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Examining PAHs Presence in Novi Sad's Ambient Air: Sources and Assessment

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Abstract: Air pollution poses a significant global health risk, with severe consequences for respiratory and cardiovascular diseases, particularly among vulnerable populations facing heightened exposure. The respiratory system is particularly susceptible to pollutants, resulting in various adverse health effects. Ambient air monitoring for benzo(a)pyrene (B(a)P) was conducted at four sites in Novi Sad throughout 2020, representing diverse environmental conditions. Sampling and analytical methods adhered to standardized protocols. B(a)P concentrations exceeded prescribed limits at most sites, with combustion processes and traffic emissions identified as primary pollution sources. Principal component analysis highlighted the dominance of combustion-related pollution, particularly during winter. Hierarchical cluster analysis revealed distinct pollution patterns across sites, with areas less burdened by traffic and combustion showing lower B(a)P levels. The study underscores the urgent need to mitigate local pollution sources, especially combustion and traffic emissions, to safeguard public health. The findings provide crucial baseline data for future monitoring efforts and highlight the importance of addressing air pollution for sustainable development and climate change mitigation.

Keywords: PAHs, benzo(a)pyrene; air pollution; sources identifications, assessment

1. Introduction

Air pollution is recognized as a significant global health risk, with severe consequences for respiratory and cardiovascular diseases, particularly among vulnerable populations facing heightened exposure [1,2]. The respiratory system is particularly susceptible to pollutants, leading to various adverse health effects [3,4]. According to the World Health Organization (WHO), nearly seven million deaths are attributed to air pollution each year, with 99% of the world's population breathing air that exceeds WHO guideline limits [1]. Vulnerable populations, including children, the elderly, and individuals with pre-existing health conditions, are particularly susceptible to the adverse effects of air pollution [5]. The respiratory system serves as the primary entry point for airborne pollutants, leading to a range of health issues, including inflammation, oxidative stress, and decreased lung function [6,7]. Long-term exposure to polluted air is associated with the development of respiratory diseases such as asthma, chronic obstructive pulmonary disease (COPD), and lung cancer [8,9,10].

Polycyclic aromatic hydrocarbons (PAHs) are recognized as a group of persistent organic pollutants that are formed through the incomplete combustion of organic materials [11]. These contaminants are ubiquitous in urban environments and have been associated with significant adverse health effects, particularly concerning respiratory and cardiovascular diseases [12]. Among the PAHs, benzo(a)pyrene (BaP) is classified as a probable human carcinogen and is frequently monitored due to its toxicity and potential for bioaccumulation [13]. The presence of PAHs in the environment can arise from various sources, including vehicular emissions, industrial activities, and residential heating [14]. These pollutants can enter the air, water, and soil, subsequently accumulating in the environment and biota [12]. Understanding the distribution and behavior of PAHs in the environment is crucial for assessing their impact on human health and ecosystems.

Novi Sad, the second largest city in Serbia, is confronted with air quality challenges due to intense traffic, industrial activities, and residential heating [15,16]. The presence of PAHs in the ambient air of Novi Sad may have serious health implications for the local population. However, limited studies have been conducted to examine the presence and sources of PAHs in this city [17,18].

Numerous studies have been conducted globally to evaluate the presence of PAHs in different environmental media. For instance, a study in China reported that concentrations of BaP in urban air ranged from 0.3 to 15.7 ng/m³, with higher levels observed during winter months due to increased heating activities [19]. In Italy, research indicated that BaP concentrations in soil varied from 0.01 to 1.5 mg/kg, with elevated levels near industrial sites and roadways [20]. A study in Japan found that BaP concentrations in river sediments ranged from 0.01 to 1.2 mg/kg, with higher concentrations detected in urban areas [21].

The primary objective of this research is to assess the presence and concentrations of polycyclic aromatic hydrocarbons (PAHs), specifically benzo(a)pyrene (BaP), in the ambient air of Novi Sad. This study aims to identify the main sources of these pollutants and evaluate their potential health risks to the local population. By employing multivariate techniques, the research will provide insights into the potential sources and distribution of PAHs in environmental. Additionally, the study seeks to contribute to the understanding of the impact of PAHs on public health and inform strategies for effective air quality management and pollution mitigation in urban environments.

