

CHARACTERISATION OF FINE PARTICULATE MATTER LEVEL, CONTENT AND SOURCES OF A KINDERGARTEN MICROENVIRONMENT IN BELGRADE CITY CENTER

by

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In the present work, we investigated polycyclic aromatic hydrocarbons, metals and ions of indoor and outdoor $PM_{2.5}$ from 80 samples collected in the microenvironment of a kindergarten located in Belgrade city center during weekdays, from March to May 2010. The daily concentrations of $PM_{2.5}$ were much higher than WHO guidance daily value. Results show similar factor profiles identified by principal component analysis (PCA) and positive matrix factorization (PMF). For indoor and outdoor environment, six principal components were identified by PCA, and six and seven factors were identified by PMF, respectively. Principal components from PCA were attributed to the following sources: combustion processes, traffic emission, coal/oil combustion, mix (stationary sources/resuspension), road salt and secondary aerosol. The resulting factors from PMF were identified as representing combustion processes, traffic emission, coal/oil combustion, soil dust, secondary aerosol and break wear. For outdoor environment, PMF identified one more source, attributed to road dust.

Key words: $PM_{2.5}$, polycyclic aromatic hydrocarbon, metals, ions, sources of pollution

Introduction

Air pollution represents one of the biggest environmental problems. The WHO estimated that air pollution was responsible for more than 550000 premature deaths in the WHO European Region in 2016, almost 6600 of which were attributed to air pollution in Serbia. Air pollution affects different groups of people in different ways. Vulnerable populations, such as children, are more susceptible to the adverse effects. In addition, air pollution causes respiratory diseases, including acute respiratory infection and chronic obstructive pulmonary disease. Further, the International Agency for Research on Cancer (IARC) has classified air pollution in general, as well as particulate matter (PM) as a separate component of air pollution mix-

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tures, as carcinogenic [1]. Therefore, reports about measurements of particles in schools and kindergartens have been recently published, as well as papers about chemical characterization of particles [2-10]. Although, in recent years in Serbia, there has been a greater interest of the public, government and scientific community for monitoring of air pollution in schools, the data on the composition of suspended particles in educational institutions are still limited [11, 12].

Health effects related to PM exposure may strongly depend on their number, size, specific surface area and chemical composition. The health effects of PM are well documented. Chronic exposure to particles contributes to the risk of cardiovascular and respiratory diseases, as well as of lung cancer [13]. Particles can contain, in addition to macro-components, heavy metals and polycyclic aromatic hydrocarbons (PAH). The PM macro-components represent the chemical species that individually constitute more than 1% of the total PM mass, such as some metals (Al, Si, K, Ca, Fe), anions (Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}). Several studies have pointed that PAH and metals represent the two main PM classes correlated with the adverse health effect [8, 14, 15]. Metals have long been suspected to be major components of ambient PM in producing adverse health effects because of their potential for oxidative activity and the production of reactive oxygen species [15]. On the other hand, PAH in air represent an increasing concern because of their carcinogenicity and mutagenicity [14]. The US Environmental Protection Agency (EPA) has selected 16 priority PAH in order to be analyzed in environmental samples. Seven PAH (benzo[a]pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) classified as probable human carcinogens (Group B2). In addition, Cd, Pb, As, and Ni, are classified in Group 1A (carcinogenic to humans) by the IARC [16, 17].

In the present work, we investigated the composition, origin and contributions to indoor and outdoor $\text{PM}_{2.5}$ from 80 samples collected in the microenvironment of a kindergarten located in Belgrade city center during weekdays in a period crossing over from the heating to non-heating season, from March to May 2010. The PCA as well as PMF were used on the PM composition data to determine the sources of air pollution and the relative contributions of resolve sources to both indoor and outdoor air quality at a Belgrade urban kindergarten.

Experimental

Sampling site

Outdoor and indoor samples of $\text{PM}_{2.5}$, were collected in Belgrade kindergarten during heating and non-heating seasons of 2010 (from March to May).



Figure 1. Map of Belgrade and sampling site (44°48'12.8"N 20°28'20.1"E)

The site was selected for this study as urban/residential site, fig. 1. The kindergarten is naturally ventilated. The kindergarten is located near to city center, and at about 4 m away from street with the medium frequency of traffic.

Sampling and analytical procedure

The samples were collected continuously during 40 workdays indoor and outdoor. All samples were collected using the low volume reference sampler Sven/Leckel (LVS), over a 24 hours period. The sampling flow rate was 2.3 m³ per hours (38 Lpm). The PM_{2.5} were collected on quartz filters (Whatman International Ltd., 47 mm). The indoor PM_{2.5} samples were collected in parallel at one classroom and one outdoor location. The sampler in the classroom was placed on the floor, about 1.2 m height and 1 m from the walls. Outdoor sampler was put on terrace, at 8 m above ground level. Totally, 40 daily samples for outdoor and 40 daily samples for indoor PM_{2.5} were collected. Air volume drawn by the sampler was used to calculate the mass concentrations of particles as well as concentrations of PAH, elements, anions and cations.

