ENVIRONMENTAL EFFECTS OF PAH'S IN URBAN AREAS OF AZERBAIJAN. STUDY CASE: YASAMAL, SABAIL, NASIMI DISTRICTS

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Abstract: Polycyclic aromatic hydrocarbons (PAH's) are chemical compounds considered as pollutants of high priority due to their carcinogenic potential. PAH's can appear in water, soil or in the atmosphere as adsorbed on particulate material or in the gas phase. An increased number of studies on atmospheric PAH's in urban areas have been published in the last decade, especially in the last years. This study describes a simple, sensitive method to determine the – PAH's in the air of the city center. Moss bags technique [active biomonitoring] was applied to assess levels of hydrocarbons in the air of the Absheron peninsula, Azerbaijan. This paper provides a brief, focused overview of what constitutes a PAH's found in mosses, highlights the harmful effects they may have on the human population, make some comments on their environmental sources and analysis.

Keywords: Gas Chromatography; Atmospheric pollution; PAH's; Active moss biomonitoring; Sphagnum girgensohnii; Health risk ecology; Urban environment;

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH's) are a class of organic pollutants existing extensively in the atmosphere and mainly formed and emitted as a result of incomplete combustion of organic matter such as fossil fuel and biomass. PAH's have been extensively studied in the urban atmosphere over the past two decades mainly due to the public health effects associated with their carcinogenic and/or mutagenic properties [1], [2], [3].

The main source of PAH is engine combustions, industrial processes, domestic heating systems or natural sources such as volcanic eruptions and wildfires [4], [5].

With the increasing awareness day by day about environmental degradation and pollution, the field of ecology has become an entirety in itself [6]. The pace with which this stream of environmental science has progressed has invented a lot of newer terms with meanings totally unrelated to the common words [7]. Ecology is all about how the environment is maintained, degrades and destroyed by man and the various harmful effect that can be associated with the ecological imbalance [7]. The gravity of this ecological imbalance has been well understood by the ecologist, one of the consequences of this is the emergence of terminologies in the science of ecology [8].

Over the past two decades, the percentage of the population who live in urban areas has risen to over 50% and this proportion is expected to increase to over 70% by 2050 [9]. In highly populated areas, anthropogenic activities can cause very high air pollutant concentrations. This includes emissions both from stationary sources such as industry and domestic combustion and mobile sources, especially road traffic. Various organic and inorganic pollutants have been studied as tracers of urban atmospheric pollutants on a regional scale [10], [11], [12], [13], [14].

Additionally, some previous studies showed that the main sources of PAH in urban areas from Asia and Europe were traffic exhaust (diesel or gasoline) and certain industrial processes, as shown by Kong et al. [15]. The health assessment document from the USEPA mentions that diesel exhaust (DE) is likely to be carcinogenic to humans by inhalation. This evidence has been shown in different studies [16], [17] and from several years ago [18]. Recent data from Liu et al. [19] had shown that diesel engine contributes to a higher amount of PAH than gasoline. However, PAH's seem to present more carcinogenic potential in gasoline [19]. Although the majority of research works show cancer as a consequence of occupational exposure due to pollution like DE, it is reasonable to presume that the hazard extends to environmental exposure levels [20].

PAH's are slowly transformed into the environment through chemical and biological processes. The chemical reactions which take place during the transformation and degradation of PAH's are particularly catalyzed by sunlight and involve volatilization and oxidation, nitration, and other chemical processes that take place in the interaction between the PAH, the atmosphere, and aqueous environments [21], [22], [23].

The volume of pollutants emitted into the atmosphere from stationary sources and cars decreased by 37.9 tons com-

pared to 2017 and amounted to 1.122.600 tons in 2018 [24] The rapid development of all spheres of economics and human activity has led to an increasingly negative impact on the environment, including the inefficient usage of natural resources. As can be seen in many other countries, Azerbaijan is interested in finding solutions to the problems of environmental protection and rational utilization of natural resources. In support of Azerbaijan's environmental protection goals, a number of important laws, legal documents, and state programs, all of which conform to European law requirements, have been developed and approved in order to improve the ecological situation in the country. Generally, there are still several environmental problems which are expressed in air pollution from industrial plants and transport vehicles, the pollution of water resources by way of introduction of contaminated water, including transnational pollution, the supply of low-quality water to inhabited regions, the loss of fresh water prior to it delivery to the end consumers, degradation of soil (erosion, desertification, etc.) and decline in biological diversity. Air pollution leads to asthma, allergies, heart failure, chronic respiratory diseases, and other diseases. Considering all this, it would be advisable to carry out measures to improve the ecological condition of the city, namely; to plant green spaces which are currently being done [25].

