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Concentration and source identification of polycyclic aromatic hydrocarbons in the metropolitan area of Belgrade, Serbia

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HIGHLIGHTS

- Analysis of PM_{10}-bound PAH has been conducted in Belgrade Metropolitan (Serbia).
- PM_{10} and PM_{10}-bound PAH concentrations have shown seasonal variation.
- PMF has been applied on PAH daily data set.
- Major PAH sources are traffic, stationary sources, wood and coal combustion.

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ABSTRACT

The aim was to determine concentrations, sources of priority PAHs in PM_{10} in ambient air and the lifetime lung cancer risk from exposure to PAHs using TEFs at different locations over Belgrade Metropolitan: traffic, rural industrial and suburban industrial. PM_{10} were collected using LVS on quartz filters in period 2010–2011 and priority PAHs were determine by GC–MS. Mean total PAHs concentrations for traffic, rural industrial and suburban industrial locations vary between nonheating and heating seasons from about 5 to 7 and 50–100 ng/m^3, respectively. Source apportionment technique as PMF and diagnostic ratio were applied and 5 emission sources were identified. Locations were under influence of traffic and stationary sources. Particular factor were identified at rural and suburban industrial locations as wood burning, while at suburban industrial site was additionally influenced by coal combustion. Health risk assessment showed that the most negative impact was found at the suburban industrial location.

1. Introduction

Air quality continues to be a very important issue for public health and the environment. Particulate matter (PM) and ozone (O_3) pollution are particularly associated with serious health risks (EEA, 2012). Among the chemical species bonded on PM surfaces polycyclic romatic hydrocarbons (PAHs) are of major significance. According to some studies a 10 μg/m^3 increase in PM_{10} concentration can be yield 1% increase in overall mortality (Lipmann, 1998).

PAHs are formed during incomplete combustion of wood or coal burning, combustion of fuels in engines, forest fires incidence, etc. These compounds consist only of carbon and hydrogen in two or more fused aromatic rings (Ravindra et al., 2008). They belong to POPs (persistent organic compounds). In the atmosphere, these compounds can be present in the vapor phase (low molecular weight PAHs) and associated with the particle phase (higher molecular weight PAHs) (Ravindra et al., 2008).

Atmospheric PAHs are human carcinogens and mutagens, a class of potentially carcinogenic substances, potentially causing respiratory problems (IARC, 2010; IARC, 2012). Particle-associated PAHs may reach and deposit in the lungs causing a negative effect on human health. USEPA listed 16 main PAHs, where some are considered probably human carcinogens. IACR in recent monograph (IARC, 2013) classified benzo[a]pyrene as human carcinogens (Group 1), benz[a]anthracene as probable human carcinogens

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(Group 2A) and chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) as possible human carcinogens (Group 2B).

Major sources of PAHs, especially in urbanized areas, are gasoline and diesel vehicles, coal and wood combustion and industrial processes (Mostert et al., 2010; Tobiszewski and Namieśnik, 2012). For each sources such as: diesel and gasoline combustion, crude oil processing products and biomass burning (Ravindra et al., 2008; Yunker et al., 2002), the PAH emission profile is different. To develop mitigation measures that will lead to the reduction of PAH's it is first necessary to identify the pollutant sources. PAH diagnostic ratios can be used to identify some potential emission sources (Okuda et al., 2010; Teixeira et al., 2012; Tobiszewski and Namieśnik, 2012). The source identification is often achieved by using receptor models. In this study we applied the positive matrix factorization (PMF) method, a sound factor analysis tool proved as successful for a reliable receptor modeling to apportion the sources of particles bounded PAHs (Moon et al., 2008; Park et al., 2011; Jang et al., 2013).

In Serbia, monitoring of PM less than 10 μm (PM_{10}) started from 2003 at three stations in Belgrade within the Local monitoring network run by the Institute of Public Health of Belgrade. Today in the Belgrade Metropolitan region in framework of Local and State Air Quality Monitoring Networks there are running 15 automatic monitoring stations, 11 of them in the city center and 4 nearby two power plants. Usually during winter season PM_{10} concentrations are much higher than during summer season. During 2011 in summer at four measurement sites in Belgrade Metropolitan region (two of them in urban traffic area and the other in rural and suburban-industrial area) the values of PM_{10} were within a range of 30.9–41.1 μg/m^3. In winter 2011 PM_{10} concentrations were within a range of 83.6–89.4 μg/m^3 at locations affected by individual domestic heating and 72.3–72.4 μg/m^3 in the urban area in city center.

In Belgrade the first data on the PAH composition of PM_{10} and smaller fractions, $PM_{2.5}$ and PM_1 started within the framework of the WeBIOPATR project (2006–2009). The database of PAH aerosol composition in ambient air in Serbia is still very limited.

2. Material and methods

The study was conducted at three sampling sites within the local monitoring network in Belgrade Metropolitan region (Fig. 1). Belgrade is one of the largest cities of Southeastern Europe (Statistical Office of Republic of Serbia, 2012). The city of Belgrade has an area of 3.222 km^2, of which 276.6 km^2 covering the river and riparian land. According to the 2011 census, 1.659.440 inhabitants live in Belgrade region. Population density is more than 500 inhabitants/km^2

The position and type of sampling sites are given in Table 1. The detail description of sampling sites and methods are presented in the Supplementary Material section.