The filters were baked at 900 °C for 4 hours before sampling, so that organic compounds could be removed, and blank values reduced. The filters were weighed before and after sampling, to determine the amount of particles captured. After gravimetric measurements, each filter was divided in three parts. One part was used for the analysis of anions and cations. Second part of the exposed filter was used for the analysis of macroelements (elements whose concentrations are one to two orders of magnitude higher than the concentrations of trace elements) and trace elements. The third part was used for PAH analysis.

The PAH were extracted from the exposed filters in microwave with mixture of solvents hexane:acetone (12.5 mL n-hexane:12.5 mL acetone) according to EPA 3546. After extraction, solvent volume was reduced by rotary evaporation under reduced pressure (55.6 kPa and with 0.2 mL isooctane as a keeper) to 1 mL. Afterwards, n-hexane solution was reduced to 0.25 mL under nitrogen stream at room temperature to 0.5 mL and analyzed on gas chromatography (GC). Known quantities of internal standard were added to estimate the method recovery. The PAH were analyzed using GC coupled with Mass Selective Detector (Agilent GC 6890/5973 MSD) according to EPA Compendium Method TO-13A with a DB-5 MS capillary column (30 m × 0.25 mm × 25 μm). Oven temperature program started on 70 °C (4 minutes) and a ramp 8 °C per minutes till 310 °C (5 minutes) was then applied. Solvent delay was 5 minutes and time of run was 46 minutes. The mass spectrometry (MS) scanning was performed from 30 to 450 m/z. Sixteen US EPA priority PAH were determined: naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ane), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DbA), benzo[g,h,i]perylene (BgP), and indeno[1,2,3-cd]pyrene (InP).

The concentration of 20 elements (Al, Ca, Fe, K, Mg, Mn, Na, Ti, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, V and Zn) and six ions (Cl⁻, NH₄⁺, PO₄³⁻, NO₂⁻, NO₃⁻, SO₄²⁻) were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and Inductively coupled plasma-MS (ICP-MS) according to standard procedure CEN/TC 264 N799. The part of the filter was placed in Teflon vessels with 3 mL HNO₃ and 2 mL H₂O and start the appropriate program of Mars 5 microwave oven (two-stage temperature program, 20-30 minutes, 235 °C). After digestion, the samples are analyzed by optical and MS. Macroelements Al, Ba, Ca, Fe, K, Mg, Na, Ti, and Zn are determined by ICP-OES method using Varian-Vista Pro spectrometer while trace elements As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, and V are determined by ICP-MS using Agilent 7500-octopole reaction system spectrometer.

The third part of filters for the analysis of cations and anions was dissolved in deionized water. Aqueous extraction was then performed for 24 hours. The aqueous solution thus obtained was further analyzed by ion chromatography using Dionex DX-500. The ions determined by this method are in accordance with the standard operating procedure SOP MDL 064, Cl^- , NH_4^+ , NO_3^- , SO_4^{2-} .

Quality control

Field blanks were collected to determine any potential background contamination during sampling, transport and storage. One blank sample was analyzed for every 10 samples. QA/QC procedures were applied to microwave digestion and multielemental analysis of samples (using ICP-OES and ICP-MS) by analysis of certified standard reference material 2783 NIST (National Institute of Standard and Technology, Gaithersburg, Md., USA). The detection limits of each PAH were estimated as three standard deviations of field blanks. The calibration curves (0.1-2 $\mu\text{g}/\text{mL}$) for all 16 PAH were obtained by spiking the seven known quantities of substances (PAH-Mix PM-831, Ultra Scientific).

Results were statistically processed using Microsoft Excel 2010. The ANOVA method was applied to the results for elements and PAH. Two outlier tests (Grubbs test and Dixon's test) were applied before further data processing. Less than 1% of data were discarded as outliers from all data sets.

The PCA and PMF analysis

The PCA are widely used in air quality studies in order to provide information about PM. The objective of PCA is to derive a new principal component (PC) as a linear combination of the original variables, which provides a description of the data with a minimum loss of information. The normality of the data was checked using the Shapiro-Wilk test and the results showed that most components are non-normally distributed. For PCA, data sets were prepared with log-transformation of indoor and outdoor data sets. Data sets for analysis were arranged in matrix, which each column corresponds to one component (PAH or elements) and each row represents sampling dates. The PCA with Varimax rotation was applied to indoor and outdoor $\text{PM}_{2.5}$ samples collected in Belgrade's kindergarten. Varimax rotation allows to obtain components more representative of the contribution of each variable to a specific PC. The PC with an eigenvalue >1 were considered in the analysis. The statistical analysis software was SPSS 20.