The aim of this study was an assessment of the Polycyclic aromatic hydrocarbons in the atmosphere of central districts of Baku.

2 MATERIALS AND METHODS

Active biomonitoring using a moss transplant (moss bags) of *Sphagnum girgensohnii Russow* was collected in appropriate amounts from relatively clean locations by the end of November 2016 from a pristine wetland area located near Dubna, Russian Federation (P349+RQ Novoye Domkino, Tver Oblast, Russia, altitude 120 m). This area is considered uncontaminated of airborne elements; materials from this area have been previously successfully used in several previous studies [26], [27]. All samples exposed in plastic bags, at Nasimi, Sabayil and Yasamal districts of Baku (Azerbaijan Republic). Exposition time was 3 months (from November 2016 to February 2017).

2.1 Study Area

For the determination of the different content of pollutants of the atmosphere, such as heavy metals, and organic matters, we studied their contents in all areas the cities of Baku and the Absheron peninsula. For this purpose, the moss-biomonitors [26] of the species *Sphagnum girgensohnii* were exposed for three months in 21 areas (Fig. 1). Studied areas included points of the intensive construction, production of asphalt bitumen, stone quarry, furniture factory is underway, enterprises to produce cast iron, concrete, asphalt, a garbage processing plant.

Fig. 1. Map of the location of moss-biomonitors in the territory of Baku and Absheron peninsula, Azerbaijan Republic.

3 EXPERIMENTAL

3.1 Sampling Program and Collection

In order to better understand the used method of active moss biomonitoring, a concise description of the moss sampling is going to be given. It is mentioned before that the transplanted moss, or active method of biomonitoring, is the use of moss in another place to quantify the extent of pollution in the investigated areas [26]. Moss samples were collected in a relevant amount from a pristine wetland area located near Dubna, Russian Federation by the end of November 2016. Moss samples were air-dried and cleaned carefully from adhering extraneous particles. Moss bags were prepared by weighing out 3 g air-dried weight and packing it loosely in nylon nets of 10 cm × 10 cm with meshes of 1 mm^2 [28, 29]. Moss bags were suspended at 5 – 10 m above the street level and simultaneously exposed for 3 months. Considering the spatial distribution of industries and features of the landscape, a total of 21 moss bags were suspended in the central zone of the Peninsula as shown in Fig. 1. After exposure time, the extraction of samples of mosses was made. Following exposure, the moss samples were removed from the nylon net, manually homogenized, and dried at 40°C to a constant weight.

3.2 Sample preparation

Approximately 0.5 g. (in some samples the weight range can be 0,3-1 g.) of each sample were selected for extraction in the glass conic bowl which is in advance cleaned with methylene chloride. Extraction was carried out under an ultrasonic bath with the use of dichloromethane. Extracts were filtered in a round-bottom flask and concentrated by means of a rotor evaporator at a temperature of a water bath of 30±5°C up to

the volume of 2 ml, then was transferred to samplers in a volume of 1 ml under a thin stream of nitrogen.

3.3 Materials and chemical reagents

During the analysis of the samples, dichloromethane solvents (Rathburn, Scotland) were used (chromatographic purity). Purposeful measures were taken to prevent contamination from glassware, teflon, steel materials. All the glassware used in the analysis were cleaned with the methylene chloride and deionized water, then kept in the oven to dry.

3.4 Instrumentation and Conditions

Qualitative analysis was carried out on the Agilent 6890N gas chromatograph, with masses the selection detector Agilent 5975, GH-MD of production of Agilent Technologies equipped with a flawless injector and a capillary column ZB-5 (Phenomenex, USA). Column ZB-5 had the following specifications: 5% -diphenyl, 95% -dimethylpolysiloxane copolymer, length - 60 m, inner diameter - 0.25 mm, film thickness - 0.25 μm. As the gas carrier helium was used. Samples were introduced using an automatic sampler. The analysis was carried out in the scanning mode (SCAN). WILLEY and NIST libraries were used as spectral databases.

4 RESULTS AND DISCUSSION

For the three above mentioned neighborhood areas, the data are shown in the below table (Table 1). The results obtained from the chromatogram are qualitative, not quantitative, only the exit time, the percentage of a single component (-%) about all components (100%). This analysis does not provide any information on the quantitative content of the studied components.

Table 1. The results of the chromatogram by using moss biomonitors in the territory of Yasamal, Sabail and Nasimi districts.

