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Ambient particulate matter source apportionment using receptor modelling in European and Central Asia urban areas

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ABSTRACT

This work presents the results of a PM2.5 source apportionment study conducted in urban background sites from 16 European and Asian countries. For some Eastern Europe and Central Asia cities this was the first time that quantitative information on pollution source contributions to ambient particulate matter (PM) has been performed. More than 2200 filters were sampled and analyzed by X-Ray Fluorescence (XRF), Particle-Induced X-Ray Emission (PIXE), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to measure the concentrations of chemical elements in fine particles. Samples were also analyzed for the contents of black carbon, elemental carbon, organic carbon, and water-soluble ions. The Positive Matrix Factorization receptor model (EPA PMF 5.0) was used to characterize similarities and heterogeneities in PM2.5 sources and respective contributions in the cities that the number of collected samples exceeded 75. At the end source apportionment was performed in 11 out of the 16 participating cities. Nine major sources were identified to have contributed to PM2.5: biomass burning, secondary sulfates, traffic, fuel oil combustion, industry, coal combustion, soil, salt and "other sources". From the averages of sources contributions, considering 11 cities 16% of PM2.5 was attributed to biomass burning, 15% to secondary sulfates, 13% to traffic, 12% to soil, 8.0% to fuel oil combustion, 5.5% to coal combustion, 1.9% to salt, 0.8% to industry emissions, 5.1% to "other sources" and 23% to unaccounted mass. Characteristic seasonal patterns were identified for each PM2.5 source. Biomass burning in all cities, coal combustion in Krakow/POL, and oil combustion in Belgrade/SRB and Banja Luka/BIH increased in Winter due to the impact of domestic heating, whereas in most cities secondary sulfates reached higher levels in Summer as a consequence of the enhanced photochemical activity. During high pollution days the largest sources of fine particles were biomass burning, traffic and secondary sulfates.

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1. Introduction

Fine particulate matter (PM2.5) – those particles with an aerodynamic diameter of less than 2.5 μm – is a key air pollutant in terms of adverse health effects. According to the document "Air Quality in Europe – 2018 report", published by the European Environment Agency (EEA), in 2016 68% of the stations located in 32 of the 37 countries reporting PM2.5 data exceeded the World Health Organization (WHO) guideline for PM2.5 annual mean (10 $\mu g/m^3$) (EEA, 2018). The 2019 edition of the same report states that in 2016, 412000 premature deaths in Europe were attributed to PM2.5 (EEA, 2019). These numbers indicate that although the great deal of improvement as a result of emission control strategies in Europe, PM2.5 is still a major risk regarding its negative impact on the citizens' health.

Apart from Europe, Asia is also a region highly affected by particulate and atmospheric pollution. Asia is experiencing rapid increases in industrialization, urbanization, and motor vehicle transport (Atkinson et al., 2012). As a result, air pollution levels in many Asian cities remain well above World Health Organization Guideline values (WHO 2006). WHO (2002) estimated that urban particulate air pollution contributed to approximately 800,000 deaths and 6.4 million lost life years worldwide in 2000, with two thirds of these losses occurring in Asia.

Several anthropogenic and natural sources emit PM2.5. Fine particles can be released directly from primary sources or indirectly through the conversion of gaseous emissions in the atmosphere (Seinfeld and Pandis, 2006). PM2.5 concentrations vary largely across Europe due to distinct climatic conditions, emission sources and dispersion patterns (Putaud et al., 2010). Depending on the location, many different sources may contribute to PM2.5 levels such as traffic, dust resuspension, biomass burning, industrial emissions, power plants, sea salt, ship emissions, etc. (Viana et al., 2008; Belis et al., 2013; Eleftheriadis et al., 2014). Understanding sources, processes and effects of high levels of PM2.5 is essential to formulate effective strategies to control PM2.5 levels and to protect human health.

Several source apportionment methods have been developed to identify sources of PM2.5 and their contribution to air quality (Belis et al., 2015a,b). Receptor models identify Particulate Matter (PM) sources and quantify their contribution using aerosol chemical composition data at a given receptor, in contrast to source-oriented dispersion models, which account for transport, dilution, and other processes that take place between the source and the receptor site. The EPA Positive Matrix Factorization model version 5.0 (EPA PMF 5.0) was developed to overcome the weak points of previous receptor models. It includes a weighting scheme considering the uncertainties of the measured concentrations that are used as point-by-point weights. Adjustment of the uncertainty estimates permits it to handle below detection limit and missing data. Furthermore, non-negative constraints are applied to generate more physically explainable factors (Manousakas et al., 2015).

A good spatial coverage of source apportionment studies over Europe, especially regarding the northern and southern regions, is observed (Karagulian et al., 2015; Viana et al., 2008; Diapouli et al., 2017a, b). However, data on particle composition and source apportionment in Eastern Europe and Central Asia countries remain sparse, despite being critical in shedding light on emission control measures of air pollutants in some of the European air pollution hotspot areas (Zwozdziak et al., 2017). To fill this gap in 2014, the International Atomic Energy Agency (IAEA) initiated the Technical Cooperation Project RER/1/013 "Supporting Air Quality Management" to assist countries in collecting and analyzing PM2.5 samples. Sixteen participating countries mainly located in eastern and southeastern Europe and central Asia have improved their competences on sampling, analyzing and utilizing the generated data to identify and quantitatively apportion PM2.5 sources. This paper presents PM2.5 mass concentration levels for all participating cities and quantitative estimation of pollution sources across 11 countries using the EPA PMF 5.0 model. For some Eastern Europe and Central Asia cities this was the first time that quantitative information on pollution source contributions to ambient PM2.5 has been performed. Thus, this paper produced unique data to address air pollution mitigation strategies and to prepare air quality plans aiming at improving air quality and public health.

2. Materials and methods

2.1. PM sampling

More than 2200 PM2.5 samples were collected in urban and sub-urban background stations from 16 European and Central Asia cities. Sampling was performed in 24-h periods, every third day, between January 2014 and December 2015. Particles were sampled on PTFE, polycarbonate, cellulose nitrate, cellulose and quartz filters by means of low and medium volume samplers Sven Leckel MVS6, LVS3 and SEQ47/50-CD, Tecora Echo PM, Gent/SFU, Partisol Plus 2025 sequential, LVS Type Comende Derenda and Digitel DHA-80. Table A1, in Appendix A, presents for each city the sampling coordinates and the details of the PM2.5 sampling and chemical analysis.

2.2. Sample treatment and chemical analysis

Before and after sampling, filters were weighed, in the laboratories located in each city, by means of a microbalance using the procedure described in EN12341. Microbalances of 1 or 10 μg resolution were used in all sites except for Kurchatov/KAZ, Dushanbe/TAZ and Chisinau/MOL where resolution was 100 μg. For the aforementioned sites, the effect of lower resolution microbalances is reflected in the source apportionment results as it will be discussed in section 3.9.

Afterwards, filters were analyzed by several analytical techniques: XRF, PIXE, and ICP-MS for the determination of major and trace elements; thermal-optical analysis, using a Semi-continuous OC-EC Field Analyzer (EUSAAR 2 protocol), for the measurement of elemental and organic carbon; reflectometry and transmittance to determine black carbon; and IC (Ion Chromatography) to analyze water soluble ions (Table A1).

Considering the high number of cities involved in this work, it was not possible to fully harmonize the used methods, which might introduce a level of uncertainty in the obtained results and especially in their comparison. To ensure the quality of PMF analysis, only the cities where the number of collected samples was higher than 75 were included in source apportionment. Additionally, within the scope of the IAEA Technical Cooperation Projects, several intercomparison exercises on sampling (Eleftheriadis, 2010) and chemical analysis (Eleftheriadis and Gini, 2012; Šega and Bešlić, 2013) of particles were performed in order to guarantee the quality of the data generated in the cities.

2.3. Source apportionment

Source apportionment of PM2.5 was performed by receptor modelling that is based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad i = 1, 2, \ldots m \quad j = 1, 2, \ldots n \tag{1}$$

where x_{ij} is the concentration of the species j in the i^{th} sample, g_{ik} is the contribution of the k^{th} source in the i^{th} sample, f_{kj} is the concentration of the species j in the chemical profile of source k, and e_{ij} is the uncertainty of each individual measurement result.

In this study the PMF (Paatero and Tapper, 1994) was used to solve Eq. (1) and the software EPA PMF 5.0 was applied to the data sets obtained in the cities. Factor contributions and profiles were derived in the EPA PMF 5.0 model by minimizing an objective function Q, without detailed prior knowledge on sources inventories (Paatero, 1999).

Details about the source apportionment methodology and the intercomparison exercise, performed within the project framework to assess the performance of the participants in the use of source apportionment tools and to ensure homogeneity of the modelling procedure, are available in Appendix B.

3. Results and discussion

The average PM2.5 concentrations measured in the 16 cities are represented as dots in Fig. 1, whereas lines represent the EU annual limit value (25 μg/m^3) at the time of the study and the WHO annual guideline (10 μg/m^3). Results show that there is a wide range of PM2.5 concentrations across the studied cities. Banja Luka/BIH, Krakow/POL, Sofia/BUL, Ankara/TUR, Skopje/MKD and Dushanbe/TAJ exhibit the highest concentrations (30, 34, 36, 55, 58 and 124 μg/m^3, respectively) exceeding the EU annual limit value. When considering the stricter WHO guidelines, all cities exceeded the PM2.5 annual mean guideline.

The observed PM2.5 levels lead to infer that there is a potential for adverse health effects (WHO, 2016) and a need to identify the PM2.5 sources and their relative contribution to support effective emission control policies and to implement multi-pollutant reduction measures that also address the PM2.5 gaseous precursors.

The EPA PMF 5.0 analysis was conducted to resolve the sources and quantify their contribution to PM2.5 in the cities where more than 75 samples were collected (11 cities). In each city between 5 and 7 sources were identified. Figures C1 to C11 (Appendix C) show the factor profiles and Table C1 (Appendix C) summarizes the identified sources for each city and the associated key species (% of the species >30%).

Sources of ambient PM2.5 have been grouped into 9 categories: biomass burning, secondary sulfate, traffic (including exhaust and road dust), fuel oil combustion, industry, coal combustion, soil, salt and "other sources". The factor labeling was made using the same criteria for all the sites to facilitate the assessment of common features and dissimilarities across them. Fig. 1 depicts an overview of the contribution of the identified sources to PM2.5 mass and Fig. 2 presents a map with the pie charts of relative source contributions in the different cities.

The sources traffic, secondary sulfate, and soil were identified in all the cities that source apportionment was performed, followed by biomass burning (identified in 9 cities). Therefore, as expected not all cities identified the same number and type of sources. The average of the sources contribution for the 11 cities was computed and when a source category was missing for a city a null contribution of this source, for the specific city, was considered in the calculation.

Results showed that from the averages of source contributions, considering all included cities, 16% of PM2.5 was generated by biomass burning, 15% by secondary sulfate, 13% by traffic, 12% by soil, 8.0% by fuel oil combustion, 5.5% by coal combustion, 1.9% by salt, 0.8% by industry, and 5.1% by "other sources". Twenty-three percent was attributed to unaccounted mass. Our results agree quite well with the findings from Karagulian et al. (2015) that compiled results from 419 source apportionment studies conducted in 51 countries. This review article showed that in Central and Eastern Europe biomass and fossil fuel combustion for domestic use (including wood, coal and gas for cooking and heating) is the main contributor to PM2.5 (32%), followed by traffic (19%), industry (17%), other sources of anthropogenic origin (mostly attributed to secondary particle formation) (17%) and natural sources (dust and sea salt) (16%). Our findings are also in line with a previous study on PM sources developed in three cities covering part of the studied area: Zagreb, Budapest and Sofia (Perrone et al., 2018). According to this study, the dominant sources in these cities

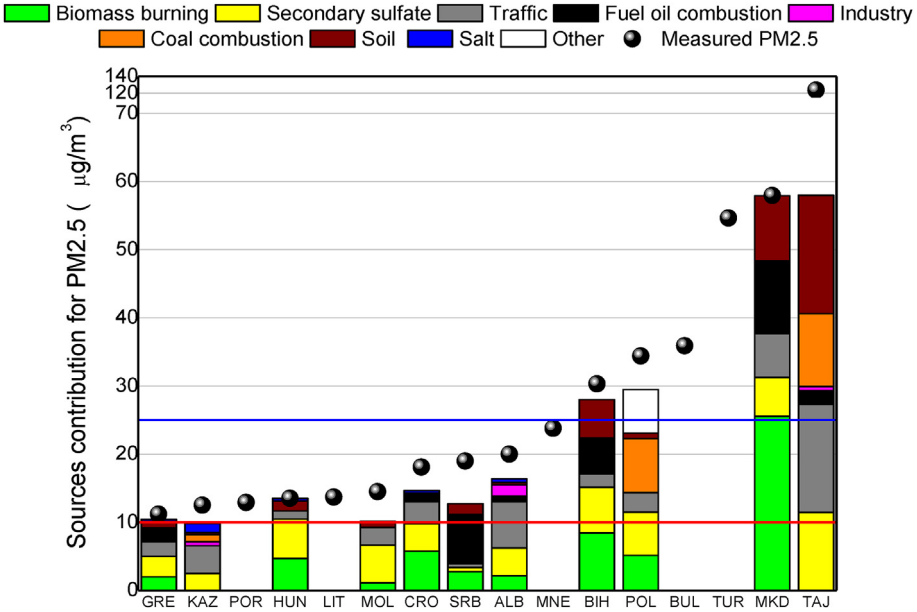

Fig. 1. Average sources contribution for PM2.5 and measured PM2.5 concentration. Values in μg/m^3. (red line – WHO annual guideline; blue line – EU annual standard). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

