СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 85, кн. 1, 2024, с. 93–99

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 85, part 1, 2024, p. 93–99

Mini-review on PAHs in airborne particulate matter: characteristics, sources, and current analytical methods

Anife Veli[1], Zilya Mustafa[1], Stela Naydenova[2], Lenia Gonsalvesh[3]

[1] Central Scientific Research Laboratory, Assen Zlatarov University, 8010 Bourgas, Bulgaria; E-mail: anife_veli@abv.bg, zmustafa@abv.bg
[2] Faculty of Natural Sciences, Department of Ecology and Environment Protection, Assen Zlatarov University, 8010 Bourgas, Bulgaria; E-mail: steltion@gmail.com
[3] Faculty of Natural Sciences, Department of Chemistry, Assen Zlatarov University, 8010 Bourgas, Bulgaria; E-mail: lenia_gonsalvesh@abv.bg

Мини-обзор върху полициклични ароматни въглеводороди в атмосферен аерозол: характеристики, източници и методи за анализ

Анифе Вели[1], Зиля Мустафа[1], Стела Найденова[2], Ления Гонсалвеш[3]

[1] Централна научно-изследователска лаборатория, Университет „Проф.д-р Асен Златаров“, 8010 Бургас, България; E-mail: anife_veli@abv.bg, zmustafa@abv.bg
[2] Факултет по природни науки, Катедра „Екология и опазване на околната среда“, Университет „Проф.д-р Асен Златаров“, 8010 Бургас, България; E-mail: steltion@gmail.com
[3] Факултет по природни науки, Катедра „Химия“, Университет „Проф.д-р Асен Златаров“, 8010 Бургас, България; E-mail: lenia_gonsalvesh@abv.bg

Резюме. Изследването на качеството на въздуха е от изключително значение, свързано с човешкото здраве и качеството на живот на населението. Един от основните индикатори е концентрацията на фини прахови частици (ФПЧ) и по-специално, техния състав и размери. Едни от най-опасните съединения, асоциирани с ФПЧ, са полицикличните ароматни въглеводороди (ПАВ) поради тяхната канцерогенност и мутагенност, като приоритетно се анализира и нормира бензо(а)пирена. Стотиците ПАВ се разделят на три групи – ниско, средно и високомолекулни, като относителното им присъствие в газова и твърда фаза се определя от техните свойства и условията на околната среда. Източниците на емисии са главно свързани с нискотемпературни процеси от естествен и антропогенен произход. Анализът на ПАВ и в двете фази е предизвикателство пред научните изследователи, основно поради ниските им концентрации. Усилията са насочени към разработването на методи, които да са точни, с висока разделителна способност, и едновременно с това да не изискват много време и усилия за пробонабиране, пробоподготовка, анализ и интерпретиране на резултатите. Използването на разнообразни филтри и техники за пробонабиране на ФПЧ от въздуха, както и на различни аналитични методи за идентифициране на съдържащите се в тях ПАВ, са свързани с оптимизиране на цялостния процес на анализ и получаване на максимално достоверни резултати, които не само показват и обобщават информацията за качеството на атмосферния въздух в световен мащаб, но и позволяват да се идентифицират източниците на замърсяване и здравния риск за населението. Последното ще позволи да се вземат адекватни управленчески решения, свързани с подобряване качество на въздуха и околната среда.

Ключови думи: качество на въздуха, фини прахови частици (ФПЧ), полициклични ароматни въглеводороди (ПАВ).

Abstract. The study of air quality is of extreme importance for human health and quality of life, especially in large cities. One of the main indicators is the concentration of particulate matter (PM), namely, its composition and size. Polycyclic aromatic hydrocarbons (PAHs) are among the most dangerous compounds associated with PM because of their carcinogenicity and mutagenicity, with benzo(a) pyrene being analyzed and standardized as a priority pollutant. Hundreds of PAHs are divided into three groups: low, medium, and high molecular weight, and their relative presence in the gas and solid phases is determined by their properties and environmental conditions. PAHs emission sources are mainly related to low-temperature processes of natural and anthropogenic origin. The analysis of PAHs in both phases is a challenge for scientific researchers, mainly due to their low concentrations. The attempts are focused on development of methods that are both accurate and with high-resolution, and at the same time do not require long time and efforts for sample collection, preparation, analysis and data interpretation. The use of various filters, sampling techniques and analytical methods for identifying the PAHs therein, are mainly aimed on optimizing the overall analysis process and obtaining the most reliable results. Data for PAHs not only give information about the quality of atmospheric air on a global scale, but also allow identifying the sources of pollution and appreciate the health risk for the population. The latter allows to take management decisions how to improve the air quality and the environment.