№	Industrial enterprises	Peak	Min.	Absorption, %	Name of substance	Percent of peak's credibility
1	**Yasamal dis-trict 1 [1a]** bakery, building, traffic intensity, publishing house, military factory.	183	429,828	0,2939	Benzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione, 2,3,8,9-tetramethoxy-	42
		202	462,424	0,0677	Naphthalene, 1-iodo-2,6-dimethoxy-5-nitro-	9
		203	464,572	0,1442	4a[2H]-Phenanthrenemethanol, 1,3,4,9,10,10a-hexahydro-6-methoxy-1,1-dimethyl-7-[1-methylethyl]-, [4aR-trans]-	45
2	**Yasamal dis-trict 3 [1b]** building construction, traffic intensity, asphalt, and concrete production, iron workshops.	57	220,722	0,048	Naphthalene, decahydro-, cis-	38
		202	430,687	0,39	2,3a-Dimethylhexahydrobenzofuran-7a-ol	35
		233	548,451	14,705	3-Methyl-1-phenyl-2-azafluorene	38
3	**Sabail district 4 [2a]** Azerbaijan TV studio, a workshop for the production of plastic doors and windows, woodworking workshop.	81	288,489	0,0408	Retene	94
		180	426,981	0,9382	Anthracene, 9,9'-[1,2-ethanediyl]bis[10-methyl-	27
		205	49,287	0,1005	10,11-Dihydro-7,12-bis-dihydroxymethylbenz[a]anthracene -trans-10,11-diol	43
4	**Sabail district 5 [2b]** construction of buildings, traffic intensity, metro	85	274,527	0,0971	Fluoranthene	76
		103	300,142	0,0292	Anthracene, 9-dodecyltetradecahydro-	14
		136	345,249	0,367	9,10-Anthracenedione, 1,8-dihydroxy-3-methoxy-6-methyl-	97
5	**Nasimi district 20, [13a]** heavy traffic, bread work-shop, boiler room, sweets workshop	49	237,904	0,0649	1,2,3,4,5,6,7,8-Octahydrotriphenylene	43

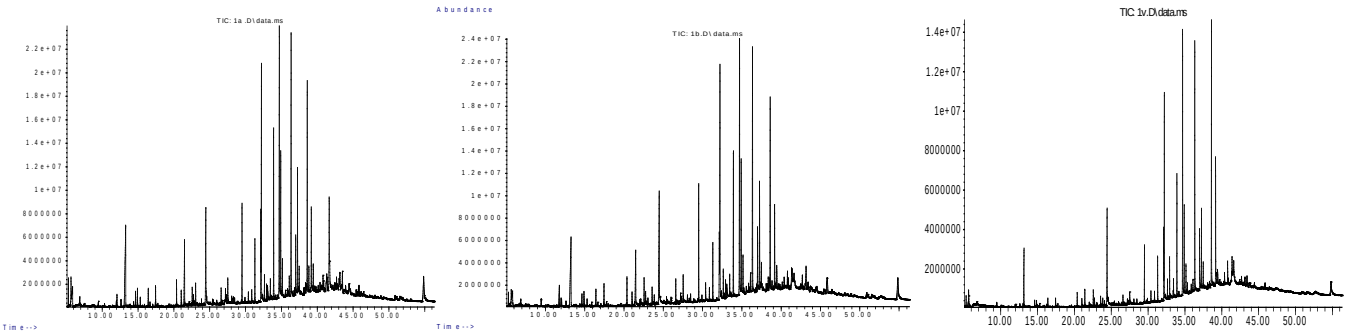

Fig. 2. Chromatogram of moss bags taken from the territory of Yasamal district [1a-1c]

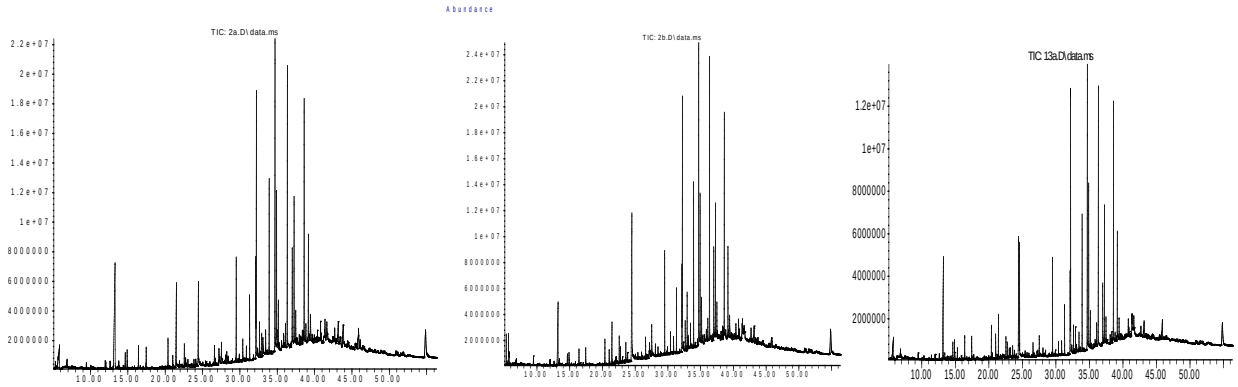

Fig. 3. Chromatogram of moss samples taken from the territory of Sabail [2a, 2b] and Nasimi [13a]

