ПРИЛОЗИ, Одделение за природно-математички и биотехнички науки, МАНУ, том **41**, бр. 1 , стр. 41–48 (2020)
CONTRIBUTIONS, Section of Natural, Mathematical and Biotechnical Sciences, MASA, Vol. **41,** No. 1, pp. 41–48 (2020)

Received: February 12, 2020
Accepted: May 15, 2020

ISSN 1857–9027
e-ISSN 1857–9949
UDC: 502.3:[504.5:621.43.064(497.711)
DOI: 10.20903/csnmbs.masa.2020.41.1.156

Original scientific paper

URBAN AIR POLLUTION IN SKOPJE AGLOMERATION – TRAFIC VS BACKGROUND CASE

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Extreme winter time air pollution episodes, fortify public concerns and put focus on air pollution as most important environmental problem in urban areas throughout the country. However, focused research efforts to derive information about pollution sources and the amount they contribute to ambient air pollution levels, are still missing, thus leaving room for dubious discussions and political, instead of scientifically based abetment strategies.

Having in mind importance of proper information on air pollution sources and utilizing the data collected during several different measurement's campaigns performed for city of Skopje, as much extensive additional lab works and modeling efforts, indicative source apportionment analysis was performed for two sites (receptors) within Skopje urban area, one source specific (traffic) and one background site.

Key words: air pollution; sources apportionment; PMF; traffic; background

INTRODUCTION

While the air pollution has become recognized globally as one of most important environmental and health problems that urban population face nowadays, Balkan capitols become largely "popular" as a urban areas with the worst air quality in Europe, with Sarajevo leading on the unofficial AirVisual list, as the sixth most "polluted" city in Europe region, with PM 2.5 yearly average of 38.4 μg/m^3. Other capitols in the region closely follow, with Skopje ranked as tenth with PM 2.5 yearly average of 34 μg/m^3, Pristina ranked as twelfth with PM 2.5 yearly average of 34 μg/m^3, Sofia (21) and Belgrade (45) with respective PM 2.5 yearly averages of 28.2 and 23.9 μg/m^3.

Limited in scope and scattered scientific data, leave room for dubious discussions about air pollution sources identification and their respective contribution, making source apportionment public and political deliberation, instead of scientifically sound modeling exercise. Reliable and quantitative information on air pollution sources is essential for the drafting and implementation of air quality plans, especially having in mind that abatement at the source is core principle of any air pollution control strategy (Directive 2008/50/EC).

Source contribution or so-called Source Apportionment (SA) procedure include deriving information about pollution sources and the amount they contribute to ambient air pollution levels, using one of the three main approaches: emission inventories, source-oriented models, and receptor-oriented models. Receptor-oriented models imply apportion of the measured mass of an atmospheric pollutant at a given site (the receptor) to its emission sources by using multivariate analysis to solve a mass balance equation Belis *et al.*[1].

The main types of receptor-oriented models include but are not limited to positive matrix factorization - PMF, principal component analysis – PCA, multivariate models, regression models and chemical mass balance (CMB) models, Viana *et al.* [2]. These tools have the advantage of providing information derived from real-world measurements, including estimations of output uncertainty, and are

extensively used for the quantification of source contributions at local and regional scales all over the world [1]. Due to well developed and freely distributed software support for PMF and CMB, application of those tools steadily growth in last years with improved source resolution and accuracy.

Compiling information's collected over a few distinctive measurement's campaigns, performed for city of Skopje, as much broad extra lab works and modeling efforts, receptor models were constructed for two sites within Skopje urban area. Samples were taken according to standard gravimetric method (EN 12341:2014) using a low volume sampler and 47 mm PTFE filters. Chemical composition was determined using Fluorescent X-ray Spectrometer (Shimadzu EDX-900HS) according to EPA/625/R-96/010a IO-3.3 method, supported with multielement ICP-MS analysis. Seasonal and diurnal variation of PM10, PM2.5, NO_2 and CO were obtained with real time monitoring during the sampling campaigns using the Air Pointers (MLU Recordum, Austria), as much a UGD AMBICON independent monitoring network. Source apportionment was performed using EPA PMF 5.0 positive matrix factorization software package.