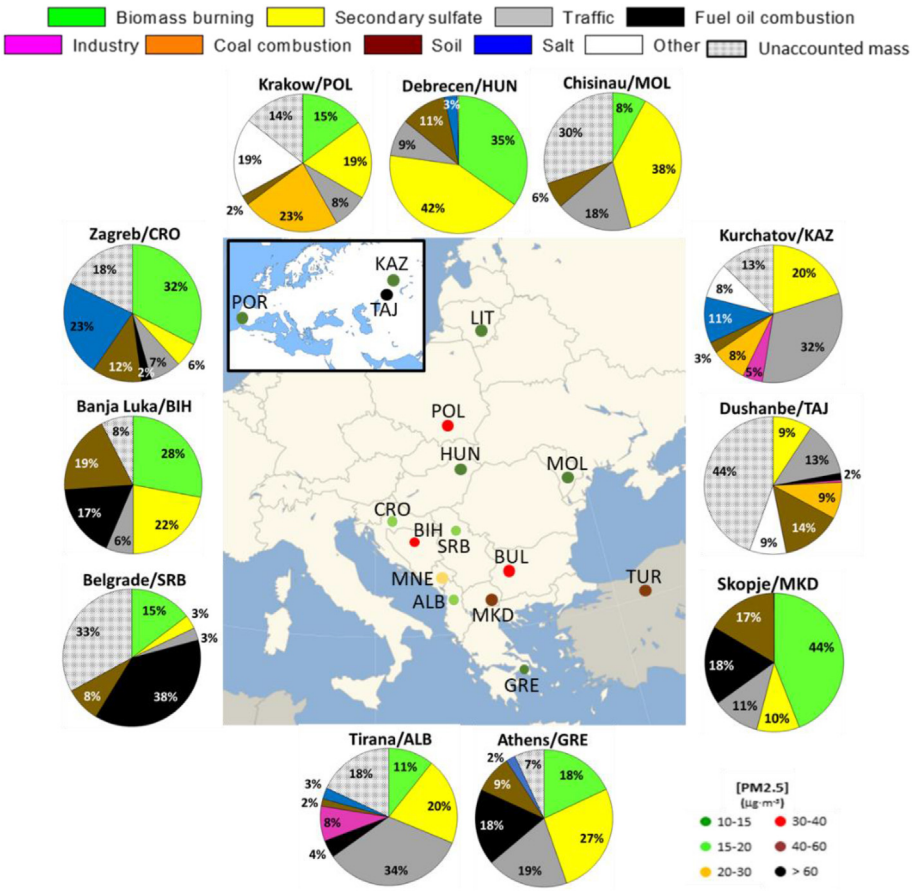

Fig. 2. Average contribution of PM2.5 sources (values in %, 11 cities). Average measured PM2.5 concentrations for the period of study (values in µg/m^3, 16 cities).

are the secondary sulfate (contribution between 22% and 34%) and the biomass burning (contribution between 24 and 28%).

Figure D1 (Appendix D) shows that the contribution of the sources presented a seasonal trend. The average of the source contribution in the warmest months (July and August) was 3.4% for biomass burning, 19% for secondary sulfate, 12% for traffic, 18% for soil, 3.1% for fuel oil combustion, 5.4% for coal combustion, 0.30% for salt, 1.0% for industry, and 0.49% for "other sources" (38% unaccounted mass). In the coldest months (December and January) the average of the source contribution was 29% for biomass burning, 9.8% for secondary sulfate, 12% for traffic, 8.9% for soil, 14% for fuel oil combustion, 7.9% for coal combustion, 0.9% for salt, 0.54% for industry, and 2.1% for "other sources" (15% unaccounted mass). Only cities that were monitored on these four months were considered for the calculation of the averages.

A detailed discussion on the specific findings for each major source category across the different cities is given below, while the monthly variability of the source contributions is displayed graphically in Fig. 3.

3.1. Secondary sulfate

The concentration of major ions was only available in the dataset from Krakow/POL, therefore S was used as the main tracer to identify secondary aerosols in the other cities.

Ideally, the secondary sulfate factor contains only the secondary inorganic species but this was seldom achieved in the PMF solutions obtained. Tabel C.1 shows that in Tirana/ALB, Dushanbe/TAJ, Chisinay/MOL, Zagreb/CRO and Skopje/MKD sulfate is the single key specie in the secondary sulfate source, whereas in Banja Luka/BIH and Kurchatov/KAZ also contains Br, in Athens/GRE and Belgrade/SRB contains Pb and in Debrecen/HUN contains Cr.

Secondary aerosols are by definition not emitted directly into the atmosphere by a single source, they are usually the result of atmospheric chemical transformations of gaseous precursors derived from combustion to PM at shorter or longer timescales, often involving heterogeneous processes and therefore they share the same marker species with anthropogenic emissions on the local- and meso-scale (Viana et al., 2008). Secondary sulfates are in many cases attributed to long-range transport events and are frequently associated with "aged air masses" due to the slow oxidation of SO_2 to SO_4^{2-} (Lazaridis et al., 2006; Manousakas et al., 2017). Consequently, in source apportionment studies secondary aerosols are often not allocated to the primary source of their precursor, which might complicate the interpretation of results (Karagulian et al., 2015).

The average secondary sulfate contribution for PM2.5 varied between 0.62 µg/m^3 in Belgrade/SRB and 11 µg/m^3 in Dushanbe/TAJ (Fig. 1). In this last city the average contribution of secondary sulfate was higher than the WHO guideline for total PM2.5 mass concentration. The highest relative contribution of this source was observed in Debrecen/HUN, Chisinau/MOL, and Athens/GRE (42%, 38%, and 27%, respectively) revealing the importance of abating emissions of gaseous precursors in designing mitigation actions for air quality. Belis et al. (2019a,b) showed that in Balkans the secondary sulfate is mainly associated to coal combustion, which is responsible for the precursor SO_2 emissions.

The ratio between the secondary sulfate source contribution in

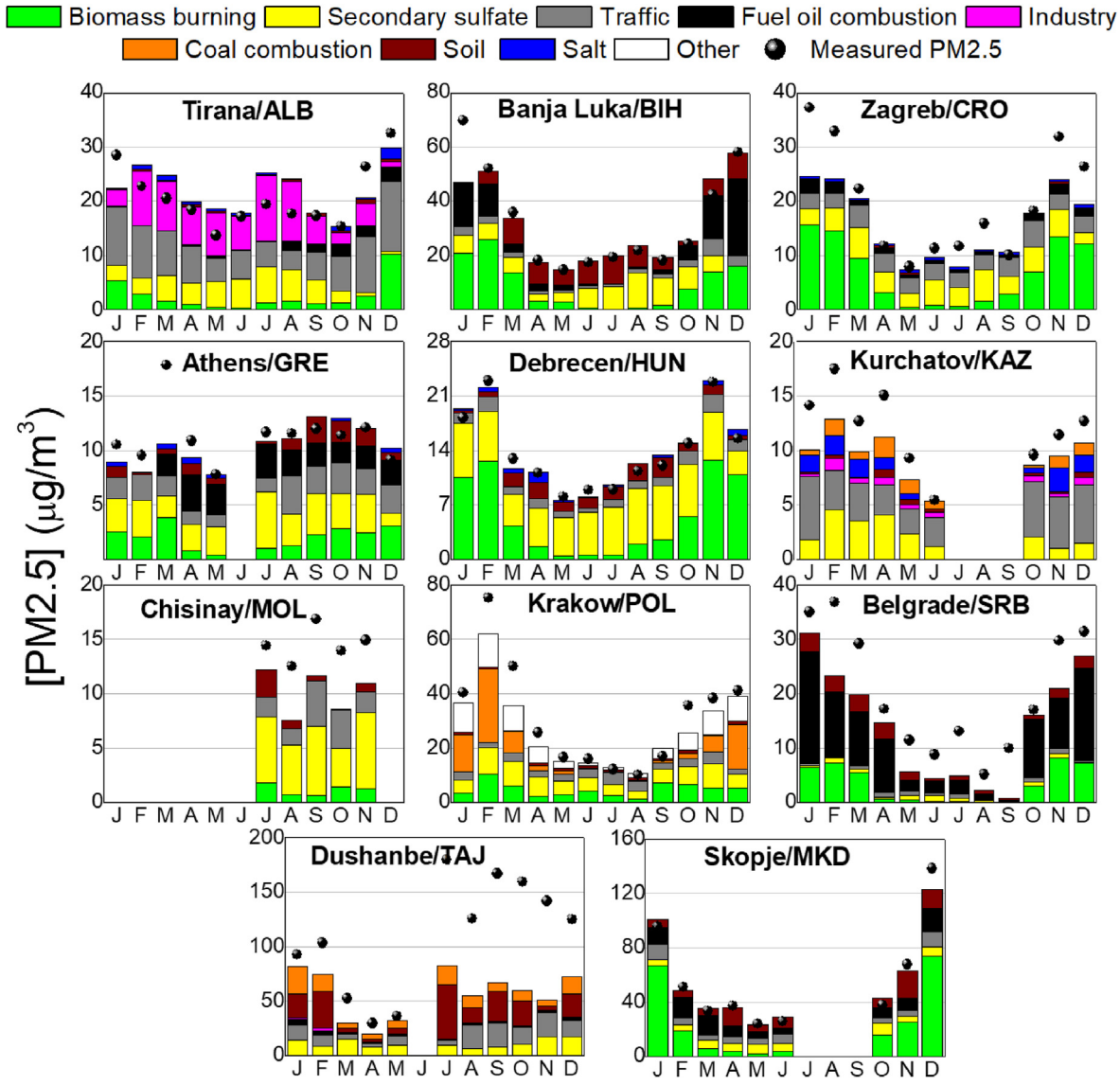

Fig. 3. Monthly source contributions for PM2.5 and measured PM2.5 concentration (values in μg/m^3).

the warmest (July and August) and in the coldest (December and January) months was calculated for the cities that were monitored during these months. Figure D2 (Appendix D) shows that the contribution of secondary sulfate was higher in the warmest months except for Krakow/POL. This may be due to the strongest solar radiation in Summer, increasing both temperature and the formation of OH radicals, promoting therefore the formation of secondary sulfate, which are transported at longer distances than the gaseous precursors (Chan et al., 1999). In Krakow/POL there was an increase of the secondary sulfate contribution in the Winter probably due to the increase of its precursors, which are associated with the combustion sources used for domestic heating whose impact in Krakow has already been described in previous studies (Junninen et al., 2009; Thunis et al., 2018). Moreover, sulfate is to a large extent originating also from cloud phase SO_2 oxidation, which occurs during Winter as well. In Krakow/POL this ratio increased from 0.71 to 2.23 when the percentage contribution of the secondary aerosol is considered instead of the concentration.

3.2. Biomass burning

Potassium appeared as the main tracer for biomass burning (Gonçalves et al., 2010; Belis et al., 2011), while in the absence of organic and elemental carbon in most of the studies it was the major component in the biomass burning profile. Other chemical species, such as Pb (in 3 cities), Cu, BC, Cl and Zn (in 2 cities), and Br and S (in 1 city) were also associated with this source (Belis et al., 2011), displaying a certain variability in the biomass types used across the study area.

Average biomass burning contribution to PM2.5 varied widely from 7.9 to 18% in Chisinau/MOL, Tirana/ALB, Belgrade/SRB, Krakow/POL, and Athens/GRE, 28% in Banja Luka/BIH, 32–35% in Zagreb/CRO and Debrecen/HUN, and 44% in Skopje/MKD. The large variability in this source contribution is mostly due to the different share of biomass burning for residential heating in the 9 cities. Some differences can be also due to the different sampling period in the various cities.

Biomass was the major source in cities from BIH, CRO, and MKD. Fig. 2 depicts that in Skopje/MKD the average biomass burning contribution (26 μg/m^3) was higher than the WHO guideline for total PM2.5 mass concentration.

Seasonal trends in the biomass burning contribution are illustrated in Fig. 3. Results reveal a seasonality of biomass burning source with maxima in Winter due to emissions from fireplaces and woodstoves for residential heating.

Fig. 4 shows that the cities with the highest percentage of days exceeding the PM2.5 EU annual limit value of 25 μg/m^3 (Skopje/MKD – 77%, and Banja Luka/BIH – 41%) presented the highest biomass burning contribution (44% and 28%, respectively). The exception was Krakow/POL (% of exceedances equal to 47%) where the biomass burning was not the dominant source (15%).

During the days with PM2.5 concentrations exceeding 25 μg/m^3, biomass burning was the main source in 36% of the studied cities and its contribution was on average 1.2 to 3.7 times higher than in the overall period (Fig. 4). During these days biomass burning increased from 8.4 to 17 μg/m^3 in Banja Luka/BIH, 5.9 to 16 μg/m^3 in Zagreb/CRO, 4.7 to 18 μg/m^3 in Debrecen/HUN, and 26 to 32 μg/m^3 in Skopje/MKD.

It should be noted that the comparison with the limits must be considered with caution when the sampling was not performed on a regular basis for the whole year. There are sites (like Chisinay/MOL, and Kurchatov/KAZ) where the samples were not taken during all the year. This introduces a considerable bias when comparing with the annual target value. For that reason, the comparison is provided as a metric of the concentration level of PM and not as direct comparison identifying the compliance with the limits.

Results show that biomass burning is a significant contributor to atmospheric fine particles especially in Eastern Europe. It is expected that several factors may contribute to a further increase of the contribution of this source, such as the efforts of the European Union to decrease the consumption of fossil fuels and increase the use of carbon neutral solutions, which is leading to a return to biomass burning (Fuller et al., 2013). EU estimates an increase in biomass burning between 57 and 110% from 2010 until 2020 (Wagner et al., 2010). Moreover, local policies are encouraging the installation of biomass stoves in newly built or refurbished homes (EEA, 2016). In addition, the economic recession and the rising prices of diesel are leading to an increased use of biomass as a residential fuel in some European regions (Saffari et al., 2013; Diapouli et al., 2017a). As there is growing evidence of adverse health effects from wood smoke (Bølling et al., 2009), it is essential to ensure that in urban areas the increased wood burning does not off-set the substantial investment in measures to reduce traffic pollution. It is expected a positive impact of the new EU Eco-design directive that will favor the development of lower emitting domestic stoves and boilers. However, incentive schemes to encourage the replacement of old equipment at local level are also needed, as well as, raising the awareness of citizens about the need to perform a correct maintenance of the stoves and to use adequate type of biomass fuel.