Considering the potential health impact of airborne PAH's, an accurate assessment of their concentration levels in target environmental settings is crucial to establish their proper management, to assess abatement strategies and to develop future policy options. As the physicochemical properties of PAH's vary between lighter and heavier compounds, they are fractionated differentially between gas phase (lighter with high volatility) and particle-phase (relatively heavy PAH's). As such, a suite of PAH's can exhibit noticeable differences in concentration levels in line with their molecular weights. For this reason, it has often been a challenge to develop precise techniques to measure their distribution in a particular environment.

As can be seen from chromatograms (Fig. 2 and Fig. 3) based on the analysis in the air of the city center districts, different derivatives of PAH's, such as Retene, Fluoranthene, Naphthalene, Anthracene, and other hazardous substances are present in the air. A recent study has shown retene, which is a component of the Amazonian organic PM10, is cytotoxic to human lung cells [30].

Fluoranthene is found in many combustion products, along with other PAH's. Its presence is an indicator of less efficient or lower-temperature combustion since non-alternant PAH's are less preferred information than alternant PAH's.

Naphthalene can enter through the air into your lungs, through the skin Exposure to a large amount of naphthalene may damage or destroy some of the red blood cells. This could cause to have too few red blood cells until the body replaces the destroyed cells.

5 CONCLUSION

Atmospheric PAH's pollution has become a serious problem in the world. More and more researchers have put effort into this field. Though there are many reports on toxicity, concentration, distribution of PAH's and their derivatives, there are still many unknown mutagenic compounds of PAH's which are too low to be detected but have high mutagenicity. How to avoid the volatilization and loss of PAH's in the sampling, the reaction between PAH's and other compounds and the redistribution among different size particles; and how to develop new, noiseless and lower-volume sampler; to realize the pretreatment automatically, innocuously, rapidly, low-cost; to protect peoples' health from PAH's; all these problems need further endeavors.

This pilot study shows air pollution in the Absheron peninsula using the moss bag technique. The complex of various measures allowing a decrease in anthropogenic loading is necessary for environmental protection. Accordingly, this data may serve as a baseline in constituting the local guidelines by regulatory bodies in the Republic of Azerbaijan.

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REFERENCES

[1] Chen, S.C. and Liao, C.M. (2006). Health Risk Assessment on Human Exposed to Environmental Polycyclic Aromatic Hydrocarbons Pollution Sources. Sci. Total Environ. 366: 112–23.

[2] Kameda, Y., Shirai, J., Komai, T., Nakanishi, J. and Masunaga, S. (2005). Atmospheric Polycyclic Aromatic Hydrocarbons: Size Distribution, Estimation of Their Risk and Their Depositions to Human Respiratory Tract. Sci. Total Environ. 340: 71–80.

[3] Lee, S.C., Ho, K.F., Chan, L.Y., Zielinska, B. and Chow, J.C. (2001). Polycyclic Aromatic Hydrocarbons (PAH's) and Carbonyl Com-

pounds in Urban Atmosphere of Hong Kong. Atmos. Environ. 35: 5949–5960.

[4] ATSDR. Polycyclic Aromatic Hydrocarbons (PAH's) (Washington, DC: U.S. Environmental Protection Agency, 2003).

[5] Mastral, A.M., J. M. López, M. S. Callén, T. García, R. Murillo, andM. V. Navarro. "Spatial and Temporal PAH Concentrations in Zaragoza, Spain." Sci. Total Environ. 307 (2003): 111–24.

[6] Kawamura K., Suzuki I, Fujii .Y., Wanatabe O. 1994. Ice core record of Polycyclic aromatic hydrocarbon over past 400 years, Naturwissenschaften 81, 502,

[7] Paterson .S, MackaY D. 1989A model illustrating the environmental fate exposure and human uptake of the persistent organic chemicals. Ecol. Modeling, 47, 85.

[8] Agency for Toxic Substance and Disease Registry (ATSDR). 2010. Public Health Statement. August 1995. Accessed 12-09

[9] WHO-UN-UNHABITAT, 2011. Hidden Cities: Unmasking and Overcoming Health Inequities in Urban Settings. WHO Library Cataloguing.

