be associated with both long-range transport and secondary processes in the atmosphere, as discussed in previous section. No other significant correlation was revealed among the resolved sources and relative humidity or wind speed variation.

The interpretation of the resolved PMF sources was also supported by the relation of factor contributions with wind direction and velocity, as derived from a number of polar plots (Openair, Carslaw and Ropkins, 2012). For example, traffic-related sources

(TRAF-EX, TRAF-NEX) clearly show higher concentrations under winds corresponding to the direction of the main roads and vehicle traffic area. Moreover, in several cases, the pattern is similar between TRAF-EX and TRAF-NEX, highlighting their common origin. A characteristic example of this, is the case of Madrid traffic and urban background sites (Fig. 3a-d). The origin of traffic emission at MAD-URBB seems to be mainly from East sector, that is the center of the city and the MAD-TRF site, without excluding the impact of local traffic emissions e.g. a direct road (especially for the NEX component).

Regarding the BIOBURN source, the highest contributions correspond to wind directions that pinpoint domestic areas (i.e. intense wood burning for heating) or areas where agricultural burning is frequent. For example, the former is clear for ATH-URBB (Fig. 4a), where N, NE (i.e. northeastern suburbs of Athens) and SSW, SW, WSW (i.e. densely populated areas of center and eastern surroundings) winds are associated with high percentages of BIOBURN contribution. The origin of the source in the case of BRNO-URBB seems to be rather local or east-southeastern where are the domestic areas (Fig. 4b). The same source for the case of Thessaloniki (Fig. 4c-d) seems to have twofold character: at THES-URBB there is a clear impact from the surrounding inhabited area (intense fireplace burning) while the THES-RUR site is affected by both fireplaces burning (southern winds) and agricultural burning from the surrounding rural area (NW sector). The latter is supported by the presence of this specific source component in both winter and summer periods while being evidenced also by previous studies for Thessaloniki area (Argyropoulos et al., 2016; Samara et al., 2014).

A clear origin from the sea is revealed for the SEASALT source in cases of ATH-TRF and THES-TRF sites (Figs. 5 a,b). In the first case, the main SEASALT influence is observed under southwestern winds (i.e. from Saronikos Gulf) while in the second, SEASALT is clearly originating from Thermaikos Gulf. Lastly, as described previously, FUELOIL source includes mainly industrial emissions and in specific cases, shipping emissions. A characteristic example of this is for Thessaloniki's sites (Figs. 6a-c): at THES-TRF site, FUELOIL contribution seems to be enhanced primarily by W and WNW winds pinpointing the harbor emissions (e.g. shipping maneuvering) and the relative activities taking place in the surrounding area. At THES-URBB, the source seems to contribute from multiple directions, but a higher component originates from the northern area, where is the Thessaloniki's industrial zone. This is more obvious at THES-RUR site, where FUELOIL is enhanced under S winds, which is the direction of the industrial zone. A remarkably different picture is observed for the FUELOIL source origin in the case of ATH-RUR, where the source is enhanced under almost all observed wind directions, possibly correlated with industrial emissions occurring in the broader area. Finally, the SOILDUST and SEC sources are associated with winds of all observed directions. This was anticipated as dust from soil is an ambiguous source while secondary formation of particles may originate or have been transported from any direction either through long-range transport or secondary particles formation resulting from local sources (i.e. traffic emissions, oil combustion) as discussed previously.