The PMF is a quantitative source analysis receptor model based on multivariate factor analysis. In this paper, EPA PMF 5.0 was used. The goal of PMF is to identify the number of factors, p , the species profile, f , of each factor, and the amount of mass, g , contributed by each factor to each individual sample that solve the chemical mass balance between measured species concentrations and factor profiles. The PMF model is described in detail elsewhere [18-20].

We decided to exclude PO_4^{3-} and NO_2^- from the analysis because more than 70% of samples were below the detection limit. In addition, volatile PAH were shown as the sum of 2+3-ring PAH because these PAH have lower concentrations, close to detection limit, because these molecules are usually present in the gas phase. Following these sample exclusion choices, a matrix of 40 $\text{PM}_{2.5}$ samples and 36 variables, for both indoor and outdoor, was analyzed by PCA. There was no missing value in input datasets. The measured concentrations and uncertainty matrices required as input files for PMF analysis were prepared from both datasets separately according to the EPA user guide [20].

Results and discussion

The $PM_{2.5}$

The indoor and outdoor $PM_{2.5}$ mass concentrations ranged from 16.54 to 63.24 $\mu\text{g}/\text{m}^3$ and from 14.63 to 97.60 $\mu\text{g}/\text{m}^3$, respectively, tab. 1. There were no statistically significant differences between $PM_{2.5}$ measured indoors and outdoors ($p = 0.05$), even the indoor concentrations were found to be lower than the outdoor concentrations during most of the time. The I/O ratio was ranged between 0.47 and 1.88 (mean 0.91), indicating that the particles measured in classrooms originate mainly from the outdoor environment. The mean and median values are comparable to those found in European schools and kindergarten [5, 21-24], but relatively higher than those found in other kindergartens in Portugal [25].

Table 1. Indoor and outdoor $PM_{2.5}$ concentrations and indoor/outdoor ratio (I/O)

	$PM_{2.5}$, $\mu\text{g}/\text{m}^3$		
	Outdoor	Indoor	I/O ratio
Mean	38.37	32.19	0.91
Standard deviation	16.55	10.66	0.33
Median	34.25	29.71	0.84
Min	14.63	16.54	0.47
Max	97.60	63.24	1.88

Taking into account results from European cohorts and other studies, WHO recently published a new ambient Air Quality Guidelines (AQG) levels for main pollutants including fine particulate matter. The 24 hour AQG for $PM_{2.5}$ in ambient air are now lower. These levels are changed from 25 $\mu\text{g}/\text{m}^3$ to 15 $\mu\text{g}/\text{m}^3$ [26]. The results indicated that the outdoor and indoor $PM_{2.5}$ daily mean values were much higher than 25 $\mu\text{g}/\text{m}^3$, fig. 2., 82.5% and 75%, respectively, and even much more when taking in account newly-established WHO AQG (more than 95%).

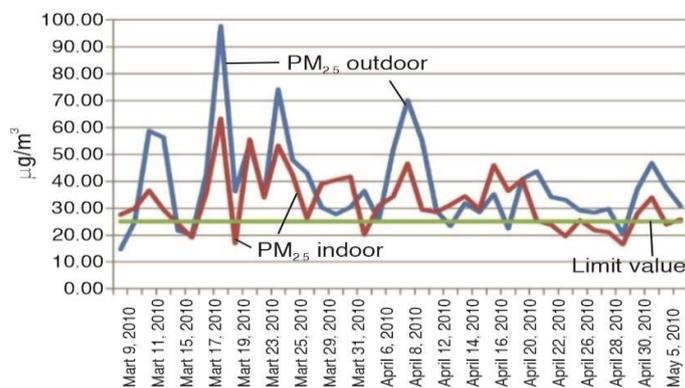


Figure 2. Indoor and outdoor daily concentrations for $PM_{2.5}$

The PAH

The concentrations of indoor and outdoor PAH in $PM_{2.5}$ are summarized in tab. 2. The sum of mean indoor PAH was 3.68 ng/m^3 mean concentration (median was 3.35 ng/m^3), which is lower than those reported by Oliveira *et al.* [27] for Portuguese schools and similar with those reported by Oliveira *et al.* [25] for Portuguese kindergartens. The sum of mean outdoor $PM_{2.5}$ -PAH concentration was 5.53 ± 3.54 ng/m^3 (median 5.05 ng/m^3). Krugly *et al.* [28] reported that ΣPAH in $PM_{2.5}$ fraction indoors and outdoors ranged from 20.3-131.1

ng/m³ and from 40.7-121.2 ng/m³, respectively, for 5 primary schools in Lithuania, and Romagnoli *et al.* [29] reported the mean total indoor and outdoor PM_{2.5}-PAH concentrations in schools in Rome as 1.84 ± 0.30 to 8.29 ± 6.67 ng/m³ and from 7.0 ± 1.53 to 9.54 ± 7.23 ng/m³, respectively. Indoor/outdoor ratios of individual PAH and ΣPAH were less than 1 which indicated that indoor PAH originated mainly from the outdoor environment. The BgP, Ind, BaP, BbF, BkF, and Chy are the most abundant in PM fractions, especially in outdoor particles. These PAH can be associated with coal combustion, industrial waste incineration and stuck and light-duty gasoline vehicles [30]. The contribution of PAH in the PM_{2.5} fraction was less than 2% for both indoor and outdoor environment.