Keywords: air quality, particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs).

https://bgd.bg/review-bgs
https://doi.org/10.52215/rev.bgs.2024.85.1.93

Introduction

Air pollution is the single largest environmental cause of various diseases and is reaching concerning levels. Air quality in large cities is deteriorating due to increased traffic emissions, urban sprawl, and population growth (Dos Santos et al., 2020). In recent years, the concentration of atmospheric aerosols, commonly called particulate matter (PM), are a matter of an increased interest and concern, because of their significant negative impacts on human health and environment (Harrison, 2020). Number of studies reveal that exposure to PM leads to increased cases of lung cancer and mortality under the problems of cardiovascular system (Abou Chakra et al., 2007; Kelly and Fussell, 2012; Harrison, 2020; Thangavel et al., 2022). Adverse health effects of PM are dependent on their size, with the smaller particles having severer health impact related to their deeper access to the human respiratory system and further penetration into blood system (Schraufnagel, 2020; Thangavel et al., 2022). PM are generally classified by their aerodynamic diameter size as “coarse” particles (aerodynamic diameter < 10 µm, PM_{10}), “fine” particles (aerodynamic diameter < 2.5 µm, $PM_{2.5}$), and “ultrafine” particles (aerodynamic diameter <100 nm or 0.1 µm, $PM_{0.1}$) (Dijkhoff et al., 2020; Veli et al., 2024). However, the negative effects of PM are related not only to their size, but also to surface properties, chemical composition, and multi-species interactions (Schraufnagel, 2020). PM consists of variety of components such as inorganic salts (ammonium sulfate, ammonium nitrate, sodium chloride, etc.), iron compounds, traces of metals and minerals, elemental and organic carbon as combustion products (Pan et al., 2022). In addition, various organic compounds have also been identified. Aldehydes, ketones, benzene, dioxins, furans, PAHs are recognized as highly harmful organic compounds present in PM (Santos et al., 2016).

PAHs Setting

PAHs are hydrophobic, lipophilic, toxic and persistent organic pollutants, by-products of incomplete combustion or pyrolysis of organic materials and fossil fuels. These compounds are ubiquitously spread in the environment and often bounded to atmospheric PM. Due to their expressed toxic, carcinogenic and mutagenic properties several world notable public health protecting organizations classify them as priority pollutants (Safo-Adu et al., 2023). Several hundred PAHs have been identified worldwide, and according to their toxicological profile the United States Environmental Protection Agency (US EPA) has classified 16 PAH species in a priority control pollutant list (Yang et al., 2021) (Fig. 1). In this regard, the European Directive (Directive 2008/50/EC 2008) defines benzo(a)pyrene as a marker for the carcinogenic risk of PAHs in atmospheric air with an annual average maximum permissible concentration of 1 $ng.m^{-3}$.

In terms of chemical structure, PAHs with 2 and 3 aromatic rings, i.e. Naphthalene (Naph), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant) and molecular weight (MW) <200 $g.mol^{-1}$, are classified as low molecular weight (LMW). PAHs with 4 aromatic rings, i.e. Fluoranthene (Fla), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), and MW ≤200 or MW <250 $g.mol^{-1}$, are classified as medium molecular weight (MMW). PAHs with 5 or more aromatic rings, i.e. Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IndP), Benzo[g,h,i]perylene (BghiP), Dibenz[a,h]anthracene (DahA), MW ≥ 250 $g.mol^{-1}$, are classified as high molecular weight (HMW) (Famiyeh et al., 2021) (Fig. 1).

LMW PAHs are characterised with a relatively high vapour pressure and mainly occur in the gaseous phase, while HMW PAHs exhibit much lower vapour pressure than that of LMW PAHs, and they are mainly bound to particle phase (Yang et al., 2021). As for the MMW PAHs, with vapour pressure between LMW and HMW PAHs, they may exist in both, the gaseous and particle phases. Phase partitioning of PAHs mainly depends on: i) properties of the individual PAHs (MW, vapor pressure, concentration); ii) ambient temperature, solar surface irradiance, relative humidity; iii) and, type of PM present in the atmosphere (Munyeza et al., 2019; Pandey et al., 2011).

