PM-ASSOCIATED PAHs DURING WINTER IN BURGAS, BULGARIA

Assist. Prof. Stela Naydenova[1]
Dr. Anife Veli[2]
Dr. Zilya Mustafa[2]
Assoc. Prof. Elena Hristova[3]
Assist. Prof. Dr. Lenia Gonsalvesh[2,4]
[1]Department of Ecology and Environmental Protection, Assen Zlatarov University, Burgas, **Bulgaria**;
[2]Central Scientific Research Laboratory, Assen Zlatarov University, Burgas, **Bulgaria**
[3]National Institute of Meteorology and Hydrology, Sofia, **Bulgaria**
[4]Chemistry Department, Assen Zlatarov University, Burgas, **Bulgaria**

ABSTRACT

The rapid development and industrialization in recent years have posed a great challenge to the environment and air quality due to the increased anthropogenic emissions of particulate matter. Both $PM_{2.5}$ and PM_{10} (particulates with aerodynamic diameters equal or less than 2.5 and 10 μm, respectively) have become the forefront focus due to their adverse effect on human health and climate. Therefore, the assessment of chemical composition of $PM_{2.5}$ and PM_{10} defining in general their toxicity and its correlation with meteorological parameters are worth to consider. The aim of the current study is to determine the concentration of 19 polycyclic aromatic hydrocarbons (PAHs), in airborne $PM_{2.5}$ and PM_{10} collected in the urban area of Burgas, Bulgaria, to investigate the PAH relationship between these two particle fractions and correlation of their concentrations with meteorological parameters. Twenty-four-hour samples of PM_{10} and $PM_{2.5}$ particle fraction were collected on quartz filters using air sampler OPSIS SM200 with flow rate about 2.3 N m^3 h^{-1}. The fractions were sampled in January, 2020, and the recovered through ultrasound-assisted extraction PAHs were analyzed by GC–MS in SIM mode. The obtained results revealed that for the studied period the mean PAHs $PM_{2.5}$ and PAHs PM_{10} concentrations are respectively 14.5 ng m^{-3} (*RSD*=53.8%) and 13.8 ng m^{-3} (*RSD*=51.9%) and represent about 0.14% and 0.06% of the weight of $PM_{2.5}$ and PM_{10}, respectively. In fact, $PM_{2.5}$, PM_{10}, PAHs $PM_{2.5}$ and PAHs PM_{10} concentrations correlate well with each other. With regards to meteorological parameters, a good linear correlation is registered with solar radiation and wind speed.

Keywords: $PM_{2.5}$, PM_{10}, PAHs, urban air quality

INTRODUCTION

Adverse Atmospheric Stability Classes, which depend on the strength of daytime incoming solar radiation, thin overcast at night and the wind speed can lead to increased concentrations of suspended particles in the atmosphere due to the formation of a

https://doi.org/10.5593/sgem2020/4.1/s19.057

floating substance in air like smoke, dust and other particles [1]. The so called photochemical smog is common not only in major industrial centres of China, India, etc., but also in the European cities subject to heavy car traffic and is a major public health concern. Recent studies have shown that the culprit for photochemical smog, namely particulate matter (PM), poses a serious risk to human health, and polycyclic aromatic hydrocarbons (PAHs), adsorbed on the surface of PM, is a persistent organic pollutant with a carcinogenic effect on humans [2]. Numerous studies have concluded that air pollution and particularly airborne PM cause respiratory illnesses, cardiovascular diseases and carcinogenic effects [3–5]. Therefore, PM_{10} and $PM_{2.5}$ are included recently in the European PM standards with an annual limit value of 40 $\mu g\ m^{-3}$ and 25 $\mu g\ m^{-3}$, respectively.

