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Exploring the patterns of particle-bound PAHs in ambient air of an urban agglomeration (first results)

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Abstract

This study examines the occurrence of polycyclic aromatic hydrocarbons (PAHs) in PM_{10} atmospheric particles in an urban environment, Ioannina, Greece (population: ~114.000). A one-year sampling campaign, spanning from March 2022 to April 2023, was conducted. Fifty-seven 24-hour samples representing both warm and cold periods were collected and sixteen PAHs, including those regulated by the revised Ambient Air Quality Directive (EU) 2024/2881, were quantified. The winter-to-summer PAH concentration ratio was calculated, and correlation analysis was conducted with PM_{10}-bound PAHs and other pollutants to identify potential common sources. Molecular diagnostic ratios of PAH isomers were employed to assess the impact of well-characterized emission sources such as vehicular traffic and biomass burning. Compounds within each ratio share identical molar masses, suggesting similar environmental behavior and fate. Low-temperature processes, such as wood burning, produce low molecular weight PAHs, while high-temperature processes, like fuel combustion in vehicles, release higher molecular weight PAHs. Meteorological parameters, including temperature, relative humidity, atmospheric pressure, precipitation and wind velocity, were also considered. The first results of the sampling campaign are presented aiming to offer insights into air quality in non-industrialized urban areas affected by PM pollution episodes during cold, steady and calm atmospheric conditions.

Keywords: PM_{10}-bound PAHs; seasonal variation; molecular diagnostic ratios; meteorology

1. Introduction

The presence of polycyclic aromatic hydrocarbons (PAHs) in ambient air, both in gas and particle phases, has emerged as a critical environmental concern in urban areas. PAHs, a group of complex organic compounds with well-documented carcinogenic properties, are primarily emitted through incomplete combustion processes such as vehicular emissions, industrial activities and residential heating. While a portion of these compounds exists in the gas phase, a significant fraction is adsorbed onto fine particulate matter, which, when inhaled, poses serious health risks to urban populations (Terzi and Samara, 2004). This study focuses on the occurrence, sources and seasonal variability of particulate-bound PAHs in urban air.

2. Methodology

2.1. Sampling

PM_{10} 24-h samples were collected at an urban background site in Ioannina; the administrative capital of the Epirus Region in northwestern Greece, with an approximate population of 114,000. The city is situated on a mountainous plateau at an elevation of 480 m above sea level. It lies adjacent to the western shoreline of Lake Pamvotis, which has a mean surface area of 19.9 km². The local topography (Fig. 1) exerts a significant influence on atmospheric dynamics and microclimatic conditions, contributing to the development of persistent temperature inversions and limited dispersion of atmospheric pollutants (Koletsis et al., 2009). The city's economic profile is dominated by the tertiary sector, encompassing retail trade, tourism, financial services, healthcare and education. The principal anthropogenic sources of atmospheric pollution are residential heating and road traffic. Industrial emissions are minimal. The region experiences a continental Mediterranean climate. A one - year sampling campaign was conducted from March 2022 to April 2023. The samples of PM_{10} were collected by filtration on PTFE membrane filters (teflo,

Figure 1. Study area and receptor site.

Pall) using a low volume (2.3 m^3/h) air sampler (Derenda LVS). The sampling height was approximately 14 m above ground. Overall, 57 samples were analyzed.

2.2. Analytical techniques

PM_{10} concentrations were determined using the gravimetric method. The average concentration of the selected PM_{10} samples was 46.43 ± 27.09 μg/m³ during the cold period and 15.39 ± 5.39 μg/m³ during the warm period. The PTFE membrane filters were subsequently analyzed for polycyclic aromatic hydrocarbons (PAHs). A two-stage extraction was performed: first, refluxing with 5 mL hexane for 30 minutes with EPA8270 internal standard (2 ng/μL), followed by ultrasonic extraction using 5 mL of hexane-acetone (1:1) for 15 minutes. Extracts were combined, concentrated to 0.1 mL under nitrogen, and analyzed by GC-MSD (Agilent 6890N/5973N) in SIM mode.