Sources of PAHs

PAHs are released into the environment through anthropogenic and natural sources, with the former being the most significant (Famiyeh et al., 2021). Anthropogenic sources are related to: i) the communal household sector including emissions from burning

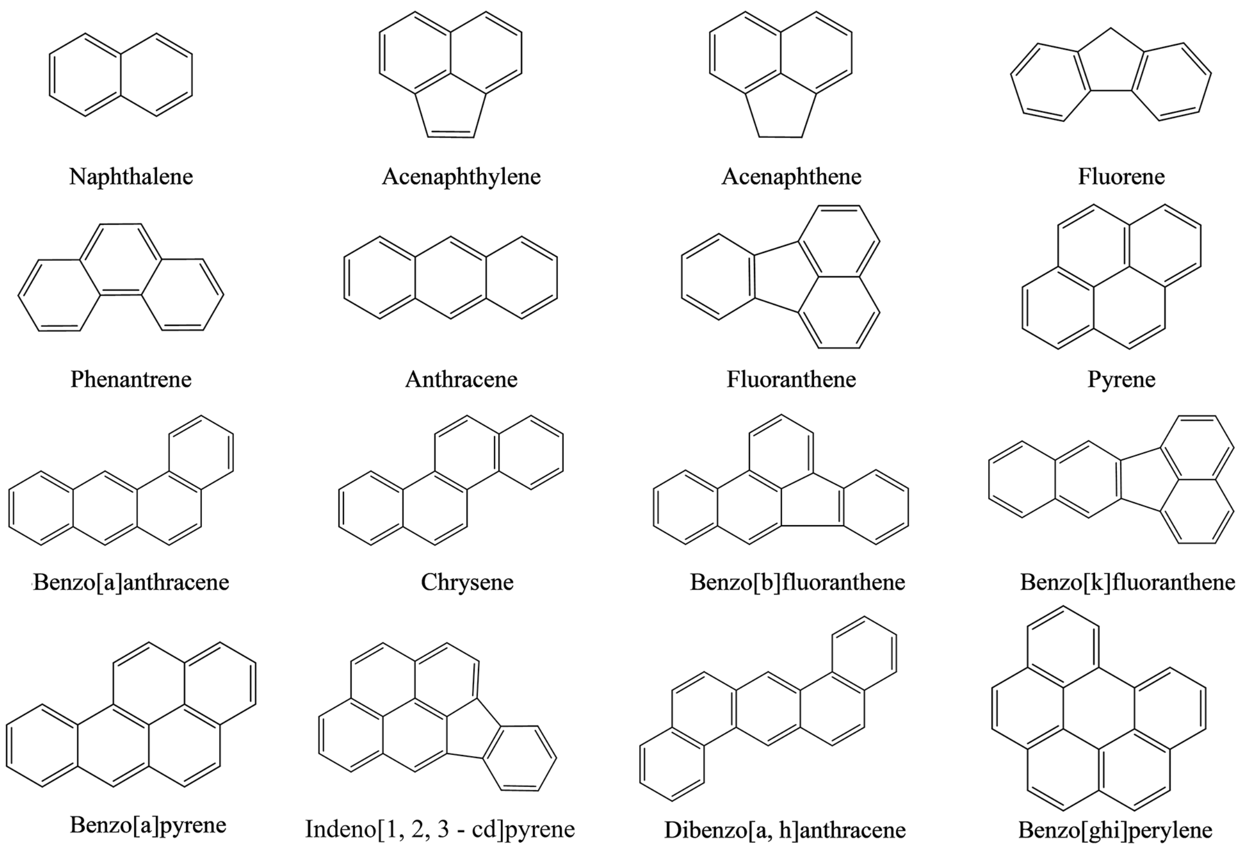

Fig. 1. Structures of 16 PAHs classified by U.S. EPA as priority pollutants

Фиг. 1. Структури на 16 полициклични ароматни въглеводороди, класифицирани от Американската агенция за опазване на околната среда като приоритетни замърсители.