The common sources of particulate matter pollution are natural processes and mainly anthropogenic activity such as combustion processes from motor vehicles, solid fuel burning and industry, and secondary particles, which formation depend on factors like precursor concentrations, reactive gaseous concentrations such as ozone, hydroxyl radical, nitrate radical, peroxy radicals, hydrogen peroxide, organic carbon, and meteorological conditions such as temperature, rainfall, wind speed and relative humidity [6]. The PM impact on health greatly depends on their chemical composition represented by a complex inorganic and organic fractions, the latter containing hundreds of compounds including primary organic compounds emitted directly from different sources to the atmosphere and secondary organic compounds formed in the atmosphere [2]. Acknowledged as unfavorable and strongly harmful organic compounds present in PM are aldehydes, ketones, benzene, dioxins, PAHs and their derivatives [7]. World notable public health protecting organizations like IARC, OSHA, EPA, NIOSH, etc. consider many of PAH compounds as highly toxic, mutagenic and/or carcinogenic and as indicators for risk evaluation. The main anthropogenic sources of PAHs are related to incomplete combustion of biomass, fossil fuels and other unconventional organic materials, fuel evaporation, oil spills, production of coke, processes in refineries and related industries, tire production, electricity generation, etc. [2,8,9]. US Environmental Protection Agency has promulgated the following 16 unsubstituted PAHs (EPA-PAHs) as priority pollutants that are found in the environmental media (air, soil, water, food and other): *acenaphthene; acenaphthylene; anthracene; benz[a]anthracene; benzo[a]pyrene; benzo[e]pyrene; benzo[b]fluoranthene; benzo[g,h,i]perylene; benzo[k]fluoranthene; chrysene; dibenz[a,h]anthracene; fluoranthene; fluorene; indeno[1,2,3–c,d]pyrene; phenanthrene; pyrene*. However, PAHs found in different PM samples may have various concentrations, profiles and pattern of distribution due to the specificity of air pollution sources and meteorological conditions. While the content and source of polycyclic aromatic hydrocarbons in PM have been a common goal in scientific research for many years, the impact of meteorological factors on the concentration and variation of PM-related PAH has only been studied in recent years. In particular, recent study indicates that not only emission sources but also regional transport and meteorological factors may have effects on concentration and distribution of $PM_{2.5}$ associated PAHs [10]. Therefore, it is important to understand the temporal and spatial behavior of PAHs, to find a correlation between the specific meteorological factors for a given region and to understand the concentration and distribution of PM associated PAH. Through a proper air quality management this may contribute to reduced PM and PAHs concentrations.

The aim of the current study is to determine the concentration of 19 polycyclic aromatic hydrocarbons (PAHs), having toxic and carcinogenic effect on human health, in airborne $PM_{2.5}$ and PM_{10} collected in the urban area of Burgas, Bulgaria and to investigate the PAH relationship between these two particle fractions and correlation of their concentrations with meteorological parameters.

MATERIALS AND METHODS

The PM_{10} and $PM_{2.5}$ particle fractions are collected in the city of Burgas, Bulgaria (42°29'43.1"N and 27°28'18.2"E) which is located on the Black Sea coast. Burgas city is characterized by a population of about 410,000 citizens, over 40,000 registered legal vehicles, a relatively well-developed industry represented by a large oil-processing company, manufacturer of wood-based panels, a large scale seaport and an airport. In other words the city is subjected to PM pollution originating from communal household sector (seasonal pollution), transportation and petrochemical industry (year-round pollution), and is influenced by the Continental Mediterranean climate. The PM sampling was carried out by the Mobile station for Air quality control of Burgas Municipality between 14th and 27th of January, 2020. The position of the sampling site is shown in Fig. 1. The PM_{10} and $PM_{2.5}$ samplers were mounted approximately 10 m above the ground. The PM fractions were collected on Whatman® QM–A quartz filters, 47 mm for 24 h, using air sampler OPSIS SM200 with flow rate about 2.3 N m^3 h^{-1}. All collected samples were stored at 3–4°C until analysis.

Fig. 1 Sampling site location (red point) in Burgas city and possible PM pollution industrial sources: 1) The largest oil-processing company on the Balkan Peninsula; 2) Wood processing plant; 3) Airport Burgas; 4) Sea Port Burgas; 5) Sea Port Burgas - Oil Terminal.