3.3. Similarity in sources chemical profiles among the sites

A tool for examining the homogeneity among the chemical profiles of the same source category identified in various receptor sites has been developed in the frame of the FAIRMODE (Forum for Air Quality Modeling) activities and presented by Belis et al., 2015. As Pearson is known to be sensitive when comparing profiles with species of high range of concentration, the combined use of two parameters as similarity indicators is proposed: the PD (Pearson distance) and SID (standardized identity distance):

$$PD = 1 - r^2,$$

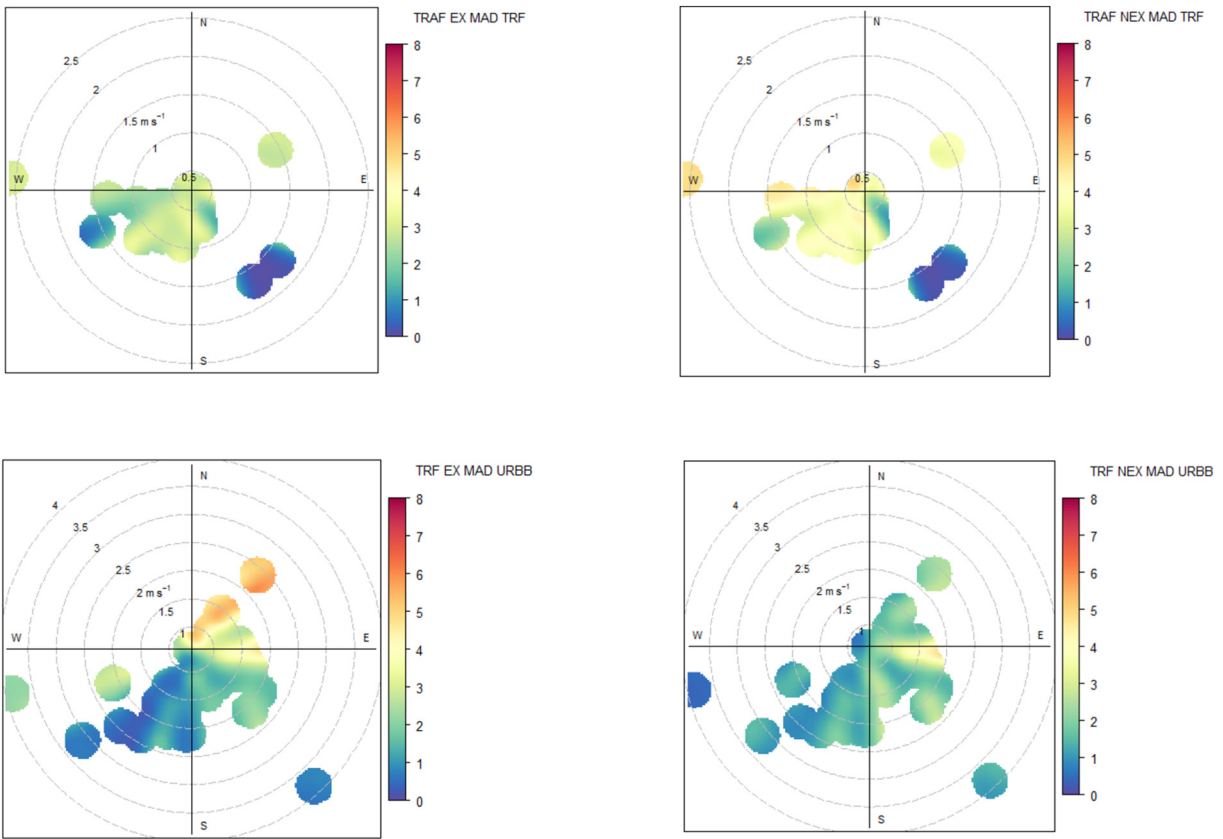


Fig. 3. a-d. Traffic sources contribution ($\mu\text{g m}^{-3}$) vs wind direction and velocity (Openair, Carslaw and Ropkins, 2012).