of wood, coal, oil, gas, dried animal manure, waste from agricultural crops or other organic substances (Famiyeh et al., 2021; Zhang et al., 2023); ii) the transport sector – including vehicle emissions as PAH emission from this type of sources is a function of engine type, vehicle power and age, fuel type and quality, lubricating oil burning (Safo-Adu et al., 2023); iii) the industrial sector – the most important industrial sources of PAHs include primary aluminum industry, coke production, incineration of industrial waste, cement production, petrochemical industry and related industries, bitumen and asphalt industry, tire production, electricity production and others (Patel et al., 2020; Safo-Adu et al., 2023); iv) the agricultural sector – related to the burning of biomass, a widely used approach for the disposal of plant and forest waste (Pham et al., 2019; Fakinle et al., 2022). PAHs emissions from natural sources are negligible and are mainly from volcanic eruption, forest fires, diagenesis, and hydrothermal processes (Famiyeh et al., 2021; Safo-Adu et al., 2023). It is important to note that the incomplete combustion of organic material, whether naturally or anthropogenically derived, has been identified as the single largest contributor of PAHs pollution in the environment (Abdel-Shafy and Mansour, 2016).

PAHs analysis - materials and methods

During the last 30 years, a significant number of studies were focused on the development of analytical methods for the qualitative and quantitative determination of PAHs present in both the gaseous and particulate phases of ambient air (Pateraki et al. 2019; Patel et al., 2020; Famiyeh et al. 2021; Galmiche et al. 2021). However, due to the complex matrix and the relatively low atmospheric concentrations of PAHs, their evaluation is still challenging and quite difficult. The main stages in their analysis are related to the sampling of atmospheric air and their storage, the need for extraction procedures, cleaning and sample concentration, as well as the necessity for an efficient technique of separation and selective/sensitive detection (Lawal, 2017).

According to EN 12341:2023 the most commonly used sampling media for PM associated PAHs includes quartz-fiber filters (QFFs), glass fiber filters (GFFs), Teflon coated glass fiber and Teflon membrane filters (Munyeza et al., 2019). The sampling media should be characterized with high adsorption efficiency, chemical stability, easy extractability of compounds of interest and low cost. Various extraction approaches (Soxhlet extraction, mechanical agitation, accelerated solvent extraction, microwave assisted extraction, supercritical fluid extraction, ultrasound assisted extraction, pressurized liquid extraction, solid-phase micro-extraction, QuEChERS), are applied to recover PAHs from the solid phase (Baek et al., 1991; Wang et al., 2017; Gao et al., 2018; Cao et al., 2019; Mueller et al., 2019; Du et al., 2018; Famiyeh et al., 2021). However, the choice of extraction procedure depends on the analytes of interest and should be balanced among high extraction efficiency, high sample throughput, less labor intensity, high cost-effectiveness, and environmentally friendliness (Famiyeh et al., 2021).

Quantitative determination of PAHs in airborne PM requires instrumental techniques with high sensitivity. Extensively used analytical techniques in this regard include high-performance liquid chromatography (HPLC) and gas chromatography (GC) coupled with suitable detection techniques. (Famiyeh et al., 2021; Soursou et al., 2023). HPLC in generally coupled to ultraviolet (UV), fluorescence (FL), diode array (DAD), and chemiluminescence (CD) detectors (Lawal, 2017; Moret et al., 2019; Bogdanović et al., 2019; Serenjeh et al., 2020). PAHs possess very characteristic UV absorbance spectra which is especially useful in their identification and quantitation (Abdel-Shafy et al., 2015). However, FL detectors are more sensitive than UV for PAHs analysis, but unfortunately some PAHs do not exhibit fluorescence (Poster et al., 2006; Famiyeh et al., 2021; Vistnes et al., 2022). Therefore, HPLC is connected simultaneously to UV and FL or DAD and FL detectors for particulate phase PAHs determination (Mo et al., 2019; Vistnes et al., 2022). Liquid chromatography with negative atmospheric pressure chemical ionization tandem mass spectrometry has also been described in analysis of PAHs in environmental samples (Wang et al., 2021). Nevertheless, GC technique is considered the most preferred over the HPLC for separation, identification, and quantification of nonpolar PAHs since it provides greater selectivity, resolution, and sensitivity compared to that achieved with HPLC (Poster et al., 2006; Famiyeh et al., 2021; Soursou et al., 2023). GC system is generally combined with mass spectrometer (MS) (Wang et al., 2019; Dos Santos et al., 2020) and flame-ionization detector (FID) (Hassan and Khoder, 2012; Safo-Adu et al. 2014). However, GC/MS is more accurate for determination of PAH than GC-FID because the MS detector offers high selectivity, minimizing the interferences of co-eluted compounds and environmental contaminants (Famiyeh et al., 2021; Veli et al., 2024). GC/MS can be utilized in two modes of operation, i.e. Total Ion Current (TIC) and Selected Ion Monitoring (SIM). Although TIC mode provides additional structural information which makes the identification of the individual PAHs easy, for the detection of ultra-trace levels of PAHs, SIM mode is preferred. The latter has advantages over TIC mode, since it provides more selective and sensitive results, as it reduces matrix effects and interference, and thus greatly simplifies the extracts cleaning step. However, in complex matrix systems, such as PM, high amount of interferences may exist, expressed as co-eluting peaks and high background noise levels at elevated GC temperatures as demonstrated by Veli et al. (2024). These challenges can be overcome via utilization of tandem mass spectrometry system (GC MS/MS) which provides additional fragmentation of the analytes ions generating "unique" ions, characteristic only for the analyte, but not for the matrix. As a result, background noise is significantly reduced and signal-to-noise ratios improved (Veli et al., 2024). Developments in the injection systems have allowed application of thermal desorption (TD), which is related to the increasing application of head space extraction techniques (Soursou et al., 2023). TD GC MS/MS is a solvent-free technique and avoids time-consuming sample preparation steps and losses related to the extraction step, and allows automation (Chu et al., 2021; Humbert et al., 2022). The use of different ionization methods, such as electron capture negative ionization, atmospheric pressure laser ionization and negative chemical ionization for selective analysis of some oxy-and nitro-PAHs have also been reported (Stader et al., 2013; Li et al., 2018; Yadav et al., 2018). Different mass analyzers in combination with GC have also been applied in PAHs analysis (Dos Santos et al., 2020; Sourso et al., 2023).