In Central Asia countries/cities participating in the current study, Kurchatov/KAZ and Dushanbe/TAJ, biomass burning was not identified as a major contributor to PM mass concentrations. Both countries are large producers of coal, and coal is a very common method of heating either domestic or used in electric power plants (Doukas et al., 2012; Karatayev and Clarke, 2014; Kerimray et al., 2017). Kazakhstan is the country with the second highest coal consumption in the world after Poland (Kerimray et al., 2017). In Kazakhstan, 40% among surveyed households used coal in 2013 (Kerimray et al., 2017). Most of the households using coal were in rural regions where natural gas and district heating is unavailable, while the proportion of rural households using biomass cook stoves for cooking and heating is currently unknown (Karatayev and Clarke, 2014). As it appears from both the findings of this study and from already published studies, coal combustion is a major source of PM emissions in the area, while biomass burning is not

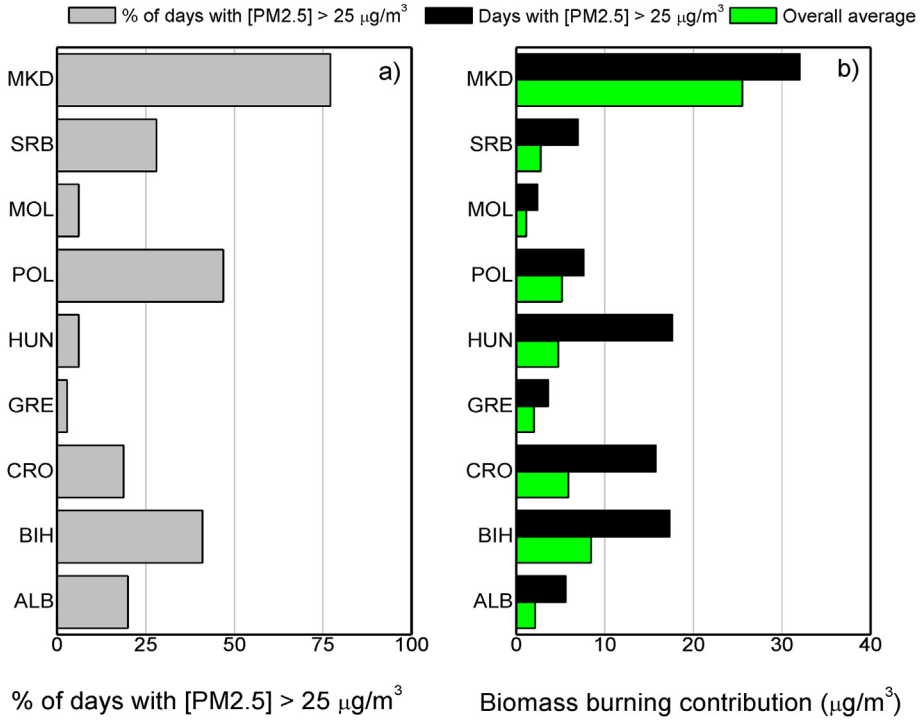

Fig. 4. a) Percentage of days with [PM2.5] > 25 μg/m^3; b) Average biomass burning contribution for all period and for days with [PM2.5] > 25 μg/m^3 (values in μg/m^3).

identified a major contributor.

3.3. Fuel oil combustion

Fuel oil combustion was identified as a standalone source in Tirana/ALB, Banja Luka/BIH, Zagreb/CRO, Athens/GRE, Belgrade/SRB, Dushanbe/TAJ, and Skopje/MKD. This source is characterized by high levels of Ni and V indicating the contribution of ship and industrial combustion emissions (Lang et al., 2017; Liao et al., 2017). Results for Athens/GRE show that the primary V–Ni bearing oil combustion particles and the secondary sulfate particles are present in the same factor. According to Amato et al. (2009), once industries and shipping typically burn high sulfur content residual oil, the sulfate related to V and Ni probably represents the direct SO_3 emission from industries and ships, condensed in particulate sulfate at the receptor site.

The average contribution of fuel oil combustion varied between 1.6% in Dushanbe/TAJ and 38% in Belgrade/SRB. A previous work developed in Belgrade presented a lower contribution of this source ranging between 13% and 25% (Mijić et al., 2010). In Skopje/MKD the average fuel oil combustion contribution (11 μg/m^3) was higher than the WHO guideline for total PM2.5 mass concentration.

In Belgrade/SRB and Banja Luka/BIH, the highest contribution of this factor in the Winter suggested oil-based small combustion units for residential heating as a potential source during the coldest months (Mijić et al., 2010). The fuel oil combustion contribution to PM2.5 increased from 3.0 μg/m^3 in Summer to 13 μg/m^3 in Winter in Belgrade/SRB and from 1.2 μg/m^3 in Summer to 14 μg/m^3 in Winter in Banja Luka/BIH. In Athens/GRE it is not observed a seasonal trend probably due to the different sources contributing to this factor, namely heating and ship emissions (Amato et al., 2016).

During the days with PM2.5 concentrations exceeding the EU annual limit value, fuel oil combustion increased significantly in Banja Luka/BIH (from 5.3 to 11 μg/m^3), and Belgrade/SRB (from 7.2 to 15 μg/m^3).

3.4. Coal combustion

The only standalone coal factor resolved by PMF was identified in Krakow/POL, Dushanbe/TAJ and Kurchatov/KAJ, with average contribution 23%, 8.6% and 8.3%, respectively. For the other sites coal combustion contribution might be incorporated in the secondary sulfate factor as SO_2 is the major precursor from coal-fired power plants.

Coal combustion in all the sites that it was identified is used as a source of power generation and domestic heating. For that reason, the contribution of the source is much higher during the cold season (for the sites that information for both seasons are available).

In Dushanbe/TAJ the average coal combustion contribution was 11 μg/m^3 which exceed the WHO guideline for total PM2.5 mass concentration. In this city the coal combustion contribution increased from 0.81 μg/m^3 in Summer to 12 μg/m^3 in Winter. In Krakow/POL, during the days with PM2.5 concentrations higher than the EU annual limit value, coal combustion contribution increased from 7.9 μg/m^3 to 16 μg/m^3. In this city the coal combustion contribution increased from 0.30 μg/m^3 in Summer to 15 μg/m^3 in Winter.

3.5. Industrial emissions

The impact of industry was identified in 3 cities: Tirana/ALB, Kurchatov/KAZ, and Dushanbe/TAJ. The average contribution of industry varied between 0.58 μg/m^3 in Kurchatov/KAZ and 1.6 μg/m^3 in Tirana/ALB. However, PM emissions from the industry are a complex mixture of stationary and diffuse emissions associated with the main processes and with general site operations. Therefore, in all the cities, industry contribution is also incorporated in other factors such as secondary sulfate, coal combustion, fuel oil combustion, and traffic.

This source is a mixed category including emissions from different types of industries and sometimes it is mixed with mineral dust, fuel combustion sources or traffic.

The ferrous/nonferrous metallurgical emissions as a local point source were identified by a mixture of several industrial species (Mn, Fe, Pb, Zn, Cu, and Cr) influenced by steel mills and nonferrous smelting emissions (Almeida et al., 2015) in Dushanbe/TAJ with an average contribution of 0.53%.

In Tirana/ALB the industrial source presented a different profile with Ca, Cr and Al and with average contribution of 8.2%. Tao et al. (2014) showed that Ca can be emitted by several anthropogenic sources such as construction and cement industry, which is present near the city of Tirana. Resuspended calcareous dust mixed with rich Ca industrial emissions (cement plants) have been reported in previous studies (Belis et al., 2011). No clear annual trends were observed for the industrial emissions, except for Tirana/ALB where Industry appears to have higher contribution during the warm season. This fact might be related with the weather conditions that favor the transportation of pollutants from the industrial site.

3.6. Traffic

Traffic source includes different kinds of emissions from several vehicle types. Besides the emissions of primary particles from exhaust and the emissions of gaseous particles precursors from the combustion of fuels and lubricants, vehicles emit substantial amounts of particles through the mechanical abrasion of brakes, clutch, tires, rotor and muffler ablation. These are deposited onto the road and then re-suspended together with mineral dust particles and road wear material. Consequently, road dust resuspension originates high human exposures to mineral matter, metalloids and heavy metals (Amato et al., 2009; Correia et al., 2020; Cunha-Lopes et al., 2019).

The vehicle exhaust source was principally constituted by carbonaceous compounds (OC, EC, and BC). The non-exhaust traffic source included trace elements (Ba, Cu, Mn, Pb and Zn) from mechanical abrasion of brakes and tires and crustal species (such as Al, Ca, Fe, Mn, Si, and Ti). Table C.1 shows that in Zagreb/CRO and Athens/GRE, the measurement of carbonaceous species enabled the distinction between vehicles exhaust and vehicle wear/road dust. However, the absence of major tracer species, such as BC or EC, in some datasets hampered the identification of the different traffic sources. Therefore, to facilitate the comparison between cities it was decided to sum the contribution of the different traffic sources in one only source named traffic.

The traffic contribution to PM2.5 varied significantly in absolute terms, from 0.55 μg/m^3 in Belgrade/SRB to 16 μg/m^3 in Dushanbe/TAJ. In Dushanbe/TAJ the average traffic contribution exceeded the WHO guideline for total PM2.5 mass concentration. The highest relative traffic contribution was measured in Tirana/ALB (34%).

The contribution of the traffic source tended to be higher on weekdays than on weekends but depended on the sampling month (Figure D3, Appendix D). The average ratio weekday/weekend varied between 1.0 in September and 1.7 in July.

During the days with PM2.5 concentrations higher than the annual limit value, traffic contribution increased from 1.2 to 3.1 μg/m^3 in Debrecen/HUN. For the other cities this large increase was not observed.

It should be emphasized that the traffic contributions presented in this work are likely underestimated. In Krakow/POL secondary

nitrate was identified and presented the expected seasonal cycle, with higher concentrations in Winter, reflecting the thermodynamic equilibrium that favors NO_3^- over nitric acid under cold temperatures when NH_3 is available (Samek et al., 2017; Almeida et al., 2013). Secondary nitrate accounted on average for 19% of the PM2.5 mass and it was classified as "other sources" in this work. The secondary nitrate imputable to traffic should be considered for the total contribution of traffic, however, the uncertainty in emission inventorying and the lack of linearity between emissions and concentrations do not permit a robust estimate (Amato et al., 2016). Moreover, diesel vehicles are important emitters of sulfates (Calvo et al., 2013) and consequently part of secondary sulfate aerosol also result from traffic.

Traffic has been identified as an important contributor to the PM2.5 burden. Cities around the world have been experiencing important changes to reduce the traffic emissions and the impacts of traffic related air pollutants. Those measures are principally focused on release of new vehicles engines and fuel regulation, on the development of new-technology vehicles using alternative fuels and on management of traffic activity, including operating restrictions and pricing, lane and speed management, traffic flow control, trip reduction strategies, car and bike-share systems and new transit systems (Bigazzi and Rouleau, 2017; Holman et al., 2015). Nevertheless, it is also essential to increase public understanding of the impacts of traffic on environment and citizens' wellbeing because public acceptance and cooperation is crucial for the implementation of the traffic management strategies. It is also important to invest on the assessment of the impacts of these measures on air quality, exposure, and public health to fully evaluate the efficacy and cost effectiveness of these projects.

3.7. Soil

Soil is characterized by elements abundant in the earth's crustal rocks and soil. In all cities, soil profiles were consistent with respect to important markers such as Al, Ca, Fe, Mn, Si, and Ti (Liao et al., 2015). Road dust, identified by markers of road wear, tires and brakes, was considered in the traffic source. However, in some cities (in Dushanbe/TAJ and Krakow/POL), the soil profiles contain an abundance of Cr, V, and Ni showing that there is an impact from deposited anthropogenic emissions such as traffic and industry or from fugitive emissions. In Debrecen/HUN two soil sources were identified: undulating sand (tracers: Si, Al, Ti) and loess (tracer: Ca), as it has already been shown in previous studies (e.g. Kertész et al., 2010).

Enrichment factors (EF) were calculated with respect to Al using the chemical profile of the source soil and the average continental crustal composition reported by Mason (1952). Results showed that EF for Ca, Fe, Mn, Si, and Ti varied between 0.3 and 5, due to the differences between local geology. Exceptions were observed for Zagreb/CRO ($EF_{Mn} = 27$ and $EF_{Fe} = 6.8$); Banja Luka/BIH ($EF_{Ca} = 8.8$) and Chisinau/MOL ($EF_{Ca} = 24.8$; $EF_{Ti} = 5.5$; $EF_{Mn} = 18.2$; $EF_{Fe} = 10.3$) suggesting a possible interference from anthropogenic sources.

Besides the soil emitted locally also long-range transport of mineral dust from the North of Africa was identified. High contributions of this source were measured simultaneously in several cities and the use of Hysplit model from the National Oceanic and Atmospheric Administration (NOAA) allowed to establish that these events were associated with the transport of mineral dust from the North of Africa. An episode of long-range transport of mineral dust was registered in 17 September 2015 with an increase of soil contribution from 2.1 to 4.8 $\mu g/m^3$ in Zagreb/CRO, 1.5–9.9 $\mu g/m^3$ in Debrecen/HUN and 0.35–3.7 $\mu g/m^3$ in Tirana/ALB (Figure E1, Appendix E).

The mean soil contribution varied between 1.8% in Tirana/ALB and 19% in Banja Luka/BIH. In Dushanbe/TAJ soil is the main source of PM2.5 accounting for 14% of the mass and the average soil contribution (17 $\mu g/m^3$) was higher than the WHO guideline for total PM2.5 mass concentration. In Athens/GRE the PM2.5 EU limit value was exceeded during three sampling periods. In two of them, 23 September 2014 and 16 October 2014, soil contribution reached up to 18 $\mu g/m^3$ and 14 $\mu g/m^3$, respectively. The Hysplit model identified transport of air masses from North of Africa for these two sampling periods in line with previous studies in Athens (Vasilatou et al., 2017) and south Europe in general (Diapouli et al., 2017b). No typical seasonal trend was observed for this source in any city.