2. Materials and methods

2.1. Sampling sites

Twenty-four-hour measurements of benzo(a)pyrene (B(a)P) were conducted during 2020 at four sampling sites in Novi Sad, a highly industrialized and populated city in Serbia with approximately half a million inhabitants. The sampling points were selected to represent different environmental conditions, including monitoring sites classified by the 2008/50/EC Directive as urban and suburban, traffic and background stations (Figure 1) [22]. Air sampling for the determination of B(a)P concentrations was carried out at the following representative measuring points:

- MM11-Kać (MZ "Kać", Kralja Petra I, no. 2 and Elementary School "Đura Jakšić", Kralja Petra I, no. 9, Kać) ("suburban traffic")
- MM2-NS1 (JKP "Vodovod i kanalizacija", Jiričekova 2, Novi Sad) ("urban background")
- MM3-NS2 (Corner of Rumenačke and Bulevar Jaše Tomić, Novi Sad (PM10)) ("urban traffic")
- MM4-SK (Sremska Kamenica, SOS Children's Village "Dr. Milorad Pavlović", Sremska Kamenica 1-14, Novi Sad) ("suburban background")

The sampling was conducted over a one-year period in accordance with the standard SRPS EN 12341:2015 and processed by experts from the Center for Hygiene and Human Ecology of the Institute of Public Health of Vojvodina.

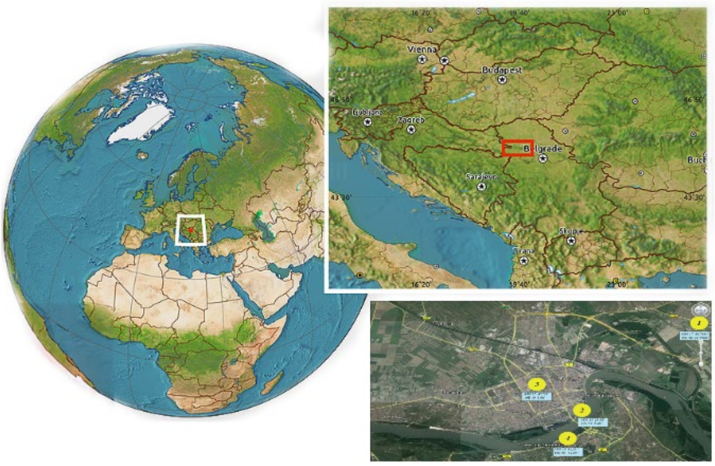

Figure 1. Measuring points for B(a)P sampling in the City of Novi Sad during 2020

2.2. Sampling and analytical methods

The concentration of benzo[a]pyrene (B[a]P) pollutants in the air was determined using a variety of air sampling equipment, including the Sven Leckel LVS3 and SEQ 47/50-RV models, provided by Comde-

Derenda GmbH. The methodology adhered to the standards outlined in SRPS EN 12341:2015, Section 5.1, for air pollutant concentration determination, while SRPS EN 15549:2010 was utilized for specific concentration measurements of B[a]P. A gas chromatograph coupled with a mass spectrometer (GC/MS) served as the analytical instrument for quantifying these pollutants. This method ensured precise detection and quantification of B[a]P in atmospheric samples, offering reliable data for subsequent analyses.

2.3. Data Analyses

Data concerning B[a]P concentrations, collected from four monitoring sites over a one-year period, were subjected to basic statistical analysis. Descriptive statistics, including mean, median, standard deviation, standard error of the mean, and range (minimum and maximum values), were calculated to summarize the data set. The standard deviation provided insight into data variability, while the standard error indicated the reliability of the sample mean. For values falling below the detection limit, a surrogate value equal to half of this limit was assigned.

Advanced statistical analyses were conducted to discern patterns among the sampling sites and to infer possible emission sources. Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were employed on the monthly average B[a]P data, utilizing Varimax rotation and Kaiser normalization to enhance interpretability. These analyses were performed using IBM SPSS Statistics 25 software. The application of PCA and HCA facilitated the visualization of data, revealing clusters of sites with similar pollution characteristics, which may indicate shared emission sources. The methodologies and results presented in this study provide a robust framework for identifying priority areas requiring further investigation, thereby informing effective decision-making and guiding remedial actions.