MATERIALS AND METHODS

As reported elsewhere, Mirakovski *et al.* [6], sampling was performed at two sites in Skopje central urban area, out if industrial or specific single source impacts (excluding traffic for roadside site). Sites were selected having in mind large spatial and temporal variation of air pollution, local topography, and meteorology, as much as references for leveling of traffic related pollutants concertation to the background within 150 m from the road, Pasquier & Andre [7]. Traffic exposed site was located within 2 meters from Ilindenska boulevard at City of Skopje Administration Buildings backyard, while background location was located at eastern corner of Ministry of Agriculture and Forestry building, facing the border of Skopje central park (Figure 1). Roadside site, experience mostly triple traffic frequency at any given day of the monitoring campaigns.

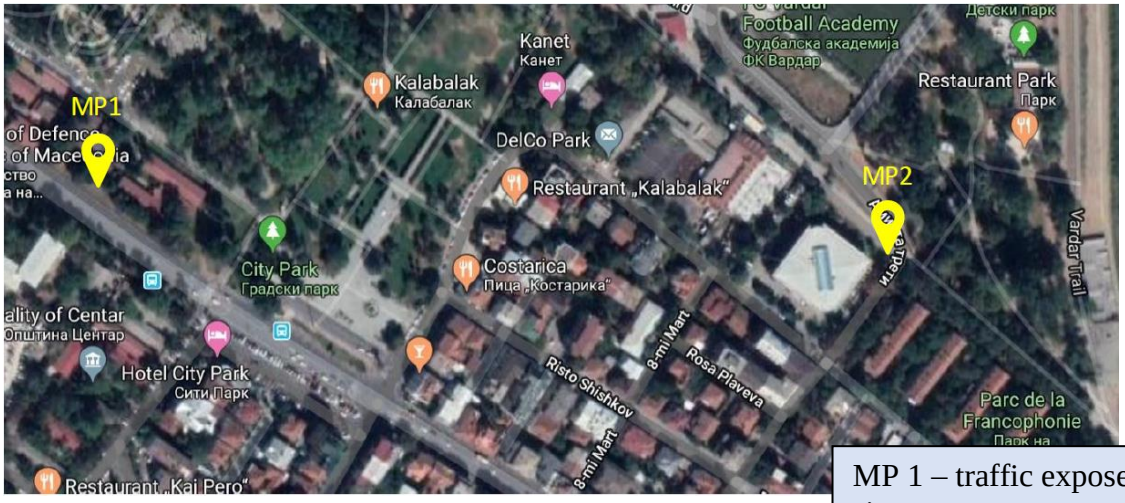

Figure 1. Sampling locations in Skopje urban area

Sampling

Both sites were equipped with sequential dust sampling systems PNS 16T-3.1 (Comde Derenda, Germany) with 16/18 filter cassettes for continuous collection of particulate matter and Air Pointers (MLU Recordum, Austria) for real time monitoring of PM10, PM2.5, NO_2 and CO using compliance or equivalent methods.

Sampling was performed at 2.2 meters height, continuously during at least 14 consecutive days in each season, starting from November 8–21.2018, January 18–31.2019, May 6–27.2019 and July 13–27.2019.

Gravimetry and elemental analysis

Particulate (PM10) samples were collected on 47 mm PTFE filters and handled and measured gravimetrically fully in line with recommendation given in EN 12341:2014 Ambient air - Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concentration of

suspended particulate matter. Quality control was performed fully in line with the requirements of EN 12341:2014 and measurement uncertainties were calculated following GUM concept (expanded relative uncertainty ≤ 11.4 %).

Elemental composition was measured by the energy dispersive X-ray fluorescence (EDXRF) using Fluorescent X-ray Spectrometer (Shimadzu EDX-900HS, Japan) for determination of Na, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Cd, Pb, Si and S fully in line with EPA/625/R-96/010a, Method IO-3.3 Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy. Measurement uncertainties were calculated based on blank and sampled filter concentrations. Expanded relative uncertainty varies for different elements between 5.2 % and 17 %.

Black Carbon or Elemental Carbon was analyzed with SootScan™ Model OT21 Optical Transmissometer Magee Scientific with dual wavelength light source (880nm providing the quantitative measurement of Elemental Carbon in PM, and a 370nm for qualitative assessment of certain aromatic organic compounds), by applying EPA empirical EC relation for TEFLON FRM filters. Measurement uncertainty was by convention set at 10%.