3.8. Salt

The salt contribution was maximum in Zagreb/CRO (23%), followed by Kurchatov/KAZ (11%), Debrecen/HUN (3.0), Tirana/ALB (2.7%), and Athens/GRE (2.2%).

Sea salt particles were found in Athens/GRE with a Winter-high pattern that may be related to the seasonal impact of the sea salt aerosols from sea breaking waves. According to Dunnett and Wallace (2009) there is a seasonal pattern in the intensity of the wave energy, characterized by higher energy density in the winter, when winds and storms are stronger.

In Kurchatov/KAZ a Winter-high trend was observed suggesting that resuspension of road salt may occur as a result of vehicles driving through salt laden puddles created from melting snow in Winter (Jeong et al., 2011). Resuspension of the dried road salt remaining on the asphalt after the snow melting and water evaporation is also observed.

3.9. Uncertainty estimation and quality assessment

Due to the scale of the study the implementation of sampling and analysis methodologies is heterogeneous in many cases. In order to assess the uncertainties that arise from this fact, the error estimation tools that are offered by EPA PMF 5.0 were used in addition to other methodologies.

The first tool that was used is the Bootstrapping (BS) analysis (Paatero et al., 2014). The results that were obtained by the test can be considered satisfactory, as for every site Base runs were reproduced at least 75% of the times (Table F1, Appendix F).

Generally, the robustness of the PMF solution is directly affected by the number of samples used (Reff et al., 2007). Another important information is the factor that presents the lowest reproducibility. This information is important because not every time that the reproducibility of a factor is low that points towards bad modeling results. A factor can be affected by a low number of observations when it describes a source of sporadic nature, or a source that it is defined by high intensity events such as dust transportation events (Manousakas et al., 2017). An additional information that can be examined is if sources of similar nature are correlated.

Industry was the factor with the lowest reproducibility for Tirana/ALB. Industry is a source with highly variant chemical profiles (Belis et al., 2020) and for that reason the profiles can often be mixed with those of other sources if they have common tracers. Soil for Banja Luka/BIH, Chisinau/MOL and Skopje/MKD and road dust for Athens/GRE were in some cases reproduced as other dust related sources. While it is possible for two sources that have a very high number of common tracers to be reproduced as one another during the resampling, which is something that becomes less apparent when a high number of samples is used. Specifically, for the case of Athens/GRE, because the distance of the sampling point to the road was relatively high, the chemical profile of road dust can be more enriched to soil related elements during transportation

leading to reduced reproducibility during resampling. For Kurchatov/KAZ and Belgrade/SRB biomass presented the lowest reproducibility and was in some cases correlated with traffic. Since both sources are combustion related sources, they have common tracers. A higher number and a better time distribution of the collected samples (allowing to capture more efficiently the variability arising from the temporal changes in source contributions) would assist towards achieving both better reproducibility and "cleaner" source profiles. Additional species in the analysis, such as nitrates, EC and OC would also assist towards a better separation of biomass and traffic profiles. For Dushanbe/TAJ and Debrecen/HUN oil and salt displayed the lowest reproducibility respectively. In this case this is attributed to the low number of species and/or samples. For example, for Debrecen/HUN salt is traced by Cl alone which increases the uncertainty of the analysis. In addition to that, the use of Cl as the only tracer of salt can lead to the underestimation of source contribution, because of the Cl depletion that commonly takes place on urban areas (Dall'Osto et al., 2013; Querol et al., 2008), even though this effect is expected to be lower when salt originates from road salting (and not the sea) which means that it remains in the atmosphere for shorter time.

Regarding the results of displacement (DIS) analysis (Table F1), they were good for all sites presenting very low Q change and zero factor swaps for the lowest dQ level. Taking the results of both uncertainty estimation tools into account, it can be concluded the level of uncertainty is acceptable for every site.

It must be noted here that the uncertainty estimation tools which are available on PMF, capture mainly the uncertainty that arises by random errors in the dataset and/or the rotational ambiguity. Even though those metrics are linked with the number of samples and species, as for example the rotational ambiguity is lowered when a higher number of samples are used (Brown et al., 2015), they cannot provide a direct/full estimation of the uncertainty that originates from the absence of key species. PMF can identify a source only if tracers of that source are available in the dataset. In order to fully comprehend the results of PMF analysis, PMF profiles need to be examined. The full PMF source profiles are provided in the supporting material (Figures C1 to C.11). It is acknowledged that generally when source apportionment results from different sites are compared, the lack of harmonization in the number of PM species is a major shortcoming. If a source is not identified due to the lack of tracers, the contribution of that source is spread in a priori unknown way among the identified sources.

An individual examination of the source profiles for every site, leads to the conclusion that due to the fact that some key species are missing from datasets used for some of the sites, some factors were mixed. Some of the identified difficulties in the source apportionment analysis are discussed in this paragraph. Because of the lack of EC and OC for many sites, it is observed that sources that originate from combustion processes are either mixed or not well defined. This methodological artifact is also recognized by BS test as was stated above. In Belgrade/SRB while oil and traffic factors have clear tracers of the processes, those tracers do not comprise enough part of the PM mass, and the contributions are probably not well defined leading to overestimated oil contribution and underestimated traffic. Additionally, road dust and traffic factors are affected by the absence of EC and OC and in most sites the factors cannot be separated and are identified not as exhaust and non-exhaust emissions but as traffic.

Generally, while it is possible to perform PMF analysis using only the elements as species, there are some documented problems in the bibliography that arise from the absence of certain species from the dataset. As it was mentioned before, it is very hard to distinguish between road dust and traffic factors without EC and OC in the input dataset, while the contribution of traffic and/or biomass can be seriously underestimated without NO_3^-. Combustion related sources (traffic, biomass, coal etc.) also suffer from the lack of EC and OC and those factors will also appear mixed in many cases. Additionally, biomass can be overestimated by using only K as a tracer under certain circumstances (Yu et al., 2018). Finally, some sources (such as secondary nitrate) cannot even be identified if certain species are absent. In this case and because PMF always assumes totality (sum of source contribution equals to 100%), the contribution that it is attributed to the source has high uncertainty, since there is not a way to predict were the contribution of the not identified sources will be apportioned to.

To assess the goodness of the fit, the observed to predicted PM concentration graphs were plotted (Figure G.1, Appendix G). The correlation between observed and predicted concentrations is considered good ($r^2 > 0.75$) for Tirana/ALB, Banja Luka/BIH, Zagreb/CRO, Athens/GRE, Debrecen/HUN, Krakow/POL, Skopje/MKD, moderate ($0.5 < r^2 < 0.75$) for Kurchatov/KAZ, Belgrade/SRB and low ($r^2 < 0.5$) for Chisinau/MOL and Dushanbe/TAJ. The low correlation for Chisinau/MOL and Dushanbe/TAJ is not attributed solely to the modeling process but to the experimental estimation of PM mass as well. For Chisinau/MOL and Dushanbe/TAZ as well as Kurchatov/KAZ, a weighting balance with lower accuracy was used (4 decimals) which resulted in less accurate estimation of PM mass.

The unaccounted mass (Fig. 3) is very high for some sites and it accounts for 30–50% of the PM mass in some cases. Since most of the sites are in urban locations, secondary NO_3^- is a very important source which cannot be identified due to the absence of that species from the list of studied PM2.5 components. A study that was conducted in five European cities (Barcelona, Porto, Athens, Florence and Milan) suggested that the contribution of nitrates was high having a range of 6–30%, while it was the source with the highest contribution in Milan (Amato et al., 2016).

Summing up, the uncertainty estimation methods that were used revealed that modelling results had in some cases high level of uncertainty, that it is mainly associated with the number of samples and species used. For that reason, the results of the analysis are considered indicative (for some sites) and representative only of the mass that was reconstructed and not the total PM mass, even if PM mass is well reconstructed by the model.

4. Conclusions

This is the first study focusing on the PM levels, chemical composition and sources from a considerable number of locations in Eastern Europe and Central Asia and showed that there is a remarkable difference in PM2.5 concentrations and sources across 16 studied cities. All cities exceeded the WHO guidelines and EPA PMF 5.0 results indicated that biomass burning, traffic and industry are important contributors to air quality degradation in the studied cities. This study provides important information for policy design in the environment, energy, transport, industry and health sectors. The investment in clean energy in households, the development of sustainable transport solutions and the reduction of industrial emissions are the key targets towards healthy cities.

5. Author Contributions

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Declaration of competing interest

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

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Appendix A. Supplementary data

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Appendix A: Sampling and analysis details

Table A.1. Sampling stations and details about PM2.5 sampling and analysis.

Country		City	Coordinates		Type of sampling station	Sampler	Flow rate ($m^3.h^{-1}$)	Filter matrix	No. samples	Species	Chemical analysis	Sampling calendar	
			X	Y								Start	End
Albania	**ALB**	Tirana	41.3479	19.8556	UB	Sven Leckel MVS6	2.3	Cellulose nitrate	219	elements, BC	XRF, reflectometry	22-Jan-14	12-Oct-15
Bosnia and Herzegovina	**BIH**	Banja Luka	44.7542	17.2425	UB	Sven Leckel MVS6	2.3	PTFE	100	elements	XRF	26-Aug-14	29-Aug-15
Bulgaria	**BUL**	Sofia	42.6553	23.3847	UB	Tecora Echo PM	2.3	PTFE	49	elements	EDXRF	05-Aug-14	30-Jan-15
Croatia	**CRO**	Zagreb	45.8352	15.9787	UB	Sven Leckel LVS3	2.3	PTFE	606	elements, BC	XRF, reflectometry	20-Jan-14	30-Sep-15
Greece	**GRE**	Athens	37.9950	23.8160	UB	Leckel sequential sampler SEQ47/50-CD	2.3	PTFE	107	elements, OC, EC	XRF, semi-continuous thermal-optical analysis	03-Jan-14	30-Dec-14
Hungary	**HUN**	Debrecen	47.5233	21.6358	UB	Gent sampler/SFU	1.0	Polycarbonate	178	elements, BC	PIXE, reflectometry	06-Jan-14	21-Set-15
Kazakhstan	**KAZ**	Kurchatov	50.7550	78.5479	UB	Sven Leckel MVS6	2.3	PTFE	78	elements	XRF	10-Oct-14	12-Jun-15
Lithuania	**LIT**	Vilnius	54.6861	25.2108	UB	Environment S.A. PM162M	1.0	PTFE	50	elements	PIXE	16-Aug-14	19-Jan-15
Montenegro	**MNE**	Nikšić	42.4652	18.5634	UB	Tecora Echo PM	2.3	PTFE	50	elements	PIXE	04-Jun-14	07-Jan-15
Poland	**POL**	Krakow	50.0646	19.9450	UB	Sven Leckel MVS6	2.3	Quartz	194	elements, WSI, BC	XRF, IC, transmitance	01-Feb-14	30-Jan-15
Portugal	**POR**	Lisbon	38.7167	-9.1333	UB	Partisol Plus 2025 sequential sampler	2.3	PTFE	50	elements	PIXE	02-Jul-14	14-Feb-15
Republic of Moldova	**MOL**	Chisinau	46.5819	28.5057	UB	Sven Leckel MVS6	2.3	PTFE	98	elements	PIXE	04-Jul-14	27-Dec-15
Serbia	**SRB**	Belgrade	44.7865	20.5217	SUB	Sven Leckel MVS6	2.3	PTFE	166	elements	PIXE	30-Apr-14	06-Aug-15
Tajikistan	**TAJ**	Dushanbe	38.5594	68.856	UB	Sven Leckel MVS6	2.3	Glass fiber and PTFE	137	elements	XRF	24-Jul-14	12-May-16
Republic of North Macedonia	**MKD**	Skopje	42.0066	21.3870	UB	LVS Type Comende Derenda	2.3	Cellulose	83	elements	XRF	20-Oct-15	23-Jun-16
Turkey	**TUR**	Ankara	40.0572	32.6076	SUB	Digitel DHA-80	6	Cellulose	50	elements	ICP-MS	27-Sep-14	03-Mar-15

(UB- Urban Background; SUB – Sub-Urban Background; WSI – Water soluble ions; BC- Black Carbon, EC – Elemental Carbon, OC – Organic Carbon)

Appendix B. Source apportionment and intercomparison exercise using PMF

Source apportionment of PM2.5 was performed by receptor modelling that is based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad i = 1, 2, \ldots m \quad j = 1, 2, \ldots . n \qquad (1)$$

where x_{ij} is the concentration of the species j in the i^{th} sample, g_{ik} is the contribution of the k^{th} source in the i^{th} sample, f_{kj} is the concentration of the species j in the source *k*, and e_{ij} is the uncertainty of each individual measurement result.

In this study the PMF (Paatero and Tapper, 1994) was used to solve Eq. (1) and the software EPA PMF 5.0 was applied to the data sets obtained in the cities. Factor contributions and profiles were derived in the EPA PMF 5.0 model by minimizing an objective function Q, without detailed prior knowledge on sources inventories (Paatero, 1999).

Firstly, the data was screened to exclude values, which could reduce the quality of the analysis. Scatter plots and time series analysis were used for data validation and to identify values that appeared anomalous when compared to the overall dataset.

Data below the limit of detection (LOD) were substituted by half of the LOD and the uncertainties were set to 5/6 of the LOD. Missing data were substituted by the geometric mean of the measured concentrations and the corresponding uncertainties were set as 4 times these geometric mean (Polissar et al., 2001).

Chemical species with high noise were down-weighted based on their signal-to-noise (S/N) ratio to reduce the influence of poor variables on the PMF analysis. Species with S/N lower than 0.5 were considered as bad variables and excluded from the analysis, and species with S/N between 0.5 and 1 were defined as weak variables and down-weighted by increasing the uncertainty (US-EPA, 2014). The summary of the input data is presented in Table B.1.