Conclusions

Over the last years different analytical procedures and instrumental techniques are developed which made far-reaching changes in the analytical determination of PAHs in environmental matrices, especially in the case of the airborne PM. This in turn induced worldwide extensive studies on the topic and contributed a lot to the accumulation of valuable information about pollution sources, their input to ambient air pollution levels, etc. Thereby the knowledge allows performing adequate pollution control, reflecting in environmental and human health protection. In the present mini-review on the composition of PAH in airborne particles the authors share their own experience in the field giving comments on the pitfalls and advantage of the experimental protocols applied.

Acknowledgements: The financial support of Bulgarian National Science Fund through contract No КП-06-Н 34/9 – 19.12.2019 is highly appreciated.

References

Abdel-Shafy, H. I., M. S. M. Mansour. 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. – *Egypt. J. Pet.*, *25*, 107–123; https://doi.org/10.1016/J.EJPE.2015.03.011.

Abou Chakra, O.R., M. Joyeux, E. Nerrière, M. P. Strub, D. Zmirou-Navier. 2007. Genotoxicity of organic extracts of urban airborne particulate matter: An assessment within a personal exposure study. – *Chemosphere*, *66*, 1375–1381; https://doi.org/10.1016/j.chemosphere.2006.06.066.

Baek, S.O., M.E. Goldstone, P.W.W. Kirk, J.N. Lester, R. Perry. 1991. Phase distribution and particle size dependency of polycyclic aromatic hydrocarbons in the urban atmosphere. – *Chemosphere*, *22*, 503–520; https://doi.org/https://doi.org/10.1016/0045-6535(91)90062-I.

Bogdanović, T., J. Pleadin, S. Petričević, E. Listeš, D. Sokolić, K. Marković. 2019. The occurrence of polycyclic aromatic hydrocarbons in fish and meat products of Croatia and dietary exposure. – *J. Food Compos. Anal.*, *75*, 49–60; https://doi.org/10.1016/J.JFCA.2018.09.017.

Cao, Z., M. Wang, Q. Chen, C. Zhu, J. Jie, X. Li. 2019. Spatial, seasonal and particle size dependent variations of PAH contamination in indoor dust and the corresponding human health risk. – *Sci. Total Environ.*, *653*, 423–430; https://doi.org/10.1016/j.scitotenv.2018.10.413.

Chu, X., T. Sasaki, A. Aono, Y. Kudo, K. Tanaka, Y. Fuse. 2021. Thermal desorption gas chromatography-mass spectrometric analysis of polycyclic aromatic hydrocarbons in atmospheric fine particulate matter. – *J. Chromatogr. A*, *1655*, 462494; https://doi.org/10.1016/J.CHROMA.2021.462494.

Dijkhoff, I. M., B. Drasler, B. B. Karakocak, A. Petri-Fink, G. Valacchi, M. Eeman. 2020. Impact of airborne particulate matter on skin: A systematic review from epidemiology to in vitro studies. – *Part. Fibre Toxicol.*, *17*, 1–28; https://doi.org/10.1186/s12989-020-00366-y.