PMF Methods

Source Apportionment (SA) studies are usually done using one of three main methods: pollution inventories, source-oriented models and receptor-oriented models. As Belis et al. explain [1], receptor-oriented models apportion the measured mass of an atmospheric pollutant at a given site (receptor), to its emission sources by using multivariate analysis. Receptor models, supported by freely distributed software packages, have gained considerable popularity in recent years, with the particulate matter as chosen metric [2]. Source contribution/apportionment of PM10 mass by Positive Matrix factorization was performed using the EPA PMF version 5.0. program, in accordance with the user's guide [8].

Positive Matrix Factorization (PMF) is a receptor model, developed by Dr. Pentti Paatero (Department of Physics, University of Helsinki) in the middle of the 1990s [8], in order to develop a new method for the analysis of multivariate data that resolved some limitations of the PCA [9]. One of the main positive aspects is the use of know experimental uncertainties as input data which allow individual treatment of matrix elements and can accommodate missing or below-detection-limit data that are a common feature of environmental monitoring [10]. PMF results have a quantitative nature and therefore it is possible to obtain the composition of the sources determined by the model [12]. Concentration and uncertainty data matrices were compiled as recommended in PMF 5.0 Fundamentals and User Guide [8]. In total 20 base runs were performed, changing between 3 to 6 factors and base random seed with 0 % extra modelling uncertainty. Using the calculated sound to noise (S/N) ratios as recommended, all variables were categorized as "Strong".

Results and discussion

In order to gain overview of the data and explore the relationships between variables, basic statistic tests were performed, including, time trends, central and dispersion statistics, correlation matrices. As expected, temporal data variability was extremely high, with maximum values for most (if not all) contaminants included in the monitoring, displayed exclusively during the autumn/winter season. Even simple overview of time trends for suspended particulates PM10 concentration, confirms that daily averages above the limits are common for heating season only, while the same are well within the limits for spring and summer season (Figure 2). This is also the case for fine particulates fraction PM 2.5, nitrogen dioxide and elemental carbon concentrations.

Time trends also reveal distinct diurnal cycles during the high pollution episodes. Specific bimodal pattern, with two peaks, one in the morning and one in the late evening are frequently found. Such patterns could be driven with natural changes in boundary layer height but are also in direct conjunction with patterns of home heating usage, which also peaks in the morning and evening hours [6]. Similar diurnal patterns are reported elsewhere, for regions where domestic wood combustion for home heating is known to be a significant contributor to PM10 concentrations during the winter [14, 15].