Ring number distribution of indoor and outdoor PAH is shown in fig. 3. The PAH concentration in PM_{2.5} samples displays the following decreasing trend: 5-rings > 6-rings > 4-rings > 3-rings > 2-rings for indoor samples and 5-rings > 4-rings > 6-rings > 3-rings > 2-rings for outdoor samples. The highest presence of 5-rings PAH and the lowest presence of 2- and 3-rings PAH were observed. The more volatile compounds (PAH with 2- and 3-rings) have lower concentrations because these molecules are usually present in the gas phase. On the other hand, the high percentage of high molecular weight PAH indicates the sources are high temperature processes, such as the combustion of fuels [30, 31].

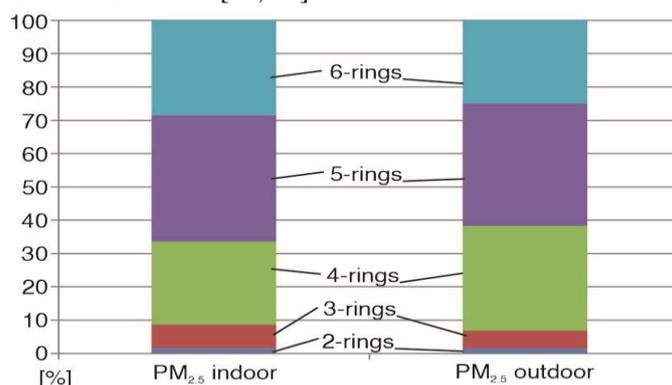


Figure 3. Ring number distribution of indoor and outdoor PM_{2.5}-PAH

Chemical elements and ions

All elements were detected in each sample, except anions PO₄³⁻ and NO₂⁻, which were not detected in 73% of the samples, and they were not included in further analyses. The mean concentrations, standard deviations and medians of PM macro-components and trace metals, as well as their contribution to total PM, are shown in tab. 3. The most abundant mac-

Table 2. Indoor and outdoor concentrations, mean ± standard deviation (median), of PAH in PM_{2.5} in ng/m³

	Indoor	Outdoor
Nap	0.06 ± 0.05 (0.05)	0.08 ± 0.05 (0.07)
Ace	0.04 ± 0.03 (0.03)	0.05 ± 0.04 (0.04)
Ane	0.04 ± 0.05 (0.02)	0.04 ± 0.06 (0.01)*
Flu	0.01 ± 0.01 (0.01)*	0.02 ± 0.01 (0.01)*
Phe	0.14 ± 0.08 (0.13)	0.17 ± 0.08 (0.16)
Ant	0.02 ± 0.01 (0.02)*	0.03 ± 0.02 (0.03)
Fln	0.21 ± 0.12 (0.18)	0.30 ± 0.14 (0.30)
Pyr	0.24 ± 0.13 (0.22)	0.36 ± 0.17 (0.38)
BaA	0.18 ± 0.13 (0.16)	0.38 ± 0.27 (0.33)
Chy	0.29 ± 0.19 (0.28)	0.69 ± 0.44 (0.60)
BbF	0.43 ± 0.33 (0.37)	0.71 ± 0.52 (0.64)
BkF	0.50 ± 0.38 (0.45)	0.80 ± 0.57 (0.77)
BaP	0.43 ± 0.35 (0.34)	0.48 ± 0.37 (0.40)
Ind	0.49 ± 0.41 (0.39)	0.64 ± 0.55 (0.57)
DahA	0.04 ± 0.04 (0.02)	0.05 ± 0.05 (0.03)
BgP	0.56 ± 0.40 (0.48)	0.73 ± 0.56 (0.66)
ΣPAH	3.68 ± 2.50 (3.35)	5.53 ± 3.54 (5.05)

* > 70% of samples was below detection limit

ro-components detected were Ca, Mg, and ions in both indoor and outdoor environments, and the most abundant trace elements detected were Zn, Ba, Cr, Cu, and Pb. Analysis of PM elements as well as ions in Belgrade kindergarten showed concentrations of Na, K, Ca, Cl⁻, NH₄⁺, NO₃⁻, SO₄²⁻ similar to the other European schools microenvironments [5, 7, 32, 33]. The Mg concentration was much higher than those reported in literature for European schools [5, 7, 21]. The concentrations of Al, Ti, and Mn were significantly lower than those reported for European schools, except for Al in Poland school where the concentration was much higher [5, 7, 8, 32, 33]. The Fe concentration was lower compared to Spanish and Belgium schools [5, 7, 32], but higher than those reported for schools in Portugal, Poland, and Sweden [2, 4, 33].