All sample filters were spiked with recovery standards and subjected to ultrasonicated extraction with 10 mL of dichloromethane for 30 min. The obtained extracts were subsequently dried and cleaned via column chromatography, as the column was packed with glass wool and 0.5 g of anhydrous sodium sulphate. The cleaned extracts were spiked with few drops of toluene, used as a PAHs keeper, and further concentrated by nitrogen purging to about 300-500 μL. Thus cleaned and concentrated extracts were

spiked with internal standards (i.e. deuterated PAHs) and diluted to exactly 1000 μL prior to GC-MS analysis. Samples were analyzed for the following PAHs: *naphthalene* (*Naph*), *acenaphthylene* (*Acy*), *acenaphthene* (*Ace*), *fluorene* (*Flu*), *anthracene* (*Ant*), *phenanthrene* (*Phe*), *fluoranthene* (*Fla*), *pyrene* (*Pyr*), *benz[a]anthracene* (*BaA*), *chrysene* (*Chr*), *benzo[a]pyrene* (*BaP*), *benzo[b]fluoranthene* (BbF), *benzo[k]fluoranthene* (*BkF*), *benzo[g,h,i]perylene* (*BghiP*), *indeno[1,2,3–c,d]pyrene* (*IndP*), *dibenz[a,h]anthracene* (*DahA*), *coronene* (*Crn*), *perylene* (*Per*) and *benzo[e]pyrene* (*BeP*). Gas chromatograph coupled with a triple quadrupole mass spectrometer (GC–MS/MS), Thermo Scientific Trace 1300/TSQ 8000 was employed for analysis under conditions described in Naydenova et al. [7]. PAHs quantification was carried out in Selected Ion Monitoring mode and internal standard calibration technique by the use of *anthracene–d10* (*d10–Ant*), *fluoranthene–d10* (*d10–Fla*), *benzo[a]pyrene–d12* (*d12–BaP*), *benz[a]anthracene–d12* (*d12–BaA*) as internal standard. The applied recovery standards were *fluorene–d10* (*d10–Flu*) and *pyrene–d10* (*d10–Pyr*). Further details concerning analysis of PAHs and calculation of $[BaP]_{eq}$ can be found in Naydenova et al. [7].

Meteorological data including temperature (TEMP), relative humidity (RH), wind speed (WS), sun radiation (RADST) and atmospheric pressure (PRESS) were measured at sampling site by the Mobile station for Air quality control of Burgas Municipality.

RESULTS AND DISCUSSION

Due to the specifics of geographical location of the Municipality of Burgas, climatic features may play an important role in shaping air quality. The proximity of the sea area is the reason for the presence of local circulation of the ground layer of air (sea and continental breeze), which has direct influence on the dispersion of atmospheric pollutants. Climatic factors can generally be divided into two main groups of indicators - favorable, which contribute to the self-purification of atmospheric air and unfavorable, which are an obstacle to self-purification. The meteorological conditions during the sampling periods as daily mean values are shown in Table 1. Wind speed was in the range of 0.1 – 1.2 m s^{-1}, temperature was about 2.9 – 9.6°C, sun radiation and atmospheric pressure were in the range of 10.7 – 45.6 W m^{-2} and 1013.2 – 1035.4 mbar, respectively, while the relative humidity, for most of the traced day, was high, i.e. above 64.7 % and up to 99.9 %, which were kind of typical for this coastal region. During sampling period precipitations were not observed.

Mass concentrations of $PM_{2.5}$, PM_{10} and PAHs bound to $PM_{2.5}$ and PM_{10} particle fractions were measured simultaneously at an urban location during the sampling period and summarized in Table 2. The concentrations of atmospheric $PM_{2.5}$ were ranged from 9.6 to 11.2 μg m^{-3} with an average value of 10.4 μg m^{-3} (*RSD*=3.5%), while PM_{10} values were in the range of 8.9 – 49.8 μg m^{-3} with a mean value of 21.8 μg m^{-3} (*RSD*=49.8%). The RSDs of the amounts of $PM_{2.5}$ and PM_{10} indicate that the registered $PM_{2.5}$ concentrations are rather homogeneous for the sampling period, while the registered PM_{10} concentrations are significantly heterogeneous and in most cases several times higher than those of $PM_{2.5}$. Higher differences (twice and more) in the concentrations of $PM_{2.5}$ and PM_{10} were registered for the days characterized by lower wind speed and higher relative humidity, with the biggest difference for the day with the lowest wind speed (0.1 m s^{-1}) and highest humidity (99.9%). Apparently this

meteorological conditions create a feasibility for particulate aggregation to form relatively bigger particulates, and thus the concentration of PM_{10} is increased compared to that of $PM_{2.5}$. However, none of the $PM_{2.5}$ and PM_{10} concentrations exceeds the set European PM standard norms.