3. Results and discussion

During 2020, at the monitoring locations in the City of Novi (MM1-Kać, MM2-NS1, MM3-NS2, and MM4-SK), the average daily concentration of benzo(a)pyrene (B[a]P) in suspended PM10 particles was determined. The values ranged from 0.22 ng/m³ at site MM4 to 19.52 ng/m³ at site MM1. Monthly concentrations of B[a]P, depicted in Figure 1, varied from 0.49 ng/m³ at site MM4 to 7.993 ng/m³ at site MM1.

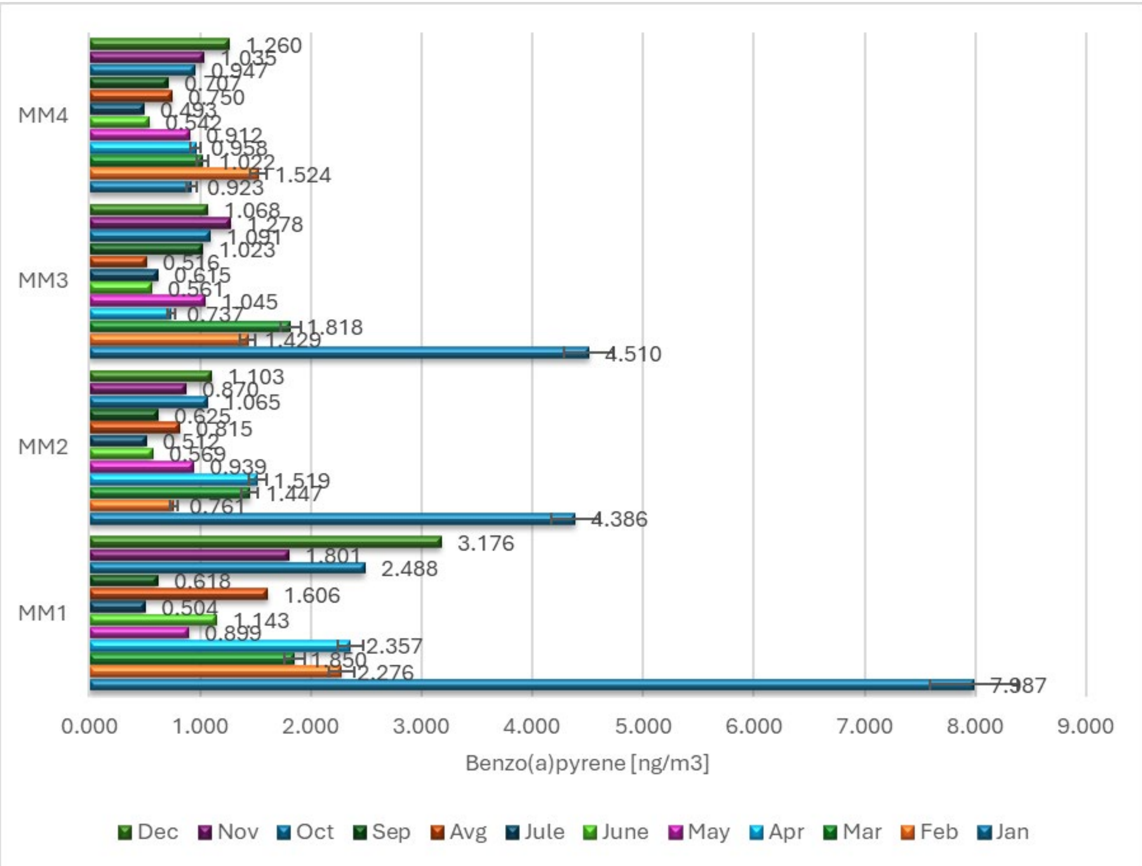

Figure 2. B(a)P air concentrations during 2020 in Novi Sad

The average monthly concentrations for MM1, MM2, and MM3 were found to be 2.23 ng/m³, 1.22 ng/m³, and 1.31 ng/m³, respectively. These values exceed the target annual level of 1 ng/m³ for total polycyclic aromatic hydrocarbons in the air, as stipulated by the relevant standards. At these measuring sites over the one-year period, the minimum daily concentration of polycyclic aromatic hydrocarbons, expressed as B[a]P on a monthly level, was below the detection limit of the analytical method employed (<0.5 ng/m³), while the maximum values recorded were 7.99 ng/m³, 4.39 ng/m³, and 4.51 ng/m³, respectively. The site MM4-SK was the only location where the prescribed average B[a]P concentration in the air (mean = 0.92 ng/m³) was not exceeded.