Table 3. Indoor and outdoor concentrations (mean ± std (median)) of macro-components and trace elements and their indoor/outdoor ratio (I/O) in PM_{2,5}

		Indoor	Outdoor	I/O
Macro-components [µgm ⁻³]	Al	0.30 ±0.10 (0.30)	0.30 ±0.14 (0.29)	1.15 ±0.53
	Ca	3.03 ±1.06 (2.82)	3.15 ±0.96 (3.01)	0.99 ±0.26
	Fe	0.28 ±0.09 (0.28)	0.43 ±0.18 (0.41)	0.72 ±0.24
	K	0.33 ±0.08 (0.33)	0.33 ±0.11 (0.34)	1.07 ±0.35
	Mg	0.57 ±0.28 (0.56)	0.59 ±0.25 (0.62)	0.99 ±0.42
	Mn	0.007 ±0.004 (0.006)	0.010 ±0.005 (0.010)	0.78 ±0.35
	Na	0.31 ±0.10 (0.34)	0.32 ±0.11 (0.36)	1.02 ±0.34
	Ti	0.005 ±0.002 (0.005)	0.008 ±0.004 (0.007)	0.80 ±0.40
	Cl-	0.26 ±0.14 (0.23)	0.88 ±0.66 (0.74)	0.44 ±0.29
	NH4+	0.49 ±0.27 (0.41)	0.38 ±0.24 (0.33)	1.55 ±0.80
	NO3-	0.08 ±0.06 (0.07)	0.94 ±0.69 (0.77)	0.16 ±0.39
	SO42-	0.23 ±0.09 (0.23)	1.29 ±0.55 (1.32)	0.22 ±0.24
Contribution	%	29.58 ±11.40	34.09 ±15.46	–
Trace elements [ngm ⁻³]	As	1.80 ±1.47 (1.38)	2.71 ±2.63 (1.79)	0.83 ±0.56
	Ba	14.88 ±4.33 (14.87)	16.06 ±5.52 (15.61)	0.98 ±0.28
	Cd	0.25 ±0.11 (0.23)	0.37 ±0.41 (0.30)	0.90 ±0.31
	Co	0.30 ±0.15 (0.25)	0.35 ±0.18 (0.29)	0.87 ±0.20
	Cr	12.49 ±4.08 (11.44)	12.81 ±3.76 (12.18)	0.99 ±0.19
	Cu	13.69 ±3.20(14.22)	14.08 ±4.29(13.99)	1.03 ±0.28
	Ni	7.01 ±2.81 (6.04)	9.09 ±4.38 (8.41)	0.84 ±0.27
	Pb	11.26 ±4.08 (11.15)	15.99 ±6.53 (16.74)	0.77 ±0.31
	Sb	0.83 ±0.41 (0.78)	1.22 ±0.65 (1.07)	0.74 ±0.23
	Se	0.55 ±0.25 (0.59)	0.70 ±0.28 (0.72)	0.79 ±0.21
	V	5.93 ±5.80 (4.58)	9.99 ±10.09 (7.39)	0.72 ±0.40
	Zn	32.12 ±14.04 (26.61)	36.72 ±21.00 (30.46)	0.96 ±0.33
Contribution	%	0.33 ±0.11	0.34 ±0.13	–

The concentrations of trace elements Cu, Cr, and Ni were similar like Belgian schools [32], but higher than Spanish and Sweden schools [4, 5]. The concentration of Cd, Co, Sb, and Se were generally higher than in other European schools. The Pb concentration was higher than those reported for Spanish and Sweden schools [4, 5, 7], but two times lower than Belgian and Poland schools [32, 33]. The levels of As, Ba, and Zn were higher than those reported by Almeida *et al.* [2] for Portuguese schools, but the level of Ba was similar like schools in Barcelona [5].

The I/O ratios for macro components and trace metals were lower than 1, except for Al, K, Na, NH_4^+ , and Cu. The I/O ratios for macro components (Al, K, and Na) were found to be about 1 or slightly higher than 1, indicating that these components may have indoor sources. But, as pointed out in other studies, the reason for the I/O ratio higher than 1 was probably resuspension of settled mineral dust during cleaning and children's activities [19, 33, 34]. At the other hand, in indoor environments ammonium nitrate becomes volatilized more quickly due to higher temperatures and adheres to room surfaces [6].