Table 1. Meteorological conditions during the sampling period

Date	WS	RH	TEMP	RADST	PRESS
	m s^{-1}	%	° C	W m^{-2}	mbar
14.01.2020	0.52	99.9	2.9	31.6	1022.7
15.01.2020	0.29	99.6	4.2	32.5	1026.7
16.01.2020	0.45	90.3	7.6	41.1	1025.8
17.01.2020	1.39	89.8	5.7	10.7	1026.0
18.01.2020	1.03	96.2	5.7	21.7	1024.3
19.01.2020	1.00	96.6	5.7	17.8	1022.5
20.01.2020	0.85	75.5	3.4	25.8	1034.3
21.01.2020	0.40	76.8	3.7	35.0	1035.4
22.01.2020	1.20	69.4	4.4	36.3	1023.8
23.01.2020	1.10	45.2	6.7	39.7	1024.0
24.01.2020	0.71	64.7	4.2	34.8	1027.4
25.01.2020	0.85	71.7	6.4	36.4	1020.6
26.01.2020	0.60	88.0	8.4	36.3	1019.7
27.01.2020	0.08	99.9	9.6	45.6	1013.2

Concentration of PAHs bound to $PM_{2.5}$ and PM_{10} particle fractions were in the ranges of 4.9 – 29.8 ng m^{-3} and 4.9 – 28.3 ng m^{-3} with an average values for the studied sampling period of 14.5 ng m^{-3} (*RSD*=53.8%) and 13.8 ng m^{-3} (*RSD*=51.9%), respectively. With regard to the studied 19 PAHs the following peculiarities are depicted: i) the pattern of distribution of PAHs in $PM_{2.5}$ and PM_{10} are somewhat similar; ii) the lowest concentrations were registered for *Ace*, *Acy*, *Flu*, *Ant* and *Per*; and iii) 4- and more rings PAHs are in higher concentration maximizing for *Chr*, *IndP* and *Fla*. These ascertainments suggest that PAHs bound to $PM_{2.5}$ and PM_{10} originate from the same pollution sources which are rather pyrogenic. Clearly it can be seen that the concentrations of PAHs in $PM_{2.5}$ and PM_{10} are relatively similar as well, but the total PAHs content as a part of PM fraction is higher for $PM_{2.5}$. Comparable to PM_{10} higher concentrations of $PM_{2.5}$ and PM_{10} bound PAHs are registered at lower wind speed and higher solar radiation. This particularity is also confirmed by data presented in Table 3 describing the linear correlation coefficients between $PM_{2.5}$, PM_{10}, PAHs in both PM fractions and meteorological parameters. Linear regression analysis revealed that concentrations of $PM_{2.5}$, PM_{10} and PAHs bound to $PM_{2.5}$ and PM_{10} particle fractions correlated well with each other ($F < 0.05$). Correlation coefficients (R) ranged from 0.74

to 0.97 (Table 3) as the greatest correlation was observed between $PM_{2.5}$ bound PAHs and PM_{10} bound PAHs suggesting once again their common source.

Table 2. Concentrations of $PM_{2.5}$, PM_{10}, sum of PAHs and sum of $[BaP]_{eq}$ in both PM fractions