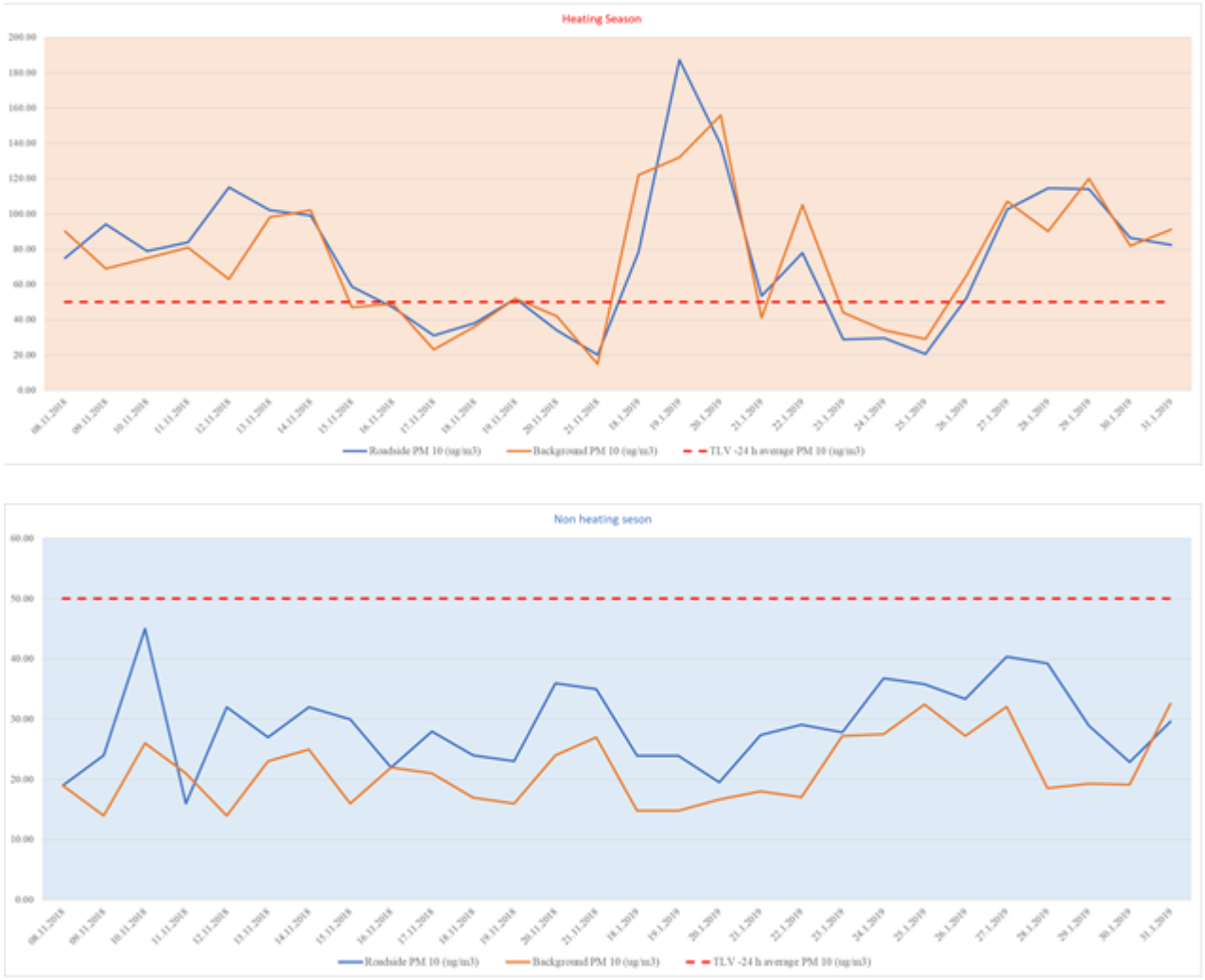

Figure 2. 24 h average for PM10 – indicative values 2019

Correlation matrices exhibit especially high correlation value (> 0.9) between suspended particulates (PM10 and PM 2.5) concentrations at both locations, as much as between concentrations of different fractions at same locations (> 0.95). Similar, although a bit lower correlation values were found for other species including nitrogen dioxide, elemental carbon, and carbon monoxide (Table 1). However, seasonal data analysis reveal that high correlation values are specific only for autumn/winter season and not for spring/summer period. Very specific is the strong correlation between particulates and background carbon monoxide concentration, frequently used as a maker for low efficient combustion processes emissions [13], found also only during the autumn/winter season.

In order to fully investigate different sources contribution, data collected for coarse particulate fraction and chemical composition were used to develop receptor model's at both sites, traffic exposed and the background site. As for each site, only 54 valid samples stretched over a 12-month period were available, PMF exercise should be seen as indication for dominant sources and cannot replace full scale source apportionment study. Low reconstructed mass percentages (around 30 %), mostly due to limited analytical exercise which does not included all usual components of ambient air particulates, like often dominant water-soluble ions (NH_4^+, SO_4^{2-} и NO_3^-), should also be taken in account for any further usage of data presented. Statistical description of the input data including average, maximum, and median concentrations of species used for source apportionment, as well as standard deviations, average uncertainties and limits of detection are given below (Table 2).

Table 1. Correlation matrix – full year data 2018/19

Full year data		Traf	Back	Traf	Back	Traf	Back	Traf	Back	Traf	Back
		PM 10 (μg/m^3)		PM 2.5 (μg/m^3)		NO2 (μg/m^3)		CO (μg/m^3)		EC (μg/m^3)	
Traf	PM 10 (μg/m^3)	1	0.91	0.97	0.91	0.76	0.86	0.51	0.80	0.89	0.81
Back	PM 10 (μg/m^3)	0.91	1	0.93	0.98	0.78	0.86	0.59	0.84	0.99	0.92
Traf	PM 2.5 (μg/m^3)	0.98	0.93	1	0.94	0.80	0.88	0.55	0.83	0.92	0.84
Back	PM 2.5 (μg/m^3)	0.91	0.98	0.94	1	0.77	0.85	0.62	0.85	0.93	0.93
Traf	NO2 (μg/m^3)	0.76	0.78	0.81	0.77	1	0.88	0.35	0.74	0.76	0.66
Back	NO2 (μg/m^3)	0.86	0.86	0.88	0.85	0.88	1	0.48	0.83	0.83	0.75
Traf	CO (mg/m^3)	-0.31	-0.22	0.09	0.08	0.54	-0.12	1	0.19	-0.69	-0.42
Back	CO (mg/m^3)	0.80	0.84	0.83	0.85	0.74	0.83	0.72	1	0.87	0.82
Traf	EC (μg/m^3)	0.89	0.91	0.92	0.92	0.76	0.83	0.66	0.87	1	0.92
Back	EC (μg/m^3)	0.81	0.91	0.84	0.93	0.66	0.75	0.68	0.82	0.92	1