3. Results and discusion

3.1. Level of PM_{10} and PAHs associated with PM_{10}

The average concentration of PM_{10}, maximum, minimum and standard deviation are shown in Table 2. The highest PM_{10} average values during winter time were measured at SLA site (88.46 ± 60.11 μg/m^3) than at LAZ (80.31 ± 55.68 μg/m^3) and finally at GRA (62.38 ± 44.34 μg/m^3). During summer the average concentration of PM_{10} was the highest at SLA (44.37 ± 17.75 μg/m^3) and the lowest at GRA (26.16 ± 15.87 μg/m^3). At GRA and LAZ, 1/3 of samples exceeded the daily limit value of 50 μg/m^3 (2008/50/EC, 2008); while at SLA the exceedance was found in more than half of the samples. The measured PM_{10} concentrations were between 2 and 3 times higher during winter (heating) seasons than in summer (non-heating) at all sampling sites.

According to data from European air quality database, AirBase the annual limit value for PM_{10} (40 μg/m^3) was exceeding most often in Poland, Italy, Slovakia, the Balkan region, Turkey and several other urban regions (EEA, 2012). The daily limit value was also exceeded in cities in these countries but also in cities in Latvia, Lithuania, Sweden, and in the United Kingdom (only in London) (EEA, 2012). Within different research studies performed in the last 15 years in European cities, the following PM_{10} concentrations for annual sampling period were identified in Thessaloniki 78–89 μg/m^3 (Voutsa et al., 2002), Athens 77 mg/m^3 (Chaloulakou et al., 2003) and 90 μg/m^3 (Valavanidis et al., 2006), Madrid 35–45 μg/m^3 (Artiñano et al., 2003), Sofia 29.7 μg/m^3, Praha 36.9 mg/m^3 (Farmer et al., 2003), Rome 10–48 μg/m^3 (Cattani et al., 2003), Birmingham 10–41.5 μg/m^3 (Harrison et al., 2003) and in A Coruña 12–21 μg/m^3 (Sanjurjo-Sánchez, 2011).

Annual concentrations of PM_{10} at sampling sites within Local and Municipal networks in Serbia in 2010 and 2011 were between 37 and 79 μg/m^3 (Table SM 1). This would be on a higher side as compared to other European cities. The annual mean PM_{10} concentrations in urban air in Belgrade for the previous period from 2004 to 2006 were within the range of some European cities (29.5–67.8 μg/m^3) with similar population density and significant traffic density (Joksic et al., 2010; Popović et al., 2007). In an earlier study conducted in Belgrade PM_{10} annual concentration of 77 μg/m^3 was reported (Rajsic et al., 2004).

List of names, abbreviations, mean and standard deviations of individual PAH's quantified in this study and total PAHs concentrations are shown in Table SM 2. The concentrations of total PAHs for all sampling site in seasonal variations is presented on Fig. 2. The total PAH concentrations for the cold season was the highest at LAZ 97.75 ± 8.08 ng/m^3 and the lowest at GRA 48.18 ± 4.0 ng/m^3. During the summer, total PAH values were lower for one magnitude order, the highest concentration was at GRA 6.81 ± 0.81 ng/m^3. No significant difference ($P < 0.05$) between sampling sites was observed for variance or for mean values of Acy, Ace, Flu, BghiP, in summer and Nap and Ant in winter campaign. Nap, Phe and BaA in summer and total PAH as well as Acy, Fly, Pyr, BaA, Chry, BbF, BkF, B[a]P Ind, DahA and BghiP, in winter were significantly different.

In one study in Spain, in Zaragoza city the mean total PAH concentration for the whole sampling period was 1.78 ± 1.86 ng/m^3-four times higher during the cold season (2.84 ± 2.09 ng/m^3) than the warm season (0.72 ± 0.60 ng/m^3) (Callen et al., 2012).

The lower PAH concentrations in summer were shown in many studies due to different photochemical decay and contribution of emission sources such as: combustion processes-coal, wood and biomass burning, oil and gas burning, vehicles engines, domestic combustion. (Ladji et al., 2009; Tobiszewski and Namieśnik, 2012; Agudelo-Castaned and Teixeira, 2014); for example in the city of Augsburg, Germany, the average total PAH concentration in winter was 11 ng m^{-3} (ranging from 0.78 to 36 ng m^{-3}) while in summer it was 1.34 ng m^{-3} (ranging from 0.27 to 3.66 ng m^{-3}) (Pietrogrand et al., 2011). The seasonal variation of PAH concentration is well known and it is due to the influence of meteorological conditions: high temperature, high photochemical degradation during summer but also reduced dissipation of pollutants and increased burning of wood and coal in domestic heating during the winter (Lammel et al., 2010, Yang et al., 2010; Lai et al., 2011 Agudelo-Castaned and Teixeira, 2014).

At urban traffic site SLA in Belgrade city center total PAH concentration was 52.89 ± 3.38 ng/m^3 in winter and 5.49 ± 0.36 ng/m^3 in summer. This is much higher than in some other study in European and world cities: in Flanders, Belgium 5.5 ng/m^3 (Brits et al.,