Date	$PM_{2.5}$	PAH $PM_{2.5}$	$[BaP]_{eq}$ $PM_{2.5}$	PM_{10}	PAH PM_{10}	$[BaP]_{eq}$ PM_{10}
	$\mu g\ m^{-3}$	$ng\ m^{-3}$ (%)*	$ng\ m^{-3}$	$\mu g\ m^{-3}$	$ng\ m^{-3}$ (%)*	$ng\ m^{-3}$
14.01.2020	10.58	29.57 (0.28)	4.03	30.02	28.26 (0.09)	3.59
15.01.2020	10.51	13.95 (0.13)	1.44	35.25	16.48 (0.05)	1.81
16.01.2020	10.42	12.37 (0.12)	1.43	25.23	12.28 (0.05)	1.41
17.01.2020	9.60	4.91 (0.05)	0.46	8.89	4.92 (0.06)	0.43
18.01.2020	10.17	5.81 (0.06)	0.64	16.22	5.93 (0.04)	0.63
19.01.2020	10.11	6.25 (0.06)	0.68	15.47	6.71 (0.04)	0.72
20.01.2020	10.21	7.00 (0.07)	0.79	10.65	5.28 (0.05)	0.56
21.01.2020	10.70	12.31 (0.12)	1.56	22.68	13.30 (0.06)	1.62
22.01.2020	10.68	15.08 (0.14)	1.68	19.60	15.84 (0.08)	1.80
23.01.2020	10.05	15.22 (0.15)	1.63	12.03	11.80 (0.10)	1.28
24.01.2020	10.49	19.29 (0.18)	2.24	19.29	15.38 (0.08)	1.77
25.01.2020	10.32	14.81 (0.14)	1.74	18.31	15.28 (0.08)	1.76
26.01.2020	10.58	16.75 (0.16)	2.01	21.40	15.08 (0.07)	1.73
27.01.2020	11.15	29.76 (0.27)	3.62	49.81	26.85 (0.05)	3.54
Mean value	10.40	14.51 (0.14)	1.71	21.77	13.81 (0.06)	1.62

*Sum of PAHs as a part of PM, %.

With regards to meteorological conditions, a significant correlation of $PM_{2.5}$, PM_{10} and PM associated PAHs with wind speed (inverse correlation, $R = 0.61 – 0.85$) and solar radiation (positive correlation, $R = 0.59 – 0.77$) was found as well. In terms of influence on PM concentration, the wind speed might be considered in several aspects: i) the absence of wind or the presence of very low speed wind may lead to increased PM concentrations mainly in the case of local pollution sources; ii) the presence of high-speed wind leads to better dispersion of pollutants and consequently to lower PM concentrations; iii) high-speed wind may lead to increased PM concentrations in case of non-local pollution sources; iv) under conditions of dry deposition of a large amount of PM on the ground and other nearby surfaces, windlessness would not affect the ambient air PM concentrations, while the high-speed winds may lead to re-dusting/resuspending and increased PM concentrations. Based on that it can be concluded that observed $PM_{2.5}$, PM_{10} and PAHs bound to $PM_{2.5}$ and PM_{10} pollution in Burgas city for the sampling period is rather to local sources of pollution. Inasmuch as in general solar radiation has a negative effect on the concentrations of PAHs in air due to their

photochemical degradation, the observed positive correlation of $PM_{2.5}$, PM_{10} and PM associated PAHs concentrations with solar radiation is kind of surprising for us and thus needs further research for clarification. However, this positive correlation gives us one more evidence that the source of pollution is rather local and close to the monitoring station, i.e. PM have not been long exposed to solar radiation due to long-distance dispersion.

The mean value of the $[BaP]_{eq}$ sums for sampling period exceeds the average annual limit of 1 ng m^{-3} set for *BaP*. However, this exceedance is not significant and should not be considered as a concern. Additionally, our previous study revealed that the mean value of the $[BaP]_{eq}$ sums registered in Burgas for the autumn and spring periods of 2019 does not exceed the average annual *BaP* limit and are in the range of 0.0018 – 0.7542 ng m^{-3} [7].

Table 3. Linear correlation coefficients between $PM_{2.5}$, PM_{10}, PAHs in both PM fractions and meteorological parameters

	$PM_{2.5}$	PAH $PM_{2.5}$	PM_{10}	PAH PM_{10}	WS	RH	TEMP	RADST	PRESS
$PM_{2.5}$	**1.00**								
PAH $PM_{2.5}$	**0.74**	**1.00**							
PM_{10}	**0.82**	**0.75**	**1.00**						
PAH PM_{10}	**0.78**	**0.97**	**0.81**	**1.00**					
WS	**-0.78**	**-0.61**	**-0.85**	**-0.66**	**1.00**				
RH	0.18	0.09	0.51	0.20	-0.41	**1.00**			
TEMP	0.19	0.17	0.32	0.11	-0.20	0.12	**1.00**		
RADST	**0.77**	**0.68**	**0.59**	**0.66**	**-0.63**	-0.28	0.37	**1.00**	
PRESS	-0.30	-0.52	-0.49	-0.51	0.14	-0.29	**-0.72**	-0.29	**1.00**

Statistically significant correlation coefficients (significance $F < 0.05$) are in bold.