Table B.1. PMF settings and diagnostics

City Code	Number of species	Extra Modelling Uncertainty %	Weak	Bad	Number of Omitted Samples	% difference Q_{true}, Q_{rob}
Tirana ALB	19	10	Na, Al, Si	Mg, Cr, Br	0	1.1
Banja Luka BIH	25	10	Mg, Br, Sr, Ba	Co, Rb, Cd, Cs, Ce	0	4.1
Zagreb CRO	21	10	N/A	Ba, Br, Cr, La	5	0.9
Athens GRE	29	5	Mg, S, K, Ca	P, Cr, Co, As, Br, Sr, Ag, Cd, Cs, Ba, Hg	2	0
Debrecen HUN	20	4	Al, Cr, Br, Ba, Pb	V, Co, Ni, Sr	0	4.8
Kurchatov KAZ	19	10	Na, Cl, Cu, Br, Ba	Mg, Sc, Cr	0	0
Krakow POL	19	10	Al, V, Cr, Cu, Br, Ni	P, Cl, As, Ba	0	4.8
Chisinau MOL	19	0	Al, V, Cr, Cu, Br, Ni	P, Cl, As, Ba	0	2.5
Belgrade SRB	19	10	Pb	P, Cr, As, Br, Ba	2	2.8
Dushanbe TAJ	23	10	Mg, As	Na, Cl, Cr, Co, As, Br, Rb	0	0
Skopje MKD	19	10	Na, Mg, Al, Si, V, Br, Sr	Cl, Cr	0	0

The uncertainty was calculated to account for every step of the analytical process that was used according to JCGM (2008). In addition to the analytical uncertainty, extra uncertainty was added in order to account for the sampling uncertainty using the methodology that is described in Amato et al. (2009). Some tests were carried out to assess rotational ambiguity in the EPA PMF 5.0 solutions. The Base Model Displacement Error Method was used to explore the rotational ambiguity in the PMF final solutions. It evaluates the largest range of source profile values without a significant rise in the Q value. To assess the rotational ambiguity, the factor profile values are adjusted to the maximum allowable level, with the constraint that the difference between the Q values associated with the original and the modified solutions (dQ) is not greater than a predefined by the model value (dQmax). Additionally, to assess the stability of the solutions the Bootstrap (BS) method was used in order to assess the uncertainty that originates from random errors in the dataset and partially from rotational ambiguity. BS estimates the random errors on the matrix by altering the original dataset. During BS some rows of the original dataset are deleted while others are repeated. The model then provides a solution for each of the new datasets

and the results are compared with the original solution. With that methodology it is possible to estimate the effect of a small set of observations in the dataset has on the solution. The number of Bootstraps was set to 100, block size to 3 and the minimum correlation value to 0.6.

Prior to applying the PMF, an inter-comparison exercise was performed within the project framework to assess the performance of the participants in the use of source apportionment tools and to ensure homogeneity of the modeling procedure (Belis et al., 2015a,b). The exercise used a synthetic dataset prepared by the European Commission - Joint Research Center to represent urban background conditions in the city of Milan (Lombardy Region, Italy). In order to reproduce real-world patterns, the database was created based on the output of a Chemical Transport Model. The dataset contained 364 PM2.5 daily average concentrations of 38 inorganic and organic chemical species, as well as PM2.5 total mass, for the year 2005. The dataset had no missing values and all the concentrations were equal or above the minimum detection limit.

The results of the inter-comparison exercise were evaluated using a series of different tests. A short summary is presented here, in order to demonstrate the performance of the participants.

Normalized target diagrams presents the sample-wise comparison between the gravimetric masses and the sum of the Source Contribution Estimates (SCEs). The inter-comparison plots are designed to summarize a great amount of information and be easy to understand. In the graphs of Figure B.1 a) and c) the area of acceptability is presented in green. All the results falling in this area are considered satisfactory. For the test on the numbers of sources represented in Figure B.1 b) there is no pre-established acceptability criterion. Therefore, the red dotted lines indicate an advisable threshold that should not be exceeded.

Figure B.1a depicts that 10 out of 11 participants ranked in the area of acceptance (represented by the green circle). In Figure 1b the number of sources (referred to as candidates), that each participant has reported is presented and compared with the reference number of sources (9). The estimations of the participants were relatively close and within the reference number of sources ±3. In Figure 1c the performance RMs z-score are presented. According to the analysis the number of successful candidates (reported sources) is 49% (total number 80). Overall, good results were observed for the following sources: biomass burning, cement industry, ammonium nitrate, ammonium sulphate and fuel oil combustion. In this exercise three different types of dust were introduced; which separation was critical due to their similar chemical composition (crustal elements). Only half of the participants reproduced the contribution of soil in the synthetic dataset satisfactorily while the majority of the participants had

problems to distinguish between road dust and desert dust that was very challenging because, in addition to the similar chemical composition, represented only a small fraction of the PM mass (2% approx.).

The inter-comparison helped to understand the degree of variability that could derive from the application of PMF by practitioners with a variable degree of expertise (Belis et al., 2020) and was, therefore, used to design a strategy for the elaboration of the entire dataset of the study based on expert users (users that obtained good performance in the intercomparison). Based on the results of the source apportionment exercise those participants who achieved the highest scores were selected to apply source apportionment for all sites. By adopting a uniform approach for the PMF and performing analysis only for the cities where a relatively large number of samples was collected, it was possible to obtain comparable contribution estimates in the different sites, within the limitations of the experimental design.

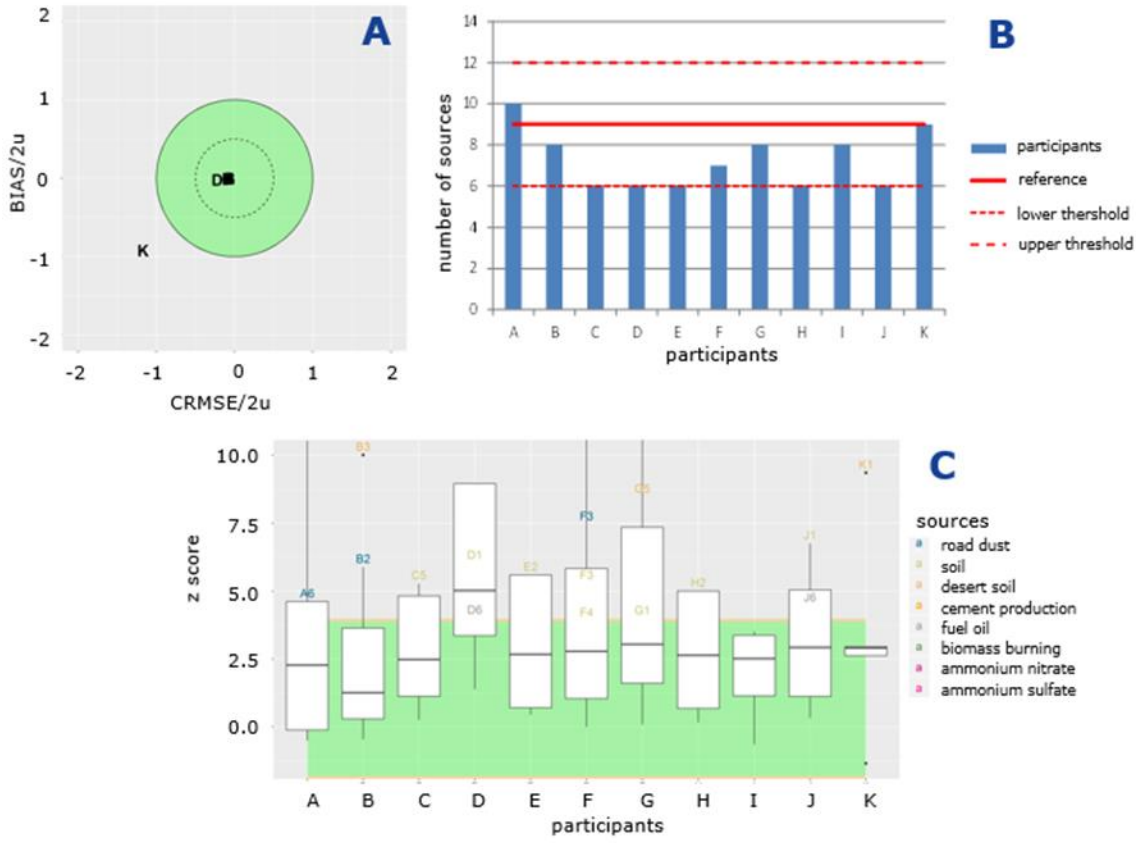

Figure B.1. (a) Target diagram summarizing the mass apportionment; (b) Number of factor/sources reported by every participant coded with letters from A to K. The horizontal solid line represents the target number of source categories, while the broken lines represent upper and lower thresholds; (c) Box and whiskers plots representing the distribution of z-scores attributed to the factor/profiles are arranged by participant (the green background indicated satisfactory scores).

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Appendix C. PMF source profiles (% of species and concentration of species)

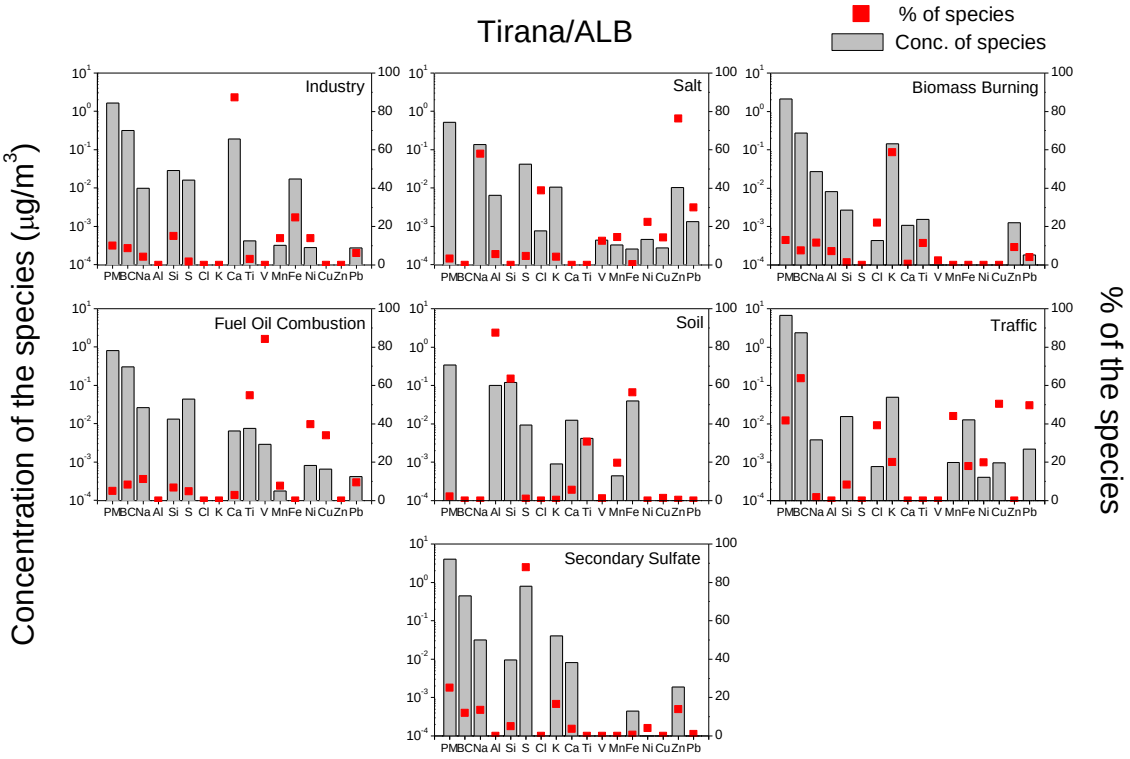

Figure C.1. Sources profile for Tirana/ALB.

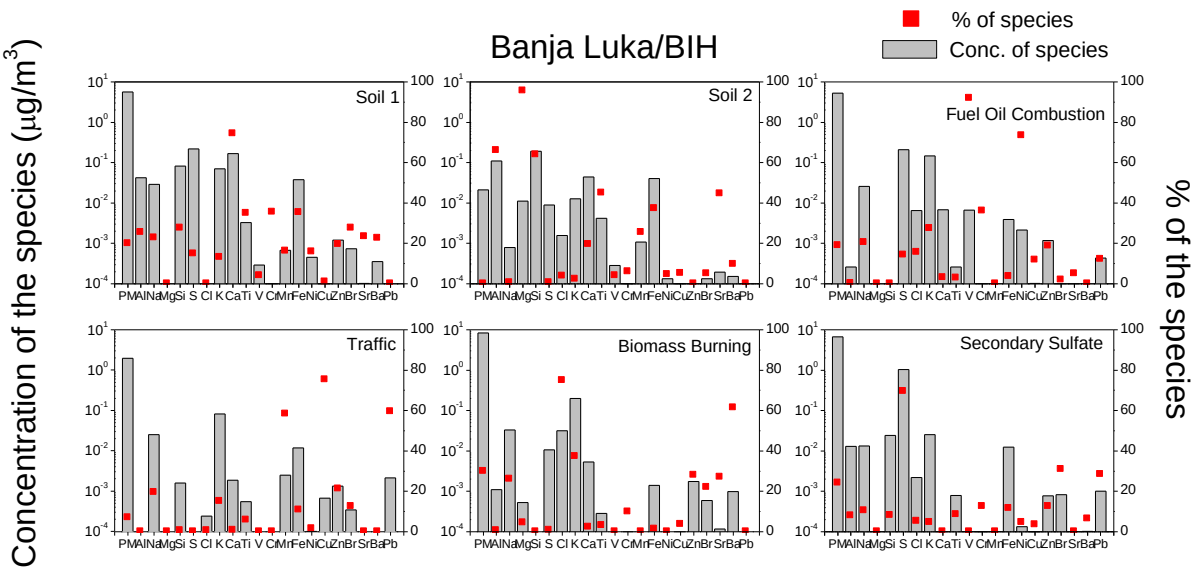

Figure C.2. Sources profile for Banja Luka/BIH.