In indoor and outdoor $\text{PM}_{2.5}$, the contributions of macro elements were 26.25% and 24.36%, while the contribution of trace elements was 0.33% and 0.34%, respectively. The contribution of ions was 3.64% in indoor $\text{PM}_{2.5}$ and 10.39% in outdoor $\text{PM}_{2.5}$.

In this study, enrichment factor (EF) values were calculated with respect to Fe and crustal compositions. The EF values of all elements were slightly higher indoor than outdoor. It can be recognized that these elements were more enriched in indoor particles, rather than outdoor particles, tab. 4. The Se was the most enriched metal (EF values > 1000), followed by Sb, Cd, As, and Pb (EF values > 100). The EF values higher than 100 indicate that these elements are anomalously enriched and are mainly originated from anthropogenic sources. Fossil fuels are a major source of Se to the atmosphere, and aerosol studies have primarily focused on using Se as tracer for coal fired power plants [35]. The Pb and Sb are primarily originated from anthropogenic sources such as vehicular exhaust and industrial emissions, while Cd and As are the characteristic trace components of fossil fuels burning in atmosphere [36]. The EF values below 1 indicate that local crust is the major origin of elements (Al and Ti). The EF values below 10 indicate that the element is not enriched and these elements are mainly contributed by crustal sources (K, Mg, Na, Ba, Co, and V). For $10 < \text{EF} < 100$, elements are moderately enriched and suggest that both natural emissions and anthropogenic sources are important (Ca, Cr, Cu, Ni, and Zn).

Table 4. The EF of elements in indoor and outdoor air

	$\text{PM}_{2.5}$	
	Indoor	Outdoor
Al	0.7	0.5
As	199.4	196.9
Ba	7.0	4.9
Ca	15.9	9.9
Cd	332.3	322.6
Co	2.4	1.8
Cr	24.4	16.4
Cu	45.5	30.7
K	3.2	2.1
Mg	4.9	3.3
Mn	1.5	1.4
Na	2.6	1.8
Ni	16.6	14.2
Pb	160.3	149.4
Sb	827.4	797.7
Se	2193.0	1831.1
Ti	0.2	0.2
V	9.9	10.9
Zn	91.5	68.6

Source apportionment

The PCA

Varimax rotation with Kaiser normalization was used to compute PC which were extracted based on an eigenvalue > 1. The KMO test and Bartlett's spherical test were adopted to determine the adequacy of variables for use in PCA analysis. The KMO test coefficient was greater than 0.6 and the significance of the Bartlett's spherical test was less than 0.01, indicating that the variables were suitable for PCA.

For indoor and outdoor environment, the PCA model extracted six varimax rotated factors that accounted for 83.74% and 86.69% of the total variance, respectively. Factor loadings are very similar for both data sets, tab. 5. The PC1 for indoor and outdoor explained 29.04% and 27.57% of the total variance, respectively, and was characterized by a high load-