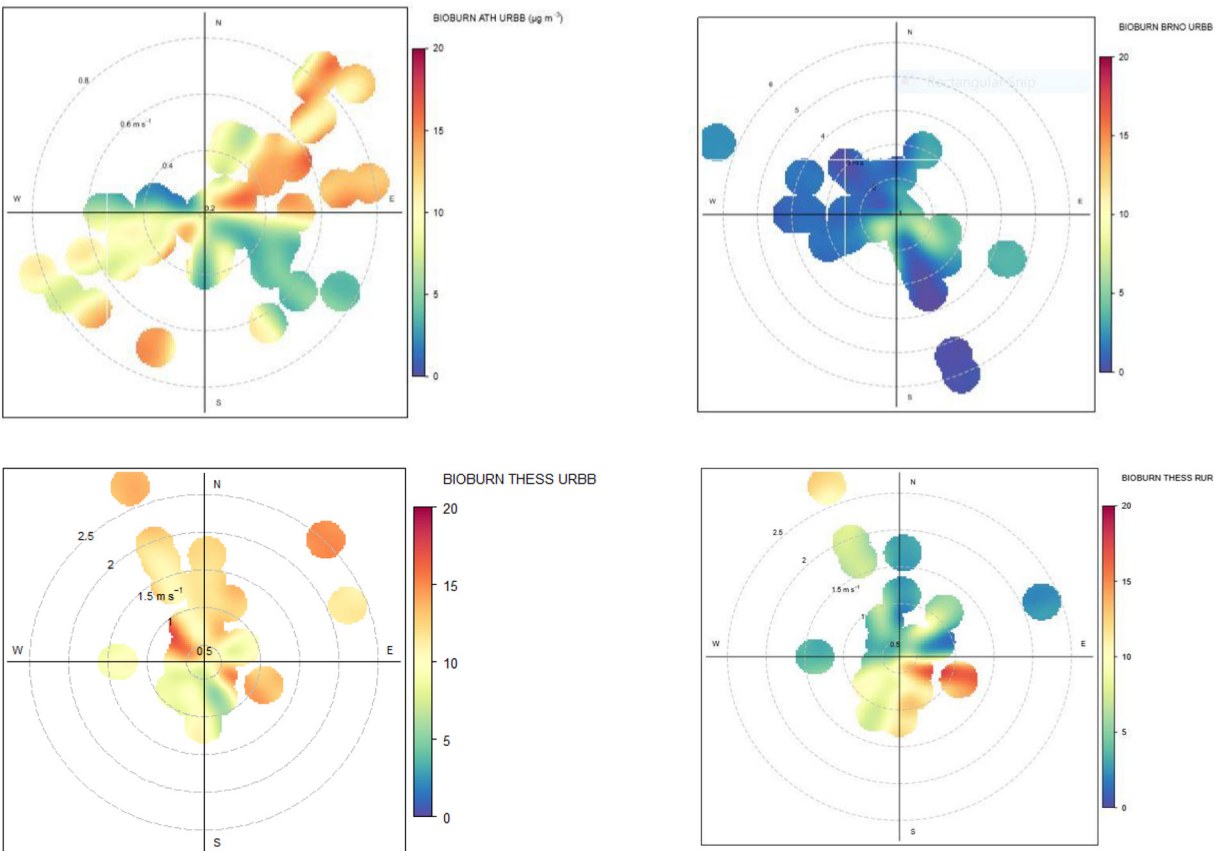


Fig. 4. a-d. BIOBURN contribution ($\mu\text{g m}^{-3}$) vs wind direction and velocity (Openair, Carslaw and Ropkins, 2012).