3.1. Identification of pollution sources

Principal Component Analysis (PCA) with Varimax rotation was employed to determine the quantitative contribution of various benzo(a)pyrene (BaP) sources, yielding highly robust results. Three principal components, accounting for 99.56% of the total variance, are depicted in Figure 3. The first principal component (PC1) explained approximately 40.85% of the variance, with significant loadings observed at site MM3, indicating contributions from **combustion processes**. The second principal component (PC2) accounted for about 38.64% of the variance, with high loadings at site MM1, suggesting **traffic emissions** resulting from the combustion of diesel and gasoline in motor vehicles. The third principal component (PC3) explained approximately 20.07% of the variance, with substantial loadings at site MM2, pointing to sources related to **industrial activities**. Site MM4 exhibited moderate loadings across all factors.

Given that Novi Sad, an urban region with substantial traffic and combustion processes, was included in the study, it can be confirmed that polycyclic aromatic hydrocarbons (PAHs) are produced from both pyrolytic and pyrolysis emission processes. The dominance of pollution sources is evident, particularly within the expected city zones. The presence of BaP, one of the most toxic PAHs, is pervasive throughout Novi Sad, which is concerning due to its carcinogenic, mutagenic, and teratogenic effects on the human population [23].

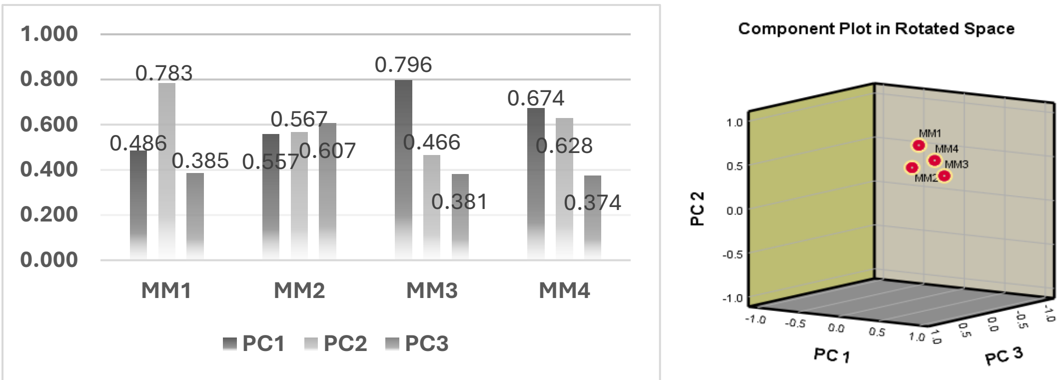

Figure 3. Principal component analysis after Varimax rotation for B(a)P

From a scientific standpoint, the results of the PCA highlight the complexity of BaP pollution in urban environments like Novi Sad. The identification of distinct sources of BaP, such as traffic emissions and biomass burning, underscores the need for targeted mitigation strategies. Traffic-related emissions are a significant contributor, suggesting that improvements in vehicle emissions standards and the promotion of public transportation could reduce BaP levels. Furthermore, the contribution from biomass burning suggests a need to address residential heating practices and promote cleaner alternatives. The findings highlight the critical importance of continuous monitoring and source apportionment studies to guide effective policy measures.