CONCLUSION

In the current study, $PM_{2.5}$ and PM_{10} samples were analyzed for 19 different PAHs, during the winter in the Municipality of Burgas, Bulgaria and the linear regression analysis and correlation assessment between concentration of $PM_{2.5}$ and PM_{10}, PM bound PAHs and the meteorological factors was performed. Analyzed data revealed a relatively similar pattern of distribution of PAHs in both PM fractions, a strong correlation between $PM_{2.5}$, PM_{10} and PAHs bound to $PM_{2.5}$ and PM_{10} concentration and most likely common source of pollution. A significant correlation between wind speed (inverse correlation, $R = 0.61 – 0.85$) and solar radiation (positive correlation, $R = 0.59 – 0.77$) with the concentration of $PM_{2.5}$ and PM_{10} and the associated PAHs was found as well assuming that their sources of pollution are rather local. The averaged concentrations of $[BaP]_{eq}$ in both PM fractions do not exceed significantly the annual limit value of 1 ng m^{-3} set for *BaP* – 1.7 ng m^{-3} $[BaP]_{eq}$ in $PM_{2.5}$ and 1.6 ng m^{-3} $[BaP]_{eq}$ in PM_{10}. However, the exceedance is due to the specifics of the heating season and the

winter meteorological conditions, and should not be considered as a concern since these circumstances are not typical for the whole year.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support for the study in the frame of the Project КП-06-Н34/9, National Science Fund, Ministry of Education and Science, Bulgaria.

REFERENCES

[1] Szep R, Keresztes R, Korodi A, Tonk S, Craciun ME. Study of air pollution and atmospheric stability in Ciuc basin-Romania. Rev Chim 2017;68:1763–7. doi:10.37358/rc.17.8.5760.

[2] Amador-Muñoz O, Martínez-Domínguez YM, Gómez-Arroyo S, Peralta O. Current situation of polycyclic aromatic hydrocarbons (PAH) in PM2.5 in a receptor site in Mexico City and estimation of carcinogenic PAH by combining non-real-time and real-time measurement techniques. Sci Total Environ 2020;703:134526. doi:10.1016/j.scitotenv.2019.134526.

[3] Pizzorno J, Crinnion W. Particulate matter is a surprisingly common contributor to disease. Integr Med 2017;16:8–12.

[4] Du Y, Xu X, Chu M, Guo Y, Wang J. Air particulate matter and cardiovascular disease: The epidemiological, biomedical and clinical evidence. J Thorac Dis 2016;8:E8–19. doi:10.3978/j.issn.2072-1439.2015.11.37.

[5] Kyung SY, Jeong SH. Particulate-matter related respiratory diseases. Tuberc Respir Dis (Seoul) 2020;83:116–21. doi:10.4046/TRD.2019.0025.

[6] Fanizza C, De Berardis B, Ietto F, Soggiu ME, Schirò R, Inglessis M, et al. Analysis of major pollutants and physico-chemical characteristics of PM2.5 at an urban site in Rome. Sci Total Environ 2018;616–617:1457–68. doi:10.1016/j.scitotenv.2017.10.168.

[7] Naydenova S, Veli A, Mustafa Z, Gonsalvesh L. Qualitative and quantitative determination of polycyclic aromatic hydrocarbons in fine particulate matter. J Environ Sci Heal - Part A Toxic/Hazardous Subst Environ Eng 2020;55:498–509. doi:10.1080/10934529.2019.1701896.

[8] Abdel-Shafy HI, Mansour MSM. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egypt J Pet 2016;25:107–23. doi:https://doi.org/10.1016/j.ejpe.2015.03.011.

[9] Ravindra K, Sokhi R, Van Grieken R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmos Environ 2008;42:2895–921. doi:https://doi.org/10.1016/j.atmosenv.2007.12.010.

[10] Yang M, Wang Y, Li H, Li T, Nie X, Cao F, et al. Polycyclic aromatic hydrocarbons (PAHs) associated with PM2.5 within boundary layer: Cloud/fog and regional transport. Sci Total Environ 2018;627:613–21. doi:10.1016/j.scitotenv.2018.01.014.