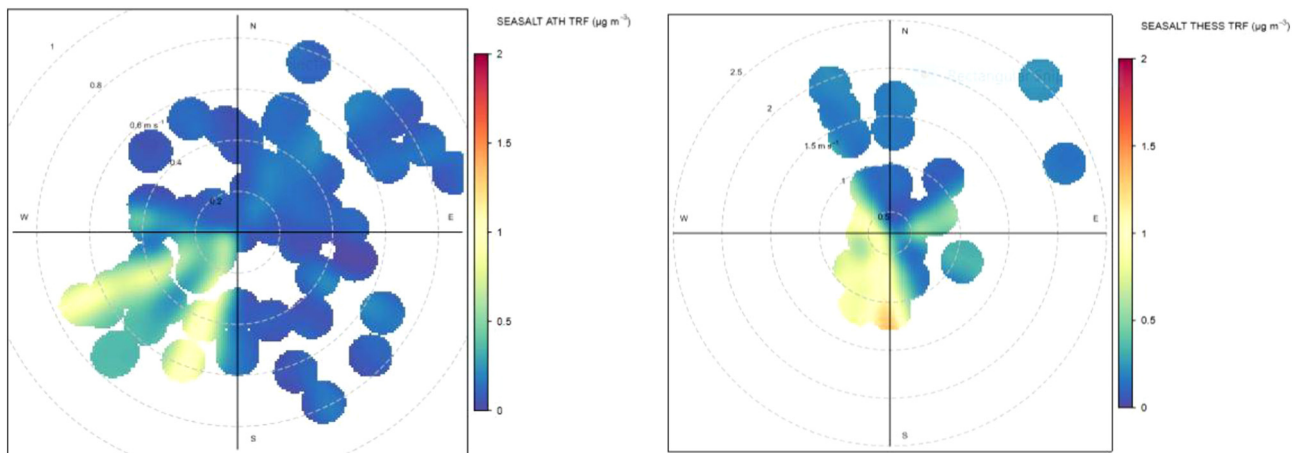


Fig. 5. a, b. SEASALT contribution ($\mu\text{g m}^{-3}$) vs wind direction and velocity (Openair, Carslaw and Ropkins, 2012).

where r^2 is the Pearson coefficient and

$$SID = \frac{\sqrt{2}}{m} \sum_{j=1}^m \frac{|x_j - y_j|}{x_j + y_j},$$

where x and y is the relative mass ($\mu\text{g}/\mu\text{g}$) to the PM of two different sources and m the number of common specie in x and y (Weber et al., 2019). Practically, SID results from the comparison of $n(n-1)/2$ possible

and unique pairs of profiles for each source. As Belis et al., 2015 underlined, SID is independent of the species concentration, but sensitive to the amplitude of the variables. Another advantage of SID is that it can be calculated for theoretical profiles of only two species, while the correlation for this specific but rather common type of profile with any other will always result in Pearson equal to 1. Based on Pernigotti and Belis, 2018, the acceptable PD and SID values for profile similarity are: $P < 0.4$ and $SID < 1$.