Table 2. PMF Input data

Valid data (N=54)	Unit	Traffic	Back.	Traffic	Back.	Traffic	Back.	Traff/Back	Traff/Back
		Min		Max		Avg		Uncertain.	Detection limit
Na (PM10)	μg/m^3	0.020	0.020	0.624	0.574	0.077	0.069	0.0020	0.0019
Cl (PM10)	μg/m^3	0.004	0.042	0.049	0.468	0.014	0.144	0.0014	0.0018
K (PM10)	μg/m^3	0.054	0.054	2.216	2.097	0.481	0.403	0.0010	0.0010
Ca (PM10)	μg/m^3	0.036	0.059	2.911	3.119	1.212	1.133	0.0021	0.0012
Mn (PM10)	μg/m^3	0.003	0.002	0.205	0.108	0.027	0.019	0.0044	0.0051
Fe (PM10)	μg/m^3	0.068	0.033	1.513	1.086	0.700	0.428	0.0071	0.0043
Ni (PM10)	μg/m^3	0.001	0.002	0.075	0.055	0.014	0.013	0.0016	0.0001
Cu (PM10)	μg/m^3	0.003	0.005	0.196	0.157	0.018	0.024	0.0041	0.0051
Zn (PM10)	μg/m^3	0.001	0.001	0.401	0.391	0.035	0.041	0.0061	0.0019
As (PM10)	μg/m^3	0.000	0.000	0.001	0.001	0.000	0.000	0.0003	0.0002
S (PM10)	μg/m^3	0.538	0.483	6.294	5.382	1.755	1.657	0.0124	0.0124
Pb (PM10)	μg/m^3	0.001	0.001	0.140	0.271	0.019	0.046	0.0004	0.0005
Si (PM10)	μg/m^3	0.059	0.059	0.658	0.918	0.178	0.201	0.0061	0.0012
PM10	μg/m^3	16.0	14.0	187.3	156.0	52.2	48.0	3	3.0
PM 2.5	μg/m^3	4.1	5.0	174.0	146.0	36.3	36.1	2	3.0
EC (PM10)	μg/m^3	3.8	3.0	43.6	43.6	15.1	14.5	0.0752	0.0100

Preforming multiple PMF runs to elemental data, optimal solution with 4 factors was obtained. Factors were identified as:

- different forms of biomass burring (open fires, small boilers and residential stoves) specific for high EC content, K, Cl and S,

- industrial sources with Ni, Si, Na, Cu and As,
- traffic source specific for Zn, Cu, Mn and EC, as much as
- crustal sources which usually include Si, Ca and Na.

Some of the elements have contribution in several sources, as some processes, like resuspending road dust or combustion sources, contribute to a mixed source profiles (crustal matter Si, Ca and Na in traffic or EC in traffic, biomass burning and industrial emissions).

Receptor models developed using EPA PMF 5.0. software, delineate specific sources contribution in coarse particulates fraction PM10, for both locations separately. As shown below (Figure 3) for traffic exposed location, largest contribution has by far come from different forms of biomass burning (69 %), followed by traffic with 22 %, industrial at 8 % and crustal dust with 1 %. Background location (Figure 3) experience similar impacts, having biomass burning as dominant contributor with almost 72 %, traffic with 14 %, industrial sources with 12 % and crustal dust with 2 %.