3. Results and discussion

In general, higher concentrations of the PAHs analyzed were observed during winter compared to summer (Table 1) primarily due to elevated emissions from the combustion of fossil fuels and biomass for residential heating, in combination with meteorological conditions unfavorable to pollutant dispersion.

Table 1. Concentration profile of PAH – first results of chemical analysis (mean ± SD). (n= number of samples)

PAHs	Molar mass (g/mol)	No of Rings	MIN (ng/m^3)	MAX (ng/m^3)	Nov-Dec-Jan Mean (ng/m^3) (n=20)	May-July-Aug-Sept Mean (ng/m^3) (n=16)
Naphthalene	128	2	0	4.2	0.72 ± 1.34	0.88 ± 1.14
Acenaphthylene	152	3	0	24.68	3.33 ± 6.77	5.28 ± 6.83
Acenapthene	153	3	0.32	1.12	0.46 ± 0.17	0.40 ± 0.06
Fluorene	166	3	0.00	4.00	0.27 ± 0.92	0.01 ± 0.02
Phenanthrene	178	3	0.00	1.80	0.59 ± 0.62	0.15 ± 0.17
Anthracene	178	3	0.00	1.82	0.60 ± 0.64	0.15 ± 0.18
Fluoranthene (FL)	202	4	0.00	24.97	7.85 ± 8.19	0.02 ± 0.03
Pyrene (PYR)	202	4	0.00	6.83	1.96 ± 2.12	0.06 ± 0.09
Benzo[a]anthracene (BaA)	228	4	0.00	5.86	2.02 ± 1.55	0.00 ± 0.02
Chrysene (Chr)	228	4	0.00	20.98	5.81 ± 5.97	0.01 ± 0.04
Benzo[b]fluoranthene	252	5	0.00	9.68	3.21 ± 2.38	1.19 ± 2.79
Benzo[k]fluoranthene	252	5	0.00	9.55	2.98 ± 5.45	1.12 ± 2.76
Benzo[a]pyrene	252	5	0.00	7.89	2.24 ± 1.65	0.77 ± 2.16
Indeno[c,d]pyrene (IP)	276	6	0.00	3.08	0.42 ± 0.69	0.00
Dibenzo[a,h]anthacene	278	5	0.00	1.36	0.13 ± 0.12	0.25 ± 0.37
Benzo[g,h,i]perylene (BghiP)	276	6	0.00	2.92	0.44 ± 0.65	0.01 ± 0.09
				Mean Σ_{16}PAHs	33.03 ± 2.20	10.29 ± 1.30

This trend aligns with previous findings in the city (Tsiodra et al, 2024). The cold-to-warm period ratio for mean Σ_{16}PAHs was 3.21. Fluoranthene, acenaphthylene, and chrysene were the most abundant PAHs. Benzo[a]pyrene exceeded the EU 2024/2881 annual target of 1 ng/m³, with a mean concentration of 1.59 ng/m³. In winter, the ratio Σ_{LMW} PAHs/Σ_{HMW}>1 indicates pyrogenic sources and moreover, the diagnostic ratios IP/IP+BghiP, FL/FL+RYR and BaA/BaA+Chr indicate biomass, wood burning and oil combustion. In warm period, the PAHs ratio $\Sigma_{LMW}/\Sigma_{HMW}$<1 and the above-mentioned diagnostic ratios suggest petrogenic origin (Tobiszewski and Namieśnik, 2012).

4. Conclusions

A one year sampling campaign was conducted at a receptor site in Ioannina, NW Greece. The first results of the chemical analysis of PM_{10} particles unveiled the concentration profile of PAHs and indicate that in winter the dominant source is residential heating, while in summer the main sources are petrogenic.

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