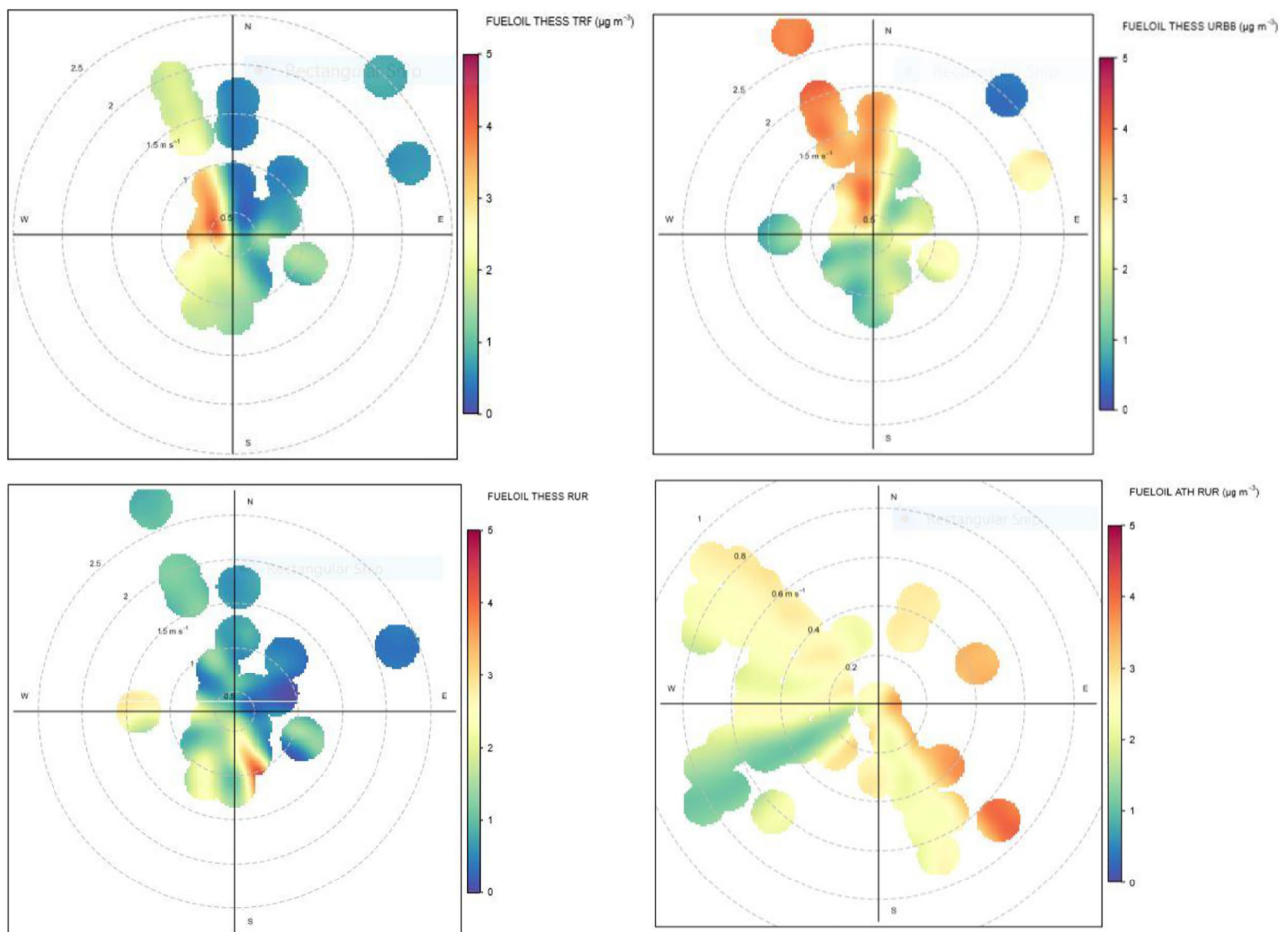


Fig. 6. a, b. FUELOIL contribution ($\mu\text{g m}^{-3}$) vs wind direction and velocity (Openair, Carslaw and Ropkins, 2012).

In the present study, 15 TRAF-EX, 15 TRAF-NEX, 15 FUELOIL, 12 BIOBURN, 14 SOILDUST, 9 SEASALT, 5 SEC-SULF and 8 SEC profiles were examined. Cases of sources mixing or sources identified only in one or two sites (fireworks in BRNO TRF) were excluded from the analysis. Fig. 7 illustrates the similarity plot (PD-SID space) for all possible pairs of profiles belonging to the same factor/source category and the acceptable area for profile similarity. The number of pairs of profiles compared for each source category is given in the parenthesis.

It is observed that SEC and SEC-SULF source profiles present both low PD and SID values inside the acceptable area ($PD < 0.4$ and $SID < 1$), revealing their homogeneity among the sampling sites. On the other side, BIOBURN, SEASALT and TRAF-EX profiles can be considered as relatively homogenous at all sites as part of PD and SID values are outside the acceptable area. TRAF-EX source is characterized by low SID values (mean and standard deviation inside the acceptable area), but high variability of PD. As PD is sensitive to the prevailing (in terms of mass) chemical components (i.e. OC and EC which contributed to 83–97% of PM mass), the variability should be attributed to the carbonaceous fractions and specifically to their ratio. Indeed, as discussed in the previous section, the OC/EC ratio value varied significantly (1.1–15.3), strongly depending on the dominant type of vehicles at each site. Similarly, the prevailing tracer for BIOBURN is OC ($56 \pm 13\%$ of PM mass), followed by EC, SO_4^{2-} and NO_3^- (characterized with wider dispersion, Fig. 7) and specific elements and PAHs (with even wider dispersion and lower contribution). As SID is sensitive to the amplitude of the variables and PD is sensitive to the prevailing (in terms of mass) chemical component, which is OC, the two parameters take also values higher than the acceptable limits for similarity. These observed differences can be attributed to different type of burning materials in each area or to the fact that agricultural burning is included in most of the cases. Inclusion of specific tracers (e.g. levoglucosan, manosan) could contribute to the separation of these two combustion sources. SEASALT, recognized in nine sites, could also be considered as relatively homogenous, possibly due to the significant variation in tracer species' (Na^+ , Cl^- , Mg^{2+}) percentages.