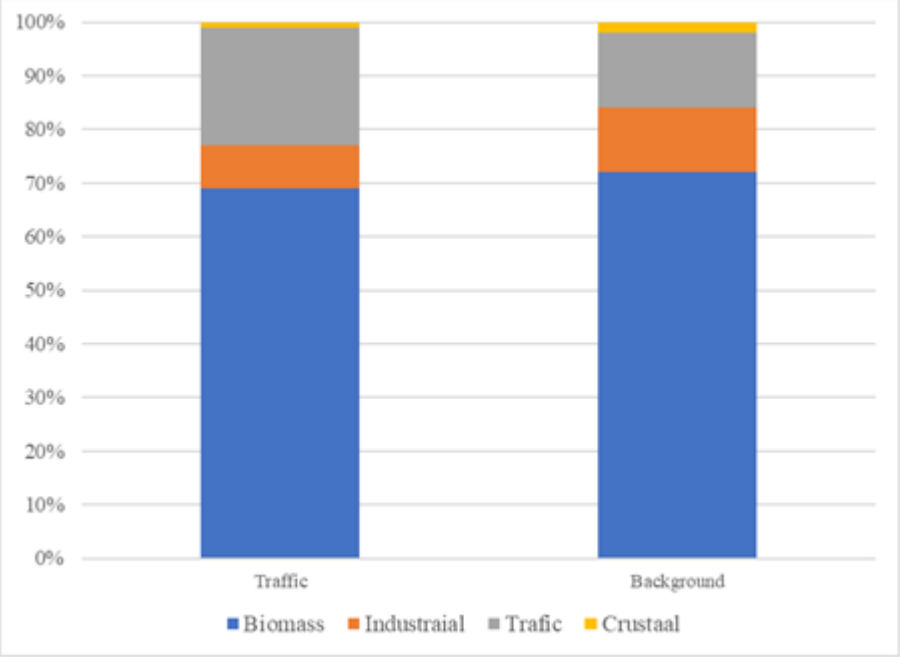

Figure 3. Factor contributions for PM10

CONCLUSIONS

Specific temporal variations (seasonal and diurnal) and correlations between different pollutant species at both locations clearly indicate domination of background sources compared to specific sources like traffic, while indicating high influence of low efficient combustion sources like residential wood stoves, open fires, and small boilers.

At both sites monitored, average yearly concentration was determined above the limits for coarse (PM10) and especially fine particulate (PM 2.5) fractions, only due to extremely high averages over the autumn/winter season, with same well within the limits out of heating season. While such pollution patterns could be explained with natural changes in boundary layer height during the cold whether season, direct conjunction with patterns of home heating, which also peaks in the morning and evening hours, is more than obvious.

In addition, source apportionment performed using Positive Matrix Factorization, clearly identify biomass burring as single dominant source at both location with high 69 % at traffic site and 72 % at background site, with no direct specific source impact. Such high contribution from biomass burning is not surprising, having in mind Skopje agglomeration emission inventory for reference 2014, where domestic heating participates with 91 %, in total PM10 emissions, while industry, energy production, traffic, waste management, agriculture and construction have altogether about 9 %, FMI & MOEPP [16].

Acknowledgement. Authors wish to acknowledge assistance from City of Skopje and Farmahem Environmental Lab for their support and participation in sampling and data collection process.

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ЗАГАДУВАЊЕ НА ВОЗДУХОТ ВО ГРАД СКОПЈЕ – СПОРЕДБА НА ПОЗАДИНСКА И НА ЛОКАЦИЈА ИЗЛОЖЕНА НА СООБРАЌАЈ

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Честите епизоди на екстремно загадување на воздухот во текот на зимските месеци, несомнено привлекуваат големо внимание и загриженост од јавноста, што веројатно го прави аерозагадувањето веројатно најважен еколошки проблем во урбаните средини ширум нашата држава. Но, за жал, речиси и да нема истражувачки напори, кои би биле фокусирани кон обезбедување на целосни информации околу поедините извори и нивното учество во вкупното загадување. Ваквите состојби, практично го лимитираат капацитетот на сите стратегии за решавање на проблемите со аерозагадувањето, кои наместо на научни се базираат на политички решенија.

Имајќи ја во предвид важноста на правилните информации за изворите на загадување на воздухот, а врз основа на податоците собрани во неколкукратни мерни кампањи во урбаната зона на град Скопје, како и

на дополнителни напори за хемиска карактеризација и конструкција на т.н. „рецепторни“ модели, беа изработени индикативни студии за пропорционирање на поединиите извори на две локации во Скопје, една изложена на интензивен сообраќај и една позадинска урбана локација.

Клучни зборови: загадување на воздухот; пропорционирање на поедини извори; позитивна факторизација; сообраќајна и позадинска локација