Directive 2004/107/EC of the European Parliament and of the Council of 15/12/2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. *Official J. of the EU*, 23, 3–16.

Dos Santos, R. R., Z. de L. Cardeal, H. C. Menezes. 2020. Phase distribution of polycyclic aromatic hydrocarbons and their oxygenated and nitrated derivatives in the ambient air of a Brazilian urban area. – *Chemosphere*, *250*, 126223; https://doi.org/10.1016/j.chemosphere.2020.126223.

Du, W, Y., G. Chen, W. Shen, S. Wang, S. Zhuo, Y. Huang. 2018. Winter air pollution by and inhalation exposure to nitrated and oxygenated PAHs in rural Shanxi, North China. – *Atmos. Environ.*, 187, 210–217; https://doi.org/10.1016/j.atmosenv.2018.06.004.

Fakinle, B. S., E. L. Odekanle, C. Ike-Ojukwu, O. O. Sonibare, O. A. Falowo, F. W. Olubiyo. 2022. Quantification and health impact assessment of polycyclic aromatic hydrocarbons (PAHs) emissions from crop residue combustion. – *Heliyon*, 8; https://doi.org/10.1016/J.HELIYON.2022.E09113.

Famiyeh, L., K. Chen, J. Xu, Y. Sun, Q. Guo, C. Wang. 2021. A review on analysis methods, source identification, and cancer risk evaluation of atmospheric polycyclic aromatic hydrocarbons. – *Sci. Total Environ.*, *789*, 147741; https://doi.org/10.1016/J.SCITOTENV.2021.147741.

Galmiche, M., O. Delhomme, Y.N. François, M. Millet. 2021. Environmental analysis of polar and non-polar polycyclic aromatic compounds in airborne particulate matter, settled dust and soot: Part I: Sampling and sample preparation. – *TrAC, Trends Anal. Chem.*, *134*, 116099; https://doi.org/10.1016/j.trac.2020.116099.

Gao, Y., L. Yang, J. Chen, Y. Li, P. Jiang, J. Zhang. 2017. Nitro and oxy-PAHs bounded in $PM_{2.5}$ and $PM_{1.0}$ under different weather conditions at Mount Tai in Eastern China: Sources, long-distance transport, and cancer risk assessment. – *Sci. Total Environ.*, *622–623*,1400–1407; https://doi.org/10.1016/j.scitotenv.2017.11.200.

Harrison, R. M. 2020. Airborne particulate matter. – *Philos. Trans. R. Soc. A*, *378*, 1–13.

Hassan, S. K., M. I. Khoder. 2012. Gas-particle concentration, distribution, and health risk assessment of polycyclic aromatic hydrocarbons at a traffic area of Giza, Egypt. – *Environ. Monit. Assess.*, *184*, 3593–3612; https://doi.org/10.1007/s10661-011-2210-8.

Humbert, K., M. Debret, C. Morin, J. Cosme, F. Portet-Koltalo. 2022. Direct thermal desorption-gas chromatography-tandem mass spectrometry versus microwave assisted extraction and GC-MS for the simultaneous analysis of polyaromatic hydrocarbons (PAHs, PCBs) from sediments. – *Talanta*, *250*, 123735; https://doi.org/10.1016/J.TALANTA.2022.123735.

Kelly, F. J., J. C. Fussell. 2012. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. – *Atmos. Environ*., *60*, 504–526; https://doi.org/10.1016/J.ATMOSENV.2012.06.039.

Lawal, A. T. 2017. Polycyclic aromatic hydrocarbons. A review. – *Cogent Environ. Sci*., *3*, 1339841; https://doi.org/10.1080/23311843.2017.1339841.

Li, J. N., Y. Zhang, J. X. Wang, H. Xiao, A. Nikolaev, Y. F. Li. 2023. Occurrence, sources, and health risks of polycyclic aromatic hydrocarbons in road environments from Harbin, a Megacity of China. – *Toxics*, *11*, 695; https://doi.org/10.3390/TOXICS11080695/S1.

Li, L., S. S. H. Ho, Y. M. Han, J. C. Chow, J. G. Watson, L. Wang. 2018. Quantification of nitrated-polycyclic aromatic hydrocarbons in atmospheric aerosol samples with in-injection port thermal desorption-gas chromatography/negative chemical ionization mass spectrometry method. – *Atmos. Environ*., *192*, 84–93; https://doi.org/10.1016/J.ATMOSENV.2018.08.049.