Further, FUELOIL, TRAF-NEX and SOILDUST profiles are considered as dissimilar according to both PD and SID values (mean and standard deviation). Indeed, as FUELOIL may include fuel oil combustion, industrial emissions or even shipping exhaust emissions, its chemical profile is expected to differ largely among the sites. SOILDUST is proved to be non-homogeneous among the sites although presenting common compounds of high contribution of certain metals (Ca, Fe or Al) and OC. Moreover, while SID presents a low variance, PD has a significantly

higher one, indicating a large discrepancy for the chemical species that represent the main mass (>40% in sum) of the profile (Weber et al., 2019). One of them is organic carbon, which may reveal the mixing of dust and organic matter during aging or by entrainment of organic materials. For similar reasons, TRAF-NEX is also characterized as non-homogeneous, with OC, EC being the dominant species, the combination of crustal species (Ca, Fe, Al) and trace elements (Zn, Cu, Mn) prevailing in each case is different. This is expected, as TRAF-NEX profile is highly dependent on the proximity to the source, surface characteristics, different type of road wear and vehicle materials, driving conditions as well as meteorological conditions (Hassan et al., 2020).

4. Conclusions

In the frame of ICARUS EU2020 project, a comprehensive database including $PM_{2.5}$ concentration and chemical composition from three sites (traffic, urban background and rural) of five European cities (Athens, Brno, Ljubljana, Madrid and Thessaloniki) was created. With the scope of a harmonized source apportionment approach, this paper presents an overview of Positive Matrix Factorization (PMFv.5) model results, focusing on dominant sources investigation while examining their statistical robustness and representativeness.

The results indicated that traffic-related sources and biomass burning prevail in terms of PM mass contribution. Particularly, the contribution of traffic exhausts source to $PM_{2.5}$ concentration was on average 23.3% at traffic sites, 13.3% at urban background sites and 8.8% at rural sites. The average contribution of traffic non exhausts to $PM_{2.5}$ concentration laid on similar levels at traffic (12.6%) and urban background (13.5%) sites while being lower (6.1%) at rural sites. The contribution of fuel oil combustion to $PM_{2.5}$ concentration did not reveal a clear predominance in a specific type of areas (13.8% at traffic, 11.6% at urban background and 18.7% at rural sites). Biomass burning contribution was on average 22% at traffic sites, 30% at urban background sites and 28% at rural sites. Regarding soil dust, a remarkable difference between traffic/urban background and rural sites is noticed, as average contribution was twofold in the latter (5% and 8% at traffic and urban background sites; 16% at rural sites). Sea salt contribution was the lowest (1–4%) while secondary particles accounted for the 16–34% of $PM_{2.5}$.