Table 5. Varimax rotated factor loadings for PM_{2.5} indoor and outdoor

	Indoor						Outdoor					
	PC1	PC2	PC3	PC4	PC5	PC6	PC1	PC2	PC3	PC4	PC5	PC6
PM _{2.5}	0.48	0.34	0.13	-0.23	0.43	0.31	0.19	0.23	0.69	-0.21	-0.07	0.42
Al	-0.17	0.78	0.13	0.32	0.12	-0.07	-0.17	0.92	0.07	0.19	0.07	-0.07
As	0.32	0.18	0.78	-0.06	0.14	0.03	0.56	0.35	0.49	0.00	0.19	-0.04
Ba	0.06	0.68	0.07	0.69	-0.01	-0.05	0.11	0.82	0.06	0.51	0.10	0.04
Ca	0.19	0.72	-0.22	0.32	-0.23	0.04	0.12	0.78	-0.21	0.23	-0.12	0.02
Cd	-0.09	0.53	0.65	0.15	-0.06	0.34	0.08	0.65	0.49	0.27	-0.04	0.34
Co	-0.02	0.12	0.10	-0.38	0.78	0.24	0.13	0.36	0.10	-0.07	0.82	0.16
Cr	0.05	0.74	0.01	0.11	-0.01	0.45	0.06	0.75	-0.07	0.39	0.21	0.18
Cu	0.30	0.84	0.02	0.11	-0.14	0.02	0.25	0.81	0.22	0.22	-0.06	-0.07
Fe	-0.11	0.88	0.33	0.10	0.04	-0.02	-0.18	0.85	0.28	0.02	0.30	-0.09
K	-0.04	0.51	0.36	0.65	0.29	0.03	0.10	0.50	0.34	0.65	0.24	0.16
Mg	-0.08	0.26	-0.12	0.88	-0.21	0.15	0.04	0.41	-0.15	0.85	-0.10	0.10
Mn	-0.09	0.78	0.32	0.17	0.04	0.01	-0.20	0.91	0.23	0.08	0.13	-0.05
Na	0.02	0.27	-0.04	0.92	-0.03	0.05	0.09	0.35	-0.05	0.88	0.05	0.14
Ni	0.48	0.17	0.49	0.01	0.37	-0.31	0.44	0.27	0.68	0.10	0.26	-0.04
Pb	0.13	0.58	0.67	0.17	-0.09	0.28	0.27	0.66	0.60	0.11	-0.06	0.18
Sb	0.15	0.41	0.83	-0.02	-0.01	0.09	0.29	0.55	0.66	0.01	0.12	0.13
Se	0.12	0.49	0.31	-0.16	-0.57	0.19	0.07	0.61	0.41	-0.07	-0.48	0.27
Ti	-0.21	0.78	0.24	0.29	0.00	-0.02	-0.23	0.90	0.09	0.07	0.07	-0.12
V	0.23	0.10	0.81	-0.12	0.24	-0.11	0.43	0.10	0.72	-0.07	0.28	0.09
Zn	0.07	0.79	0.31	-0.19	0.19	-0.10	0.13	0.82	0.26	-0.12	0.30	0.10
Cl	-0.41	0.13	0.21	0.14	0.65	-0.06	-0.17	0.18	0.23	0.15	0.75	0.16
NO ₃	0.30	-0.19	0.37	0.02	0.57	0.11	0.32	-0.03	0.23	0.10	0.19	0.76
SO ₄	0.10	0.06	-0.01	0.32	0.09	0.88	0.00	0.06	-0.03	0.38	0.11	0.85
NH ₄	0.23	0.01	0.14	-0.13	0.05	0.89	0.46	-0.11	0.26	-0.11	0.01	0.65
2+3-ring	0.79	-0.15	-0.15	-0.08	0.32	0.16	0.86	-0.08	-0.06	0.03	0.19	0.12
Flu	0.95	-0.03	0.08	0.00	-0.07	0.06	0.95	-0.06	0.14	0.10	-0.03	0.04
Pyr	0.96	-0.02	0.07	0.03	-0.08	0.07	0.95	-0.10	0.14	0.13	0.02	0.01
BaA	0.97	0.02	0.12	0.09	0.01	0.11	0.90	-0.12	0.27	0.18	0.16	0.09
Chr	0.94	0.09	0.14	0.10	-0.13	0.06	0.92	-0.06	0.27	0.19	0.01	0.06
BbF	0.96	0.02	0.14	-0.06	0.01	0.04	0.92	-0.04	0.25	-0.04	-0.07	0.15
BkF	0.93	0.08	0.14	0.14	-0.18	0.08	0.87	0.01	0.23	0.07	-0.33	0.10
BaP	0.97	-0.03	0.09	-0.03	0.10	0.07	0.95	0.01	0.23	0.01	0.06	0.13
Ind	0.96	0.02	0.08	-0.14	0.04	0.03	0.80	0.29	-0.20	-0.21	-0.21	0.13
DaA	0.66	-0.06	0.25	-0.27	0.34	-0.16	0.68	0.10	0.39	-0.17	0.33	0.18
Bpe	0.95	0.04	0.05	-0.04	-0.08	-0.01	0.78	0.31	-0.23	-0.16	-0.31	0.06
Eigenvalues	11.44	8.95	3.99	2.22	1.99	1.55	13.29	9.10	3.14	2.60	1.85	1.24
% of Variance	29.04	19.62	11.51	9.73	7.32	6.52	27.57	25.31	11.51	8.48	6.98	6.85

ing of all PAH and As in outdoor data set. The heavier PAH (with 5- and 6-rings) are associated with light-duty vehicles and low-molecular weight PAH are associated with diesel tracks. On the other hand, Chr and BkF are markers for coal combustion [30]. Therefore, this PC1 indicates combustion processes. The PC2 explained 19.62% indoor and 25.31% outdoor of the total variance and was characterized by typical traffic markers (Zn, Pb, Cu, Cr) and elements from road dust, include soil dust and resuspension (Ca, Mg, Al, Ti, Fe) [37, 38]. The kindergarten is located near to street, and it is to be expected that traffic has a significant impact on air quality. Hence, PC2 associated with vehicle emissions along with road dust resuspension. The PC3 was characterized by As, Cd, Pb, Sb, and V, explained 11.51% and 11.51% of the total variance indoor and outdoor, respectively. The high loadings of these metals rep-