Mo, Z., Z. Wang, G. Mao, X. Pan, L. Wu, P. Xu. 2019. Characterization and health risk assessment of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in 5 urban cities of Zhejiang Province, China. – *Sci. Rep*., *9*, 1–11; https://doi.org/10.1038/s41598-019-43557-0.

Moret, S., C. Conchione, A. Srbinovska, P. Lucci. 2019. Microwave-based technique for fast and reliable extraction of organic contaminants from food, with a special focus on hydrocarbon contaminants. – *Foods*, *8*, 503–508; https://doi.org/10.3390/FOODS8100503.

Mueller, A., N. Ulrich, J. Hollmann, C. E. Zapata Sanchez, U. E. Rolle-Kampczyk, M. von Bergen. 2019. Characterization of a multianalyte GC-MS/MS procedure for detecting and quantifying polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives from air particulate matter for an improved risk assessment. – *Environ. Pollut*., *255*, 112967; https://doi.org/10.1016/j.envpol.2019.112967.

Munyeza, C. F., E. R. Rohwer, P. B. C. Forbes. 2019. A review of monitoring of airborne polycyclic aromatic hydrocarbons: An African perspective. – *Trends Environ. Anal. Chem*., *24*, e00070; https://doi.org/10.1016/j.teac.2019.e00070.

Pan, S., Y. Qiu, M. Li, Z. Yang, D. Liang. 2022. Recent developments in the determination of $PM_{2.5}$ chemical composition. – *Bull. Environ. Contam. Toxicol.*, *108*, 819–823; https://doi.org/10.1007/s00128-022-03510-w.

Pandey, S. K., K. H. Kim, R. J. C. Brown. 2011. A review of techniques for the determination of polycyclic aromatic hydrocarbons in air. – *TrAC, Trends Anal. Chem*., *30*, 1716–1739; https://doi.org/10.1016/j.trac.2011.06.017.

Patel, A. B., S. Shaikh, K. R. Jain, C. Desai, D. Madamwar. 2020. Polycyclic aromatic hydrocarbons: sources, toxicity, and remediation approaches. – *Front. Microbiol*., *11*, 562813; https://doi.org/10.3389/FMICB.2020.562813/BIBTEX.

Pateraki, S., K. M. Fameli, V. Assimakopoulos, A. Bougiatioti, T. Maggos, N. Mihalopoulos. 2019. Levels, sources and health risk of $PM_{2.5}$ and PM_{10}-bound PAHs across the Greater Athens Area: The role of the type of environment and the meteorology. – *Atmos. (Basel)*, *10*, 622–640; https://doi.org/10.3390/atmos10100622.

Pham, C. T., Y. Boongla, T. D. Nghiem, H. T. Le, N. Tang, A. Torib. 2019. Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from open burning of rice straw in the north of Vietnam. – *Int. J. Environ. Res. Public Health*, *16*, 2343; https://doi.org/10.3390/IJERPH16132343.

Poster, D. L., M. M. Schantz, L. C. Sander, S. A. Wise. 2006. Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: A critical review of gas chromatographic (GC) methods. – *Anal. Bioanal. Chem*., *386*, 859–881; https://doi.org/10.1007/s00216-006-0771-0.

Safo-Adu, G. F., G. Ofosu, D. Carboo, Y. Serfor. 2014. Health risk assessment of exposure to particulate polycyclic aromatic hydrocarbons at a Tollbooth on a Major Highway. – *Am. J. Sci. Ind. Res.*, *5*, 110–119; https://doi.org/10.5251/ajsir.2014.5.4.110.119.

Safo-Adu, G. F., I. Attiogbe, F. EmahI, G. Ofosu. 2023. A review of the sources, distribution sequences, and health risks associated with exposure to atmospheric polycyclic aromatic hydrocarbons. – *Cogent Eng*., *10*, 2199511; https://doi.org/10.1080/23311916.2023.2199511.

Santos, A. G., A. C. D. Regis, G. O. da Rocha, M. de A. Bezerra, R. M. de Jesus, J. B. de Andrade. 2016. Simple, comprehensive, and miniaturized solvent extraction method for determination of particulate-phase polycyclic aromatic compounds in air. – *J. Chromatogr. A*, *1435*, 6–17; https://doi.org/https://doi.org/10.1016/j.chroma.2016.01.018.