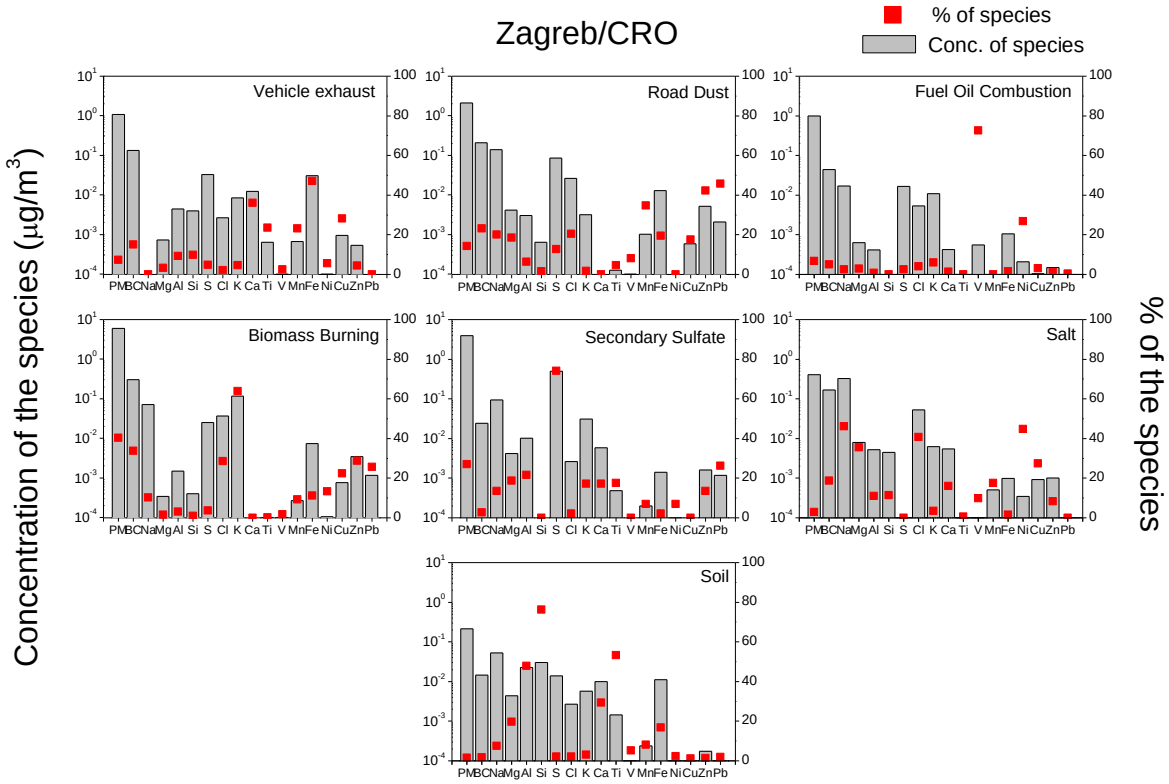

Figure C.3. Sources profile for Zagreb/CRO.

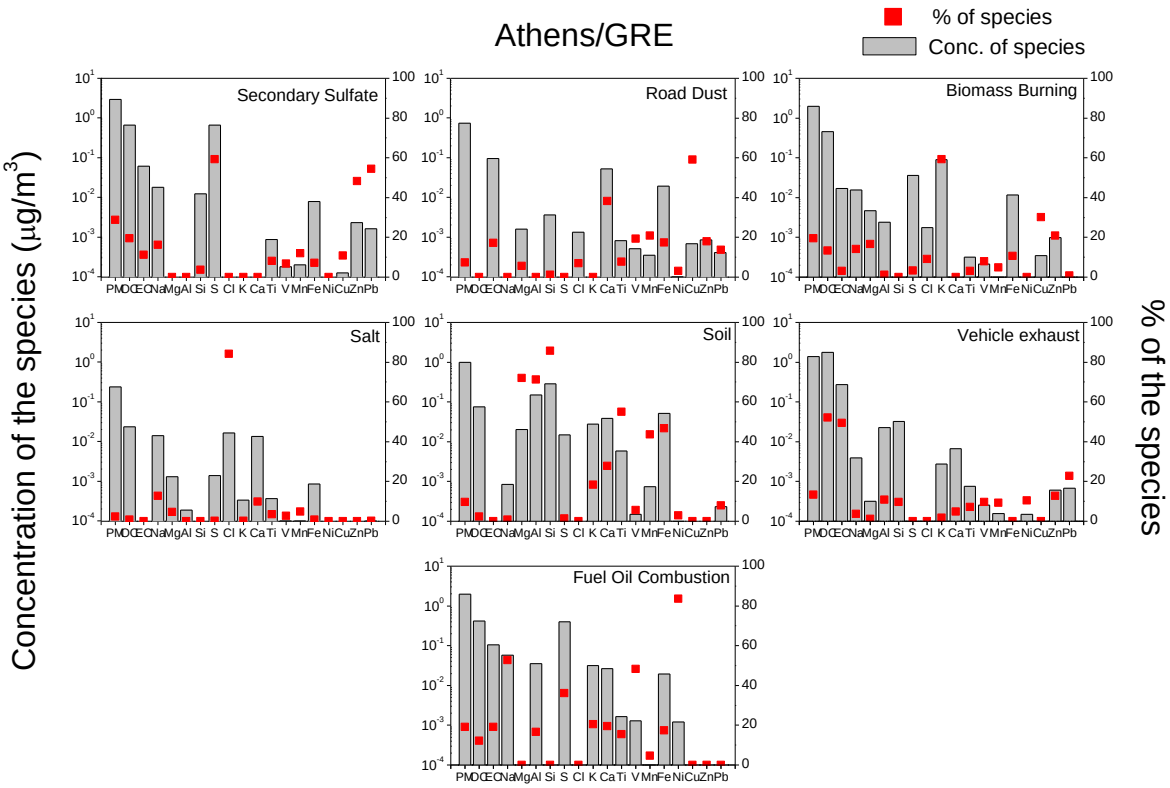

Figure C.4. Sources profile for Athens/GRE.

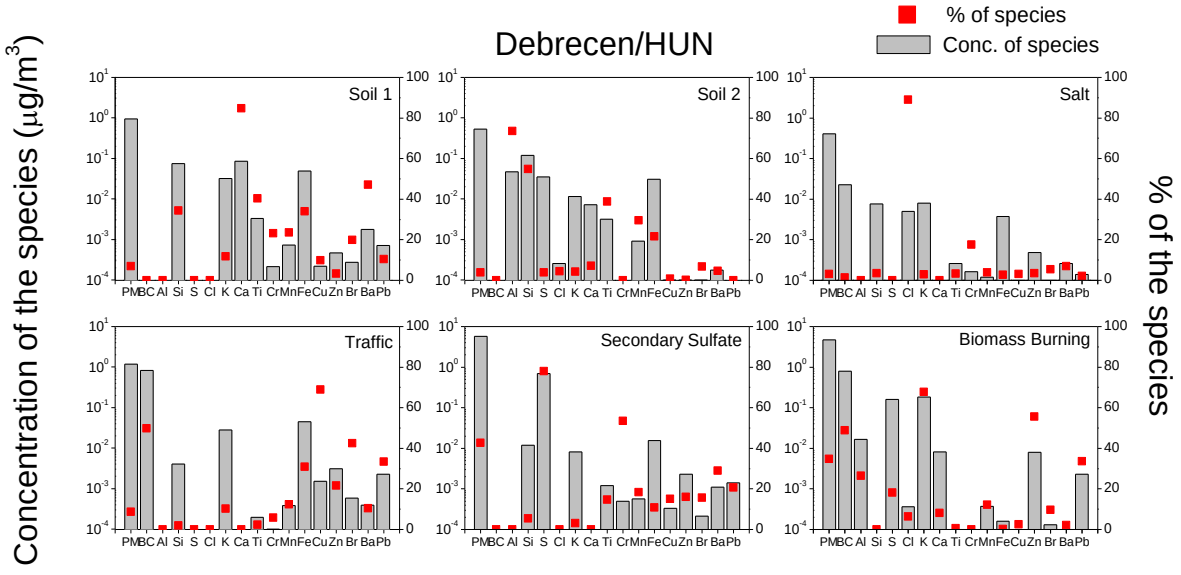

Figure C.5. Sources profile for Debrecen/HUN.

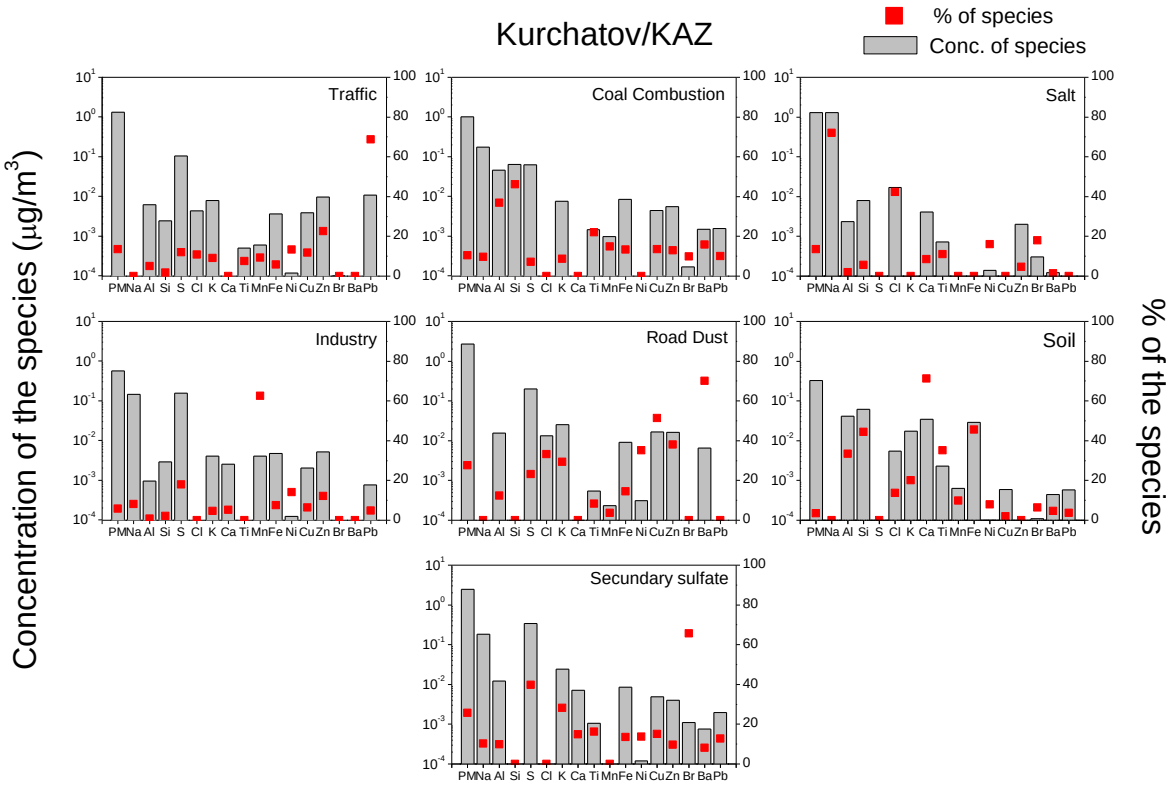

Figure C.6. Sources profile for Kurchatov/KAZ.

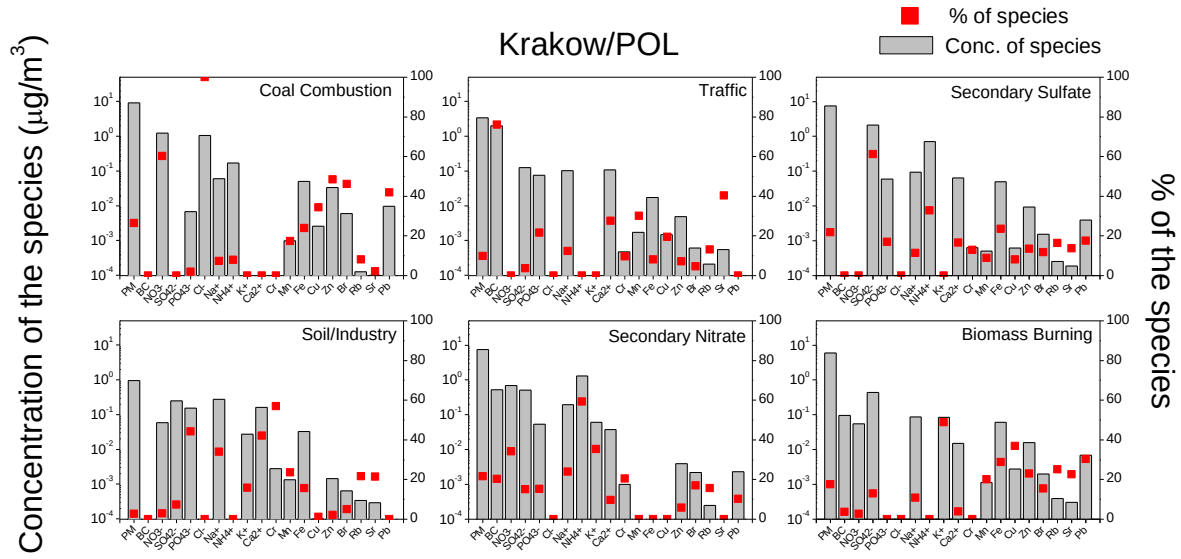

Figure C.7. Sources profile for Krakow/POL.