resent the coal/oil emission sources. The Ni and V are metals of high abundance in residual oil fly ash, which is a combustion by-product of oil used as a fuel source. They are sourced primarily from fuel oil combustion. High levels of V are present in residual and fuel oils and are also found in the lubricating oils of all types of engines. Petroleum refineries are another significant source of V to the atmosphere [38, 39]. On the other hand, As is associated with coal combustion [37]. The PC4 explained 9.31% and 8.48% of the variance indoor and outdoor, respectively, and was characterized by Ba, K, Mg, Na. Coals are often enriched in Na and K, while K have also been associated with biomass burning [39]. The Mg and Ba are indicative of crustal origin (include resuspension). This PC can be designated as mix of stationary sources and resuspension. The PC5 was responsible for 7.32% and 6.98% of total variance indoor and outdoor, respectively. It is characterized by higher contribution of Co and Cl^- . Sources of Co in the atmosphere include coal-fired power plants and incinerators [40], while NO_3^- and Cl^- could represent open burning processes as well as waste incineration [41]. Chlorine can be also attributed to road salt during winter and cleaning product containing chlorine in indoor environment. It seems that these sources are not separated by PCA. The PC6 for indoor and outdoor explained 6.52% and 6.85% of the total variance, respectively. It was characterized by a high loadings of NO_3^- , SO_4^{2-} , NH_4^+ which indicate secondary aerosol [39, 41].

The PMF

The PMF model was run multiple times to find the optimal number of factors for indoor and outdoor data sets. The reasonable result was selected according to the ratios of the Q_{true} and Q_{robust} , Q/Q_{exp} value, source profiles, and R^2 values for predicted vs. observed chemical species. For indoor data set, two variables (Cl^- and NO_3^-) were weighted as *bad* due to low S/N values (<0.5). For both data sets, $\text{PM}_{2.5}$ is included as the total variable, which by definition is weighted as *weak*. The DaA was weighted as *weak* because it had S/N < 1 in both data sets. All other variables were weighted as *strong*.

Six and seven factors were selected as the optimal solutions for indoor and outdoor, respectively, based on the distributions of scaled residuals and the interpretability of the resulting source profiles. In addition, displacement (DISP) and bootstrap (BS, $n = 100$) analyses were used to investigate the profile uncertainties of resulting solutions. The F_{peak} rotation was not needed because a unique solution could be obtained.

High loadings of PAH identified Factor 1 (indoor) and Factor 4 (outdoor) as a combustion source, figs. 4. and 5. The reasons were similar to PCA analysis for rotated PC1. The percentage contribution of this factors was 18.91% for indoor and 23.40% for outdoor. Factor 2 for both indoor and outdoor was responsible for 18.92% and 10.13% of all factors contribution and was identified as coal/oil combustion based on loadings of V and As. Similar like for PC2, Factor 3 (indoor) and Factor 7 (outdoor) were identified as related to traffic emissions. Factor 4 (indoor) and Factor 6 (outdoor) were dominated by NO_3^- , SO_4^{2-} , NH_4^+ , and the percentage contribution was 15.14% and 11.18%, respectively. The predominance of these ions has been attributed to secondary aerosol [38, 39]. The relatively high levels of Co in Factor 4, as well as moderate levels of lighter PAH (with 2-, 3-, and 4-ring) in Factor 6 (outdoor), providing evidence for stationary emission sources (coal-fired power plants and incinerators) [30, 40]. This suggests stationary emissions as a major source of pollutants responsible for secondary aerosol in kindergarten. Factor 5 for indoor environment and Factor 3 for outdoor environment were dominated by Fe, Mn, Ni, and Zn. These factors were thus attributed to brake wear [37, 39], and the percentage contribution was 9.57% for indoor and 17.51% for

For indoor and outdoor environment, six PC were identified by PCA, attributed to the following sources: combustion processes, traffic emission, coal/oil combustion, mix (stationary sources/resuspension), road salt and secondary aerosol. Overall, the PCA and PMF models achieved reasonable results with respect to their ability to identify the possible sources of pollution in the selected kindergarten in Belgrade. PMF identified six factors for indoor and seven factors for outdoor environments. The resulting factors were identified as representing combustion processes, traffic emission, coal/oil combustion, soil dust, secondary aerosol and break wear. For outdoor environment, PMF identified one more source, attributed with road dust. Although the source profiles by PCA and PMF were quite similar, there were certain differences. The PMF model appears to be more suitable to separate traffic emission and break wear than PCA. It seems that PMF differentiated sources more finely than PCA analysis.

The authors would like to emphasize that the presented data refer only to PM_{2.5} fraction, as well as the sampling period covers a limited part of the heating and non-heating seasons, therefore it may not represent realistic pollutant levels throughout the year. Also, the gas phase of PAH was not analyzed, so it was not possible to determine the actual levels of PAH, especially the volatile PAH, and their distribution between gas and particle phases. However, despite these gaps, this work can be considered to contribute to deeper understanding of the chemical composition of particles and the identification of main sources of air pollution in the selected kindergarten in Belgrade.

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