Schraufnagel, D. E. 2020.The health effects of ultrafine particles. – *Exp. Mol. Med*., *52*, 311–317; https://doi.org/10.1038/s12276-020-0403-3.

Serenjeh, F. N., P. Hashemi, A. R. Ghiasvand, F. Rasolzadeh, N. Heydari, A. Badiei. 2020. Cooling assisted headspace microextraction by packed sorbent coupled to HPLC for the determination of volatile polycyclic aromatic hydrocarbons in soil. – *Anal. Chim. Acta*, *1125*, 128–134; https://doi.org/10.1016/J.ACA.2020.05.067.

Soursou, V., J. Campo, Y. Picó. 2023. Revisiting the analytical determination of PAHs in environmental samples: An update on recent advances. – *Trends Environ. Anal. Chem.*, *37*, e00195; https://doi.org/10.1016/j.teac.2023.e00195.

Stader, C., F. T. Beer, C. Achten. 2013. Environmental PAH analysis by gas chromatography-atmospheric pressure laser ionization-time-of-flight-mass spectrometry (GC-APLI-MS). – *Anal. Bioanal. Chem*., *405*, 7041–7052; https://doi.org/10.1007/S00216-013-7183-8/METRICS.

Thangavel, P., D. Park, Y. C. Lee. 2022. Recent insights into particulate matter ($PM_{2.5}$)-mediated toxicity in humans: An overview. – *Int. J. Environ. Res. Public Health*, *19*, 3390; https://doi.org/10.3390/IJERPH19127511.

Veli, A., Z. Mustafa, S. Naydenova, I. Smoljo, E. Hristova, L. Gonsalvesh. 2024. GC MS/MS method for PAHs analysis in ambient air $PM_{2.5}$. – *J. Chem. Technol. Metall.*, *59*, 251–268; https://doi.org/10.59957/jctm.v59.i2.2024.3.

Vistnes, H., N. A. Sossalla, A. Røsvik, S. V. Gonzalez., J. Zhang, T. Meyn. 2022. The determination of polycyclic aromatic hydrocarbons (PAHs) with HPLC-DAD-FLD and GC-MS techniques in the dissolved and particulate phase of road-tunnel wash water: A case study for cross-array comparisons and applications. – *Toxics*, *10*, 1–15; https://doi.org/10.3390/toxics10070399.

Wang, C., J. Liu, Y. Chen, L. Zhang, L. Li, R. Xu. 2021. Quantitation of ultra-trace nitrated polycyclic aromatic hydrocarbons isomers in water by online solid-phase extraction coupled-liquid chromatography-mass spectrometry. – *J.*

Chromatogr. A, *1635*, 461738; https://doi.org/10.1016/J.CHROMA.2020.461738.

Wang, J., H. Xu, B. Guinot, L. Li, S. S. H. Ho, S. Liu. 2017. Concentrations, sources and health effects of parent, oxygenated- and nitrated-polycyclic aromatic hydrocarbons (PAHs) in middle-school air in Xi'an, China. – *Atmos. Res*., *192*, 1–10; https://doi.org/10.1016/j.atmosres.2017.03.006.

Wang, Y., M. Bao, Y. Zhang, F. Tan, H. Zhao, Q. Zhang. 2020. Polycyclic aromatic hydrocarbons in the atmosphere and soils of Dalian, China: Source, urban-rural gradient, and air-soil exchange. – *Chemosphere*, *244*, 125518; https://doi.org/10.1016/j.chemosphere.2019.125518.

Yadav, I. C., N. L. Devi, V. K. Singh, J. Li, G. Zhang. 2018. Concentrations, sources and health risk of nitrated- and oxygenated-polycyclic aromatic hydrocarbon in urban indoor air and dust from four cities of Nepal. – *Sci. Total Environ*., *643*, 1013–1023; https://doi.org/10.1016/J.SCITOTENV.2018.06.265.

Yang, L., H. Zhang, X. Zhang, W. Xing, Y. Wang, P. Bai, L. Zhang, K. Hayakawa, A. Toriba, N. Tang. 2021. Exposure to atmospheric particulate matter-bound polycyclic aromatic hydrocarbons and their health effects: A review. – *Int. J. Environ. Res. Public Health*, *18*, 2177; https://doi.org/10.3390/IJERPH18042177.

Постъпила на 28.05.2024 г., приета за печат на 10.06.2024 г.
Отговорен редактор Йоцо Янев