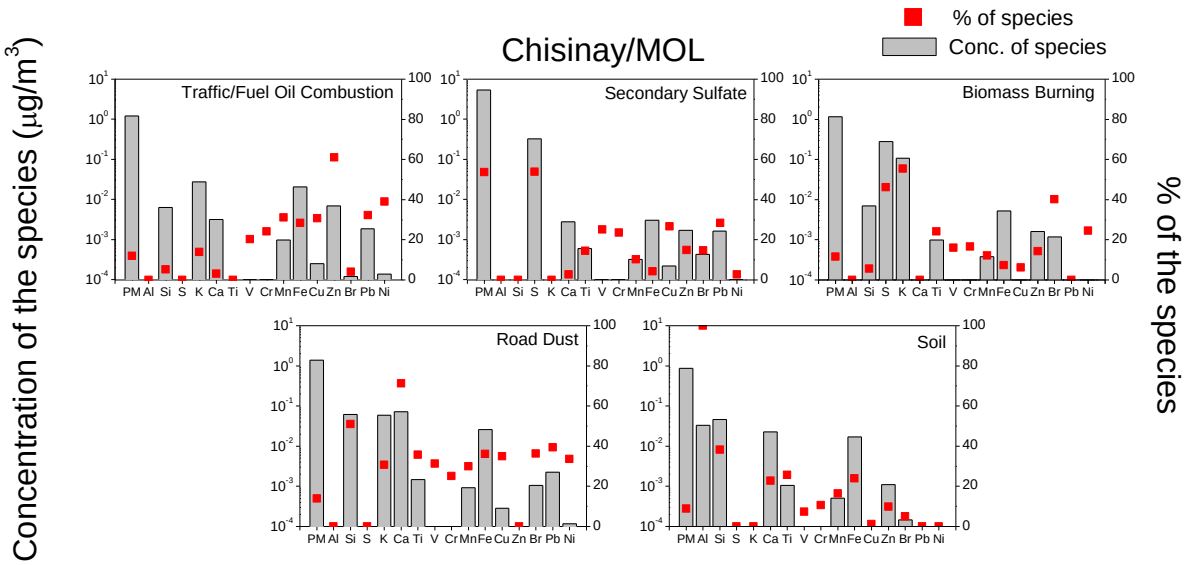

Figure C.8. Sources profile for Chisinay/MOL.

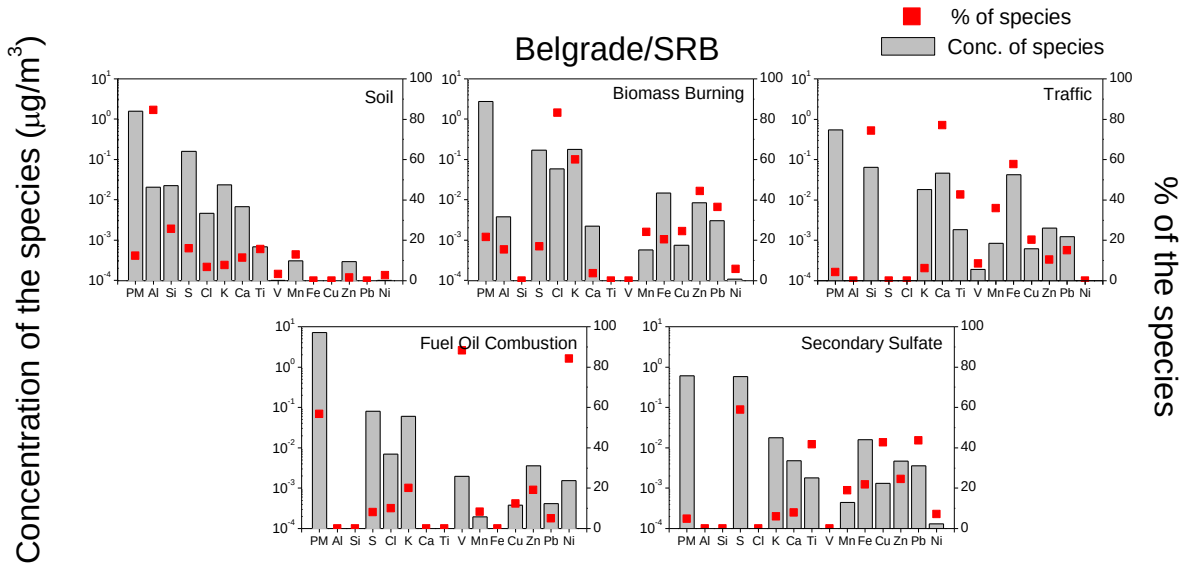

Figure C.9. Sources profile for Belgrade/SRB.

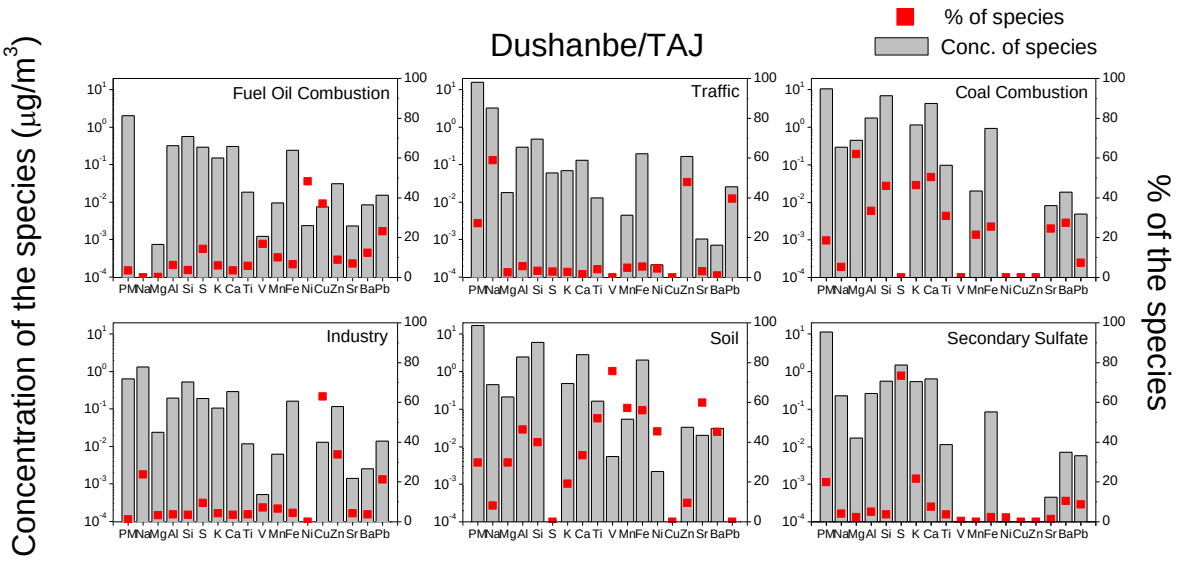

Figure C.10. Sources profile for Dushanbe/TAJ.

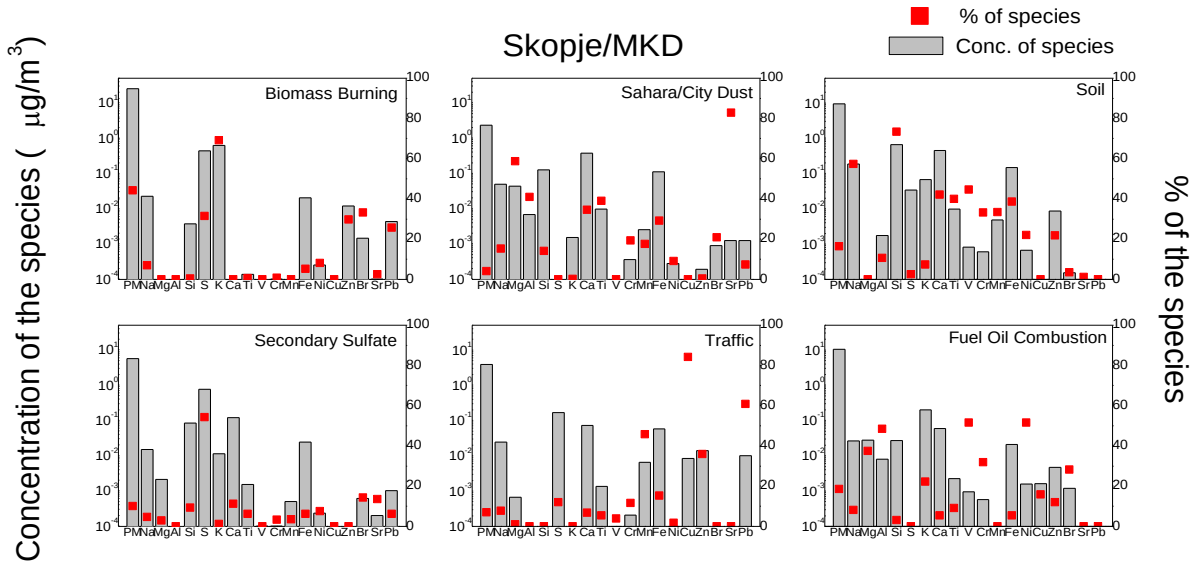

Figure C.11. Sources profile for Skopje/MKD.

Table C1: Summary of the identified factors and associated key species (% of the species > 30).

	Source	Key species		Source	Key species		Source	Key species
Tirana/ALB	Traffic	BC,Cu,Pb,Mn,Cl	**Banja Luka/BIH**	Biomass burning	Cl,Ba,K	**Zagreb/CRO**	Biomass burning	K,BC
	Secondary sulfate	S		Secondary sulfate	S,Br		Salt	Na,Ni,Cl,Mg
	Biomass burning	K		Fuel oil combustion	V,Ni,Cr		Soil	Si,Ti,Al
	Industry	Ca		Soil 1	Ca,Cr,Fe,Ti		Secondary sulfate	S
	Fuel oil combustion	V,Ti,Ni,Cu		Traffic	Cu,Pb,Mn		Road dust	Pb,Zn,Mn
	Salt	Zn,Na,Cl		Soil 2	Mg,Al,Si,Ti,Sr,Fe		Fuel oil combustion	V
	Soil	Al,Si,Fe,Ti					Vehicle exhaust	Fe,Ca
Athens/GRE	Secondary sulfate	S,Pb,Zn	**Debrecen/HUN**	Secondary sulfate	S,Cr	**Kurchatov/KAZ**	Road dust	Ba,Cu,Ni,Zn,Cl
	Biomass burning	K,Cu		Biomass burning	K,Zn,BC,Pb		Secondary sulfate	S,Br,K
	Fuel oil combustion	Ni,Na,V,S		Traffic	Cu,BC,Br,Pb,Fe		Salt	Na, Cl
	Vehicle exhaust	OC,EC		Soil 1	Ca,Ba,Ti,Si,Fe		Traffic	Pb,Zn
	Soil	Si,Mg,Al,Ti,Fe,Mn		Soil 2	Al,Si,Ti		Coal combustion	Si,Al,Pb
	Road dust	Cu,Ca		Salt	Cl		Industry	Mn
	Salt	Cl					Soil	Ca,Fe,Si,Ti,Al
Krakow/POL	Coal combustion	Cl^-,NO_3^-,Zn,Br,Pb,Cu	**Chisinay/MOL**	Secondary sulfate	S	**Belgrade/SRB**	Fuel oil combustion	V,Ni
	Secondary sulfate	SO_4^{2-},NH_4^+		Road dust	Ca,Si,Pb,Br,Fe,Ni,Cu,Ti,V,K		Biomass burning	Cl,K,Zn,Pb
	Other source: Secondary nitrate	NH_4^+,K^+,NO_3^-		Traffic/Fuel oil combust.	Zn,Ni,Pb,Mn,Cu		Soil	Al
	Biomass burning	K^+,Cu,Pb		Soil	Al,Si		Secondary sulfate	S,Pb,Cu,Ti
	Traffic	BC,Sr,Mn		Biomass burning	K,S,Br		Traffic	Ca,Si,Fe,Ti,Mn
	Soil/Industry	Cr,PO_4^{3-},Ca^{2+},Na^+						
Dushanbe/TAJ	Soil	V,Sr,Mn,Fe,Ti,Al,Ni, Ba,Si, Ca	**Skopje/MKD**	Biomass burning	K,Br,S			
	Traffic	Na,Zn,Pb		Fuel oil combustion	Ni,V,Al,Mg,Cr			
	Secondary sulfate	S		Soil	Si,Na,V,Ca,Ti,Fe,Mn,Cr			
	Coal combustion	Mg,Ca,K,Si,Al,Ti		Secondary sulfate	S			
	Fuel oil combustion	Ni,Cu		Traffic	Cu,Pb,Mn,Zn			
	Industry	Cu,Zn		Sahara/city dust	Sr,Mg,Al,Ti,Ca			

Species are presented in decreasing order of the % of the species. Sources are presented in decreasing order of the source contribution to PM2.5.