Furthermore, in the majority of the cases, traffic, biomass burning, fuel oil combustion and sea salt sources revealed a clear dependence on the wind direction. On the contrary, secondary particles and soil dust sources' origin was ambiguous as they are associated with long-range transport or even secondary particles formation resulting from

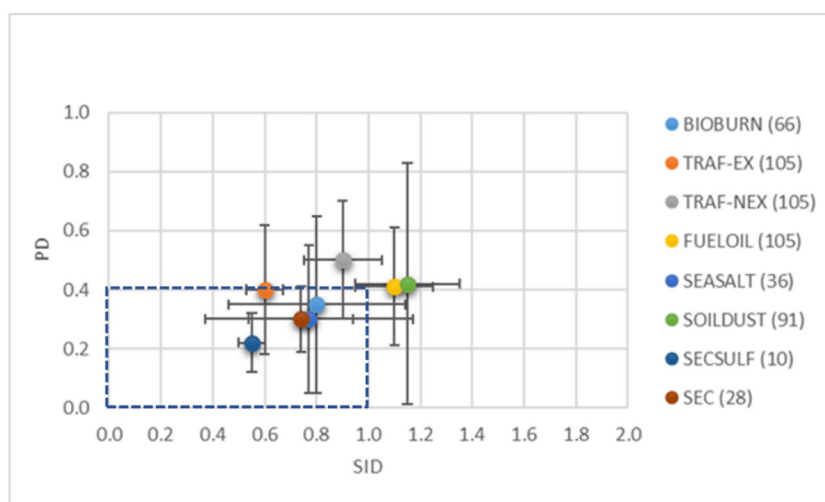


Fig. 7. Similarity plot (PD-SID space) for all pairs of profiles belonging to the same factor/source category and the acceptable area for profile similarity. The number of pairs of profiles compared for each source category is given in the parenthesis.

local sources. The profiles similarity test indicated that fuel oil combustion, traffic non-exhausts and soil dust source profiles are considered as dissimilar while biomass burning, sea salt and traffic exhaust can be characterized as relatively homogenous. Only secondary aerosol sources have been found to be characterized by similar profiles.

Taking into consideration the air pollution patterns observed over the last decades, the projected trends based on the socio-economic data along with the evolution of the environmental legislation, it becomes apparent that future efforts need to be targeted on specific sources, in terms of the quantitative assessment of their contribution in the observed PM levels. Abatement of pollution at its source is one of the overarching principles of the Thematic Strategy on Air Pollution (TSAP; Dir. 2008/50/EC). Consequently, reliable and quantitative information on pollution sources is essential for the implementation of the Air Quality Directives and protection of climate and population health. In this direction, more efforts for harmonized source apportionment results across Europe and the consequent linking of them to policy making towards air pollution abatement are needed.

CRedit authorship contribution statement

D. Saraga: Conceptualization, Methodology, Writing - original draft. **T. Maggos:** Conceptualization, Methodology, Writing - review & editing. **C. Degrendele:** Investigation, Writing - review & editing. **J. Klánová:** Investigation, Resources. **M. Horvat:** Investigation, Resources. **D. Kocman:** Investigation, Writing - review & editing. **T. Kanduč:** Investigation, Writing - review & editing. **S. Garcia Dos Santos:** Investigation, Resources. **R. Franco:** Investigation. **P. Morillo Gómez:** Investigation, Resources. **M. Manousakas:** Investigation, Writing - review & editing. **K. Bairachtari:** Investigation. **K. Eleftheriadis:** Investigation. **M. Kermenidou:** Investigation. **S. Karakitsios:** Investigation. **A. Gotti:** Conceptualization, Methodology. **D. Sarigiannis:** Conceptualization, Methodology.

Declaration of competing interest

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

Acknowledgements

This work has received funding from the European Union's Horizon 2020 Programme for research technological development and demonstration under grant agreement No 690105 (Integrated Climate forcing and Air Pollution Reduction in Urban Systems (ICARUS)). This work reflects only the authors' views and the European Commission is not responsible for any use that may be made of the information it contains. Part of this work was carried out in the RECETOX (LM2018121) and ACTRIS CZ (LM2018122) research infrastructures supported by the Czech Ministry of Education, Youth and Sports and the European Structural and Investment Funds (CZ.02.1.01/0.0/0.0/16_013/0001315). Co-financing of the project in Slovenia was provided by the Slovenian Research Agency through the programme P1-0143.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.141855>.

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