3.2. Identification of hot-spot

The results of the cluster analysis are graphically represented as a dendrogram, illustrating the grouping of sampling sites (Figure 4). The analysis identified two distinct clusters: the first cluster comprises sampling sites MM1, MM2, and MM3, while the second cluster consists solely of the MM4 site, distinguished by reduced concentrations of benzo(a)pyrene (BaP). The first group of locations is characterized by a significant presence of BaP in the ambient air, predominantly during the winter months, when combustion processes are most intense. This includes emissions from individual heating systems at MM1 and substantial contributions from the "NIS Gazprom Neft" Oil Refinery, its production facilities, oil and gas processing, transportation of oil derivatives, and a nearby cogeneration system affecting MM2 and MM3. These factors collectively result in heightened BaP concentrations at these sites.

Conversely, MM4, located in Sremski Karlovci, is identified as less impacted by BaP emissions. This locality benefits from reduced traffic compared to the city center sites (MM2 and MM3) and fewer individual heating sources compared to MM1, making it a comparatively safer and less polluted area concerning BaP emissions. The findings of this cluster analysis provide valuable insights into the spatial distribution of air pollution sources and highlight the potential health risks associated with BaP exposure in urban environments.

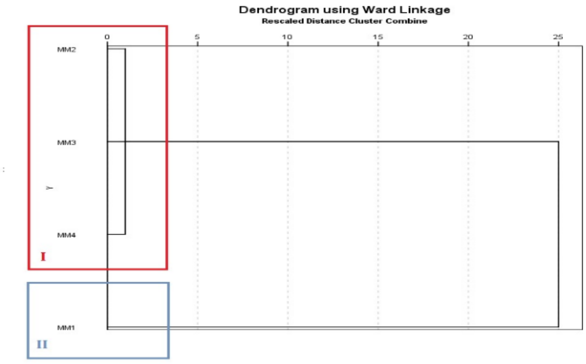

Figure 4. Dendrogram of monthly B(a)P air concentrations

Correlation relations between benzo(a)pyrene (BaP) concentrations at selected monitoring sites in Novi Sad were assessed using Pearson's correlation analysis.

Table 1: Pearson correlation coefficients for benzo(a)pyrene concentrations at selected monitoring sites in Novi Sad

Pearson Correlation				
	MM1	MM2	MM3	MM4
MM1	1	.948**	.901**	.957**
MM2	.948**	1	.938**	.959**
MM3	.901**	.938**	1	.964**
MM4	.957**	.959**	.964**	1

**. Correlation is significant at the 0.01 level (2-tailed).

The results revealed extremely high mutual correlations, indicating a strong connection in the distribution of BaP across the urban area. Such correlations suggest that the emission sources of BaP are likely similar or that the atmospheric conditions affecting its dispersion are consistent. For instance, elevated BaP levels are frequently associated with common sources such as traffic emissions and industrial activities (Ravindra et al., 2008). When correlation coefficients exceeding 0.90 are recorded, it implies that these locations may experience comparable pollution levels due to shared emission sources or similar meteorological conditions. Identifying these high correlations can help in targeting specific areas for interventions to reduce BaP exposure, thereby informing regulatory measures aimed at improving air quality and protecting public health.

4. Conclusion

This study provides a comprehensive assessment of the presence and sources of polycyclic aromatic hydrocarbons (PAHs), specifically benzo(a)pyrene (BaP), in the ambient air of Novi Sad. Through the application of advanced analytical techniques and statistical analyses, including Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), the study identifies key emission sources contributing to air pollution in the region. The PCA revealed that combustion processes, traffic emissions, and industrial activities are the primary contributors to BaP concentrations, with site-specific variations observed. The cluster analysis delineated two distinct groups of sampling sites, highlighting the spatial distribution of pollution sources. The urban locations, particularly MM1, MM2, and MM3, exhibited elevated BaP levels, primarily due to industrial activities, vehicular emissions, and increased heating during winter. In contrast, the MM4 site in Sremski

Karlovci demonstrated lower BaP concentrations, underscoring the influence of reduced anthropogenic activities.

These findings emphasize the significant impact of urbanization and industrialization on air quality and the associated health risks posed by PAHs. The study underscores the need for targeted regulatory measures and pollution control strategies to mitigate BaP emissions and improve air quality in Novi Sad. Continuous monitoring and comprehensive assessment of PAH sources are crucial for informed decision-making and effective environmental management in urban areas.

Acknowledgements

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