Appendix D: Sources Contribution

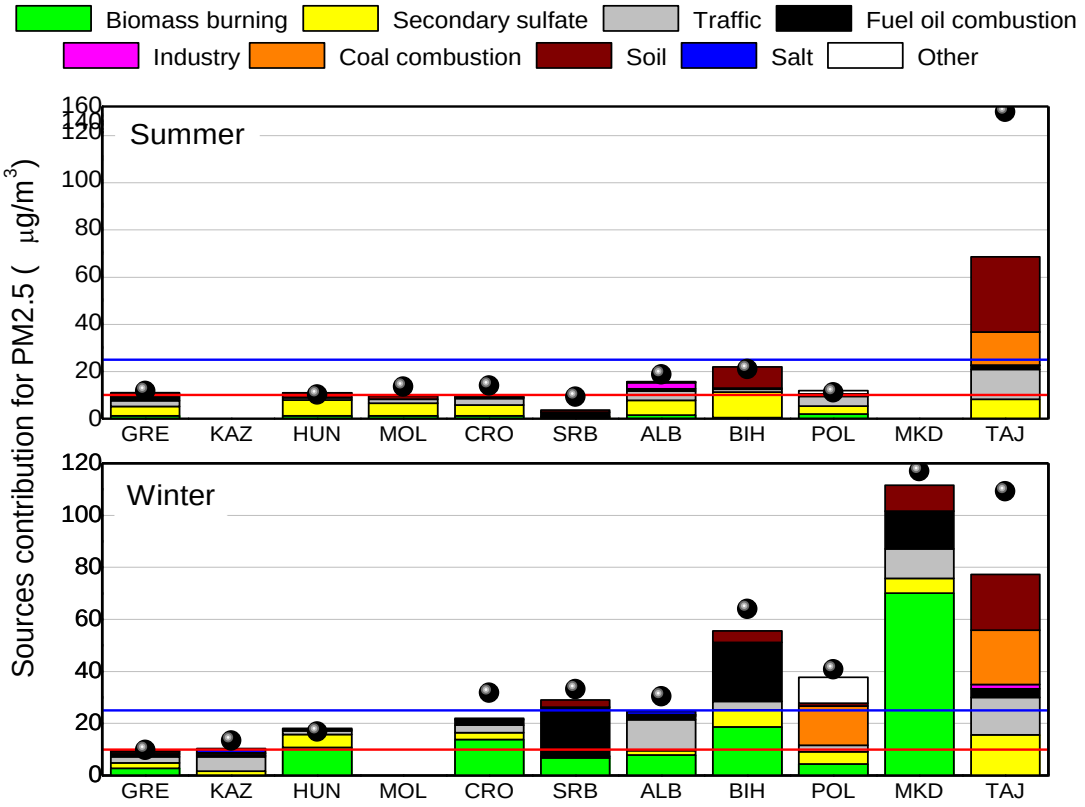

Figure D.1. Average sources contribution for PM2.5 in Winter (December and January) and Summer (July and August) (red line – WHO annual guideline; blue line – EU annual standard). Values in µg/m^3.

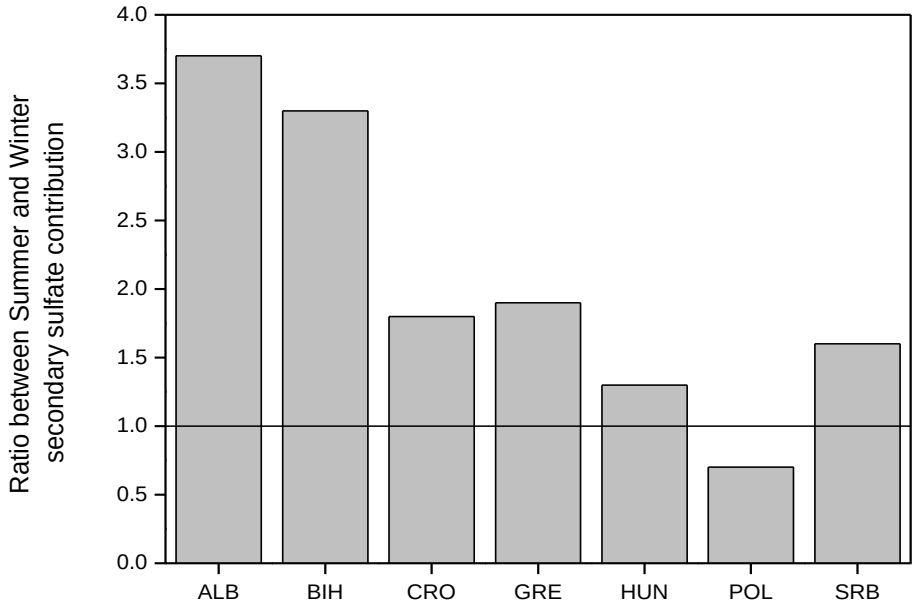

Figure D.2. Ratio between the secondary aerosol contribution in Summer (July and August) and in Winter (December and January)

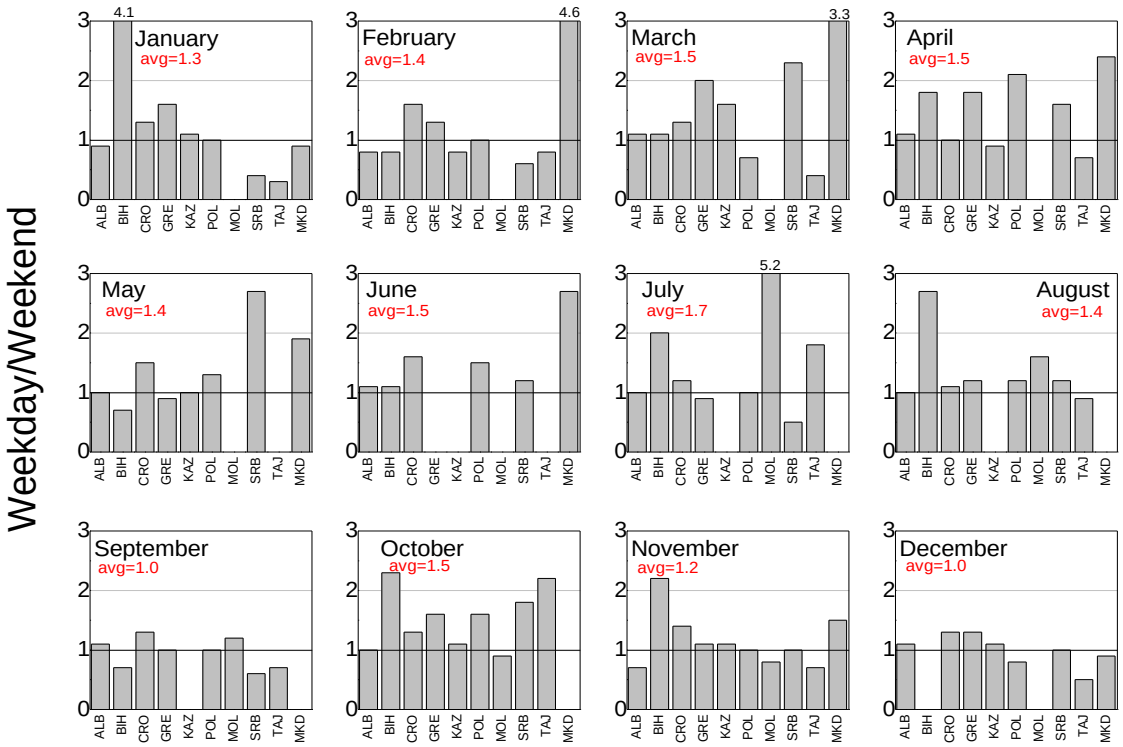

Figure D.3. Ratio between the traffic contribution during the weekdays and weekends. The average ratio for all cities is presented in red.

Appendix E. Long range transport

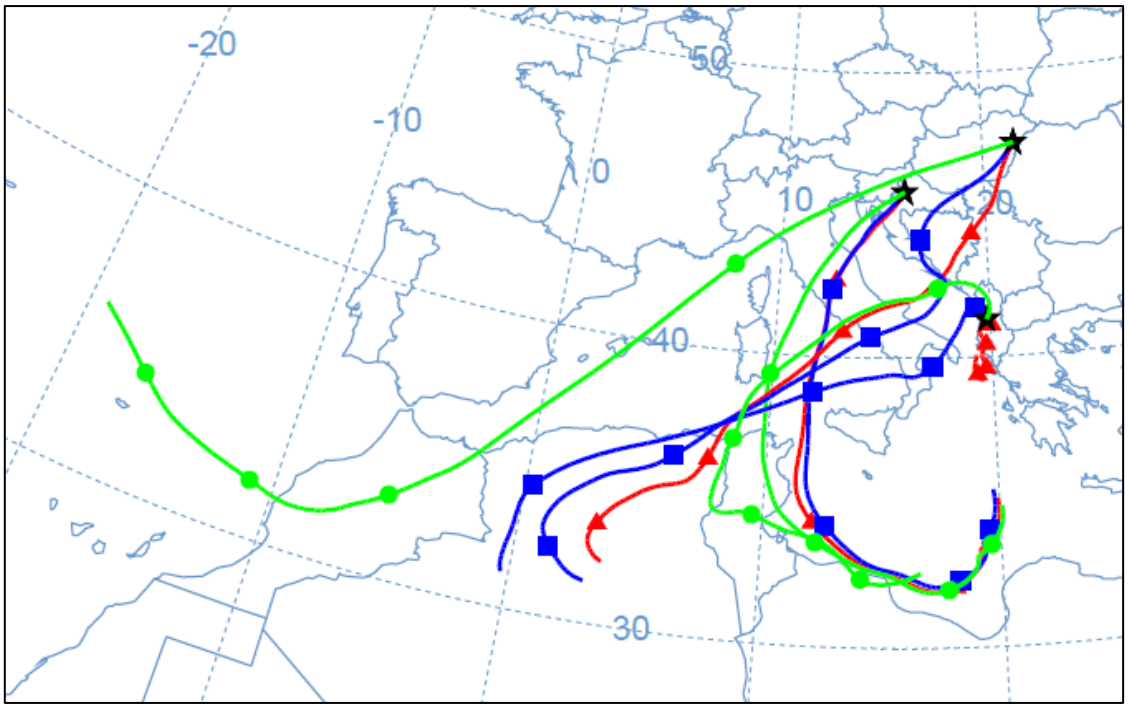

Figure E.1. Backward trajectories using Hysplit from NOAA: end at 17 September 2015 in Zagreb/CRO, Debrecen/HUN and Tirana/ALB. Green, blue and red lines refer to starting height equal to 3000 m, 1000 m and 500 m, respectively.

Appendix F. PMF base error estimation summary

Table F.1. Bootstrap (BS) and Displacement (DIS) results summary

City Code	BS Reproducibility Range	BS Unmapped	BS LR Source	DIS Swaps	DIS dQ%
Tirana ALB	85-100	0	Industry	0	
Banja Luka BIH	88-100	0	Soil	0	-0.02
Zagreb CRO	98-100	0	N/A	0	0
Athens GRE	84-100	0	Road dust	0	-0.01
Debrecen HUN	75-100	0	Salt	0	-0.03
Kurchatov KAZ	81-100	0	Biomass	0	0
Krakow POL	90-100	0	Combustion	0	0
Chisinau MOL	78-100	0	Soil	0	-0.02
Belgrade SRB	80-100	0	Biomass	0	0
Dushanbe TAJ	94-100	0	Oil	0	0
Skopje MKD	90-100	0	Sahara	0	0

LR Source: source that displayed the lowest reproducibility

Appendix G. Observed vs Predicted PM2.5 Concentrations

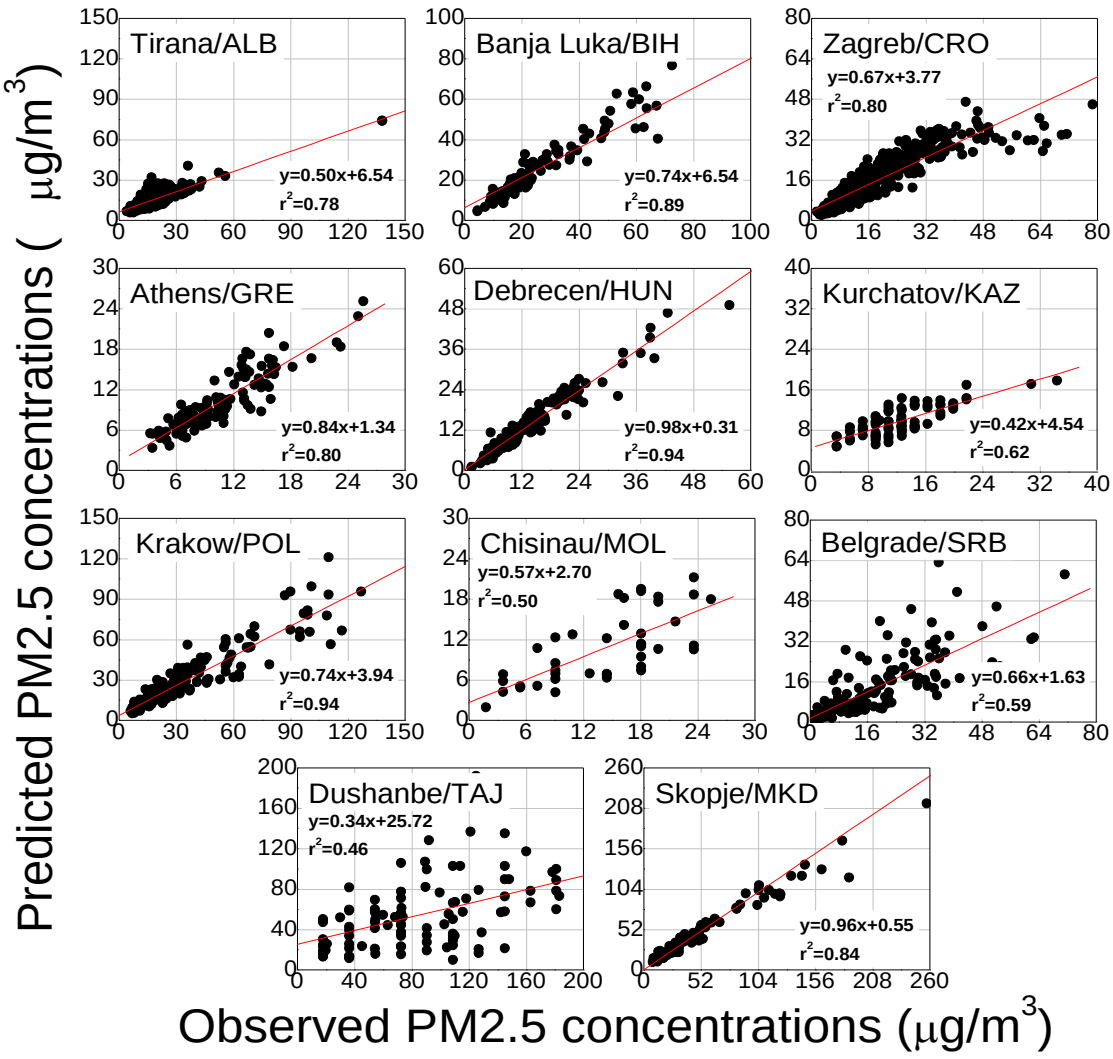

Figure G.1. Observed vs predicted $PM_{2.5}$ concentrations. Values in $\mu g/m^3$.