[10] Marr, L.C., Grogan, L.A., Wöhrnschimmel, H., Molina, L.T., Molina, M.J., Smith, T.J., Garshick, E., 2004. Vehicle traffic as a source of particulate polycyclic aromatic hydrocarbon exposure in the Mexico City metropolitan area. Environmental Science & Technology 38, 2584-2592.

[11] Li, J., Zhang, G., Li, X.D., Qi, S.H., Liu, G.Q., Peng, X.Z., 2006. Source seasonality of polycyclic aromatic hydrocarbons (PAH's] in a subtropical city, Guangzhou, South China. Science of The Total Environment 355, 145-155.

[12] Duan, J., Bi, X., Tan, J., Sheng, G., Fu, J., 2007. Seasonal variation on size distribution and concentration of PAH's in Guangzhou city, China. Chemosphere 67, 614-622.

[13] Sharma, H., Jain, V.K., Khan, Z.H., 2007. Characterization and source identification of polycyclic aromatic hydrocarbons (PAH's) in the urban environment of Delhi. Chemosphere 66, 302-310.

[14] Ma, W.L., Li, Y.F., Qi, H., Sun, D.Z., Liu, L.Y., Wang, D.G., 2010. Seasonal variations of sources of polycyclic aromatic hydrocarbons (PAH's) to a northeastern urban city, China. Chemosphere 79, 441-447.

[15] Kong, S., X. Ding, Z. Bai, B. Han, L. Chen, J. Shi, and Z. Li. "A Seasonal Study of Polycyclic Aromatic Hydrocarbons in PM2.5 and PM2.5–10 in Five Typical Cities of Liaoning Province, China." J. Hazardous Mater. 183 (2010): 70–80.

[16] Manzetti, S. "Polycyclic Aromatic Hydrocarbons in the Environment: Environmental Fate and Transformation." Polycyclic Aromatic Compd. 33 (2013): 311–30.

[17] Bakeas, E.,Karavalakis, G., and Stournas, S. "Biodiesel Emissions Profile inModern DieselVehicles. Part 1: Effect of Biodiesel Origin on the Criteria Emissions." Sci. Total Environ. 409 (2011): 1670–6.

[18] Rhead, M. M., and Hardy, S. A. "The Sources of Polycyclic Aromatic Compounds in Diesel Engine Emissions." Fuel 82 (2003): 385–93.

[19] Liu, G.-R., X. Peng, R.-K. Wang, Y.-Z. Tian, G.-L. Shi, J.-H. Wu, P. Zhang, L.-D. Zhou, and Y.-C. Feng. "ANewReceptorModel-Incremental Lifetime Cancer Risk Method to Quantify the Carcinogenic Risks Associated with Sources of Particle-Bound Polycyclic Aromatic Hydrocarbons from Chengdu in China." J. Hazardous Mater. 283 (2015): 462–8.

[20] Environmental Protection Agency (US-EPA]. Health Assessment Document For Diesel Engine Exhaust. (Washington, DC: National Center for Environmental Assessment, 2002).

[21] Fu, P. P., Q. Xia, X. Sun, and H. Yu. "Phototoxicity and Environmental Transformation of Polycyclic Aromatic Hydrocarbons (PAH's)-Light-Induced Reactive Oxygen Species, Lipid Peroxidation, and DNA Damage." J. Environ. Sci. Health C Environ. Carcinog. Ecotoxicol. Rev. 30 (2012): 1–41.

[22] Kamens, R. M., Z. Guo, J. N. Fulcher, and D. A. Bell. "The Influence of Humidity, Sunlight, and Temperature on the Daytime Decay of Polyaromatic Hydrocarbons on Atmospheric Soot Particles." Environ. Sci. Technol. 22 (1988): 103–8.

[23] Kim, S. K., D. S. Lee, W. J. Shim, U. H. Yim, and Y. S. Shin. "Interrelationship of Pyrogenic Polycyclic Aromatic Hydrocarbon (PAH) Contamination in Different Environmental Media." Sensors (Basel) (2009): 9582–602.

[24] The State Statistical Committee of the Republic of Azerbaijan: Motorways, road transport and number of motor vehicles. 2018

[25] Impact of cellular metabolısm on the bıologıcal effects of benzo(a)pyrene and related hydrocarbons Kimberly P. Et al. 2001

[26] Aničić M, Tomašević M, Tasić M, Rajšić S, Popović A, FrontasyevaMV, Lierhagen S, Steinnes E (2009b) Monitoring of trace element atmospheric deposition using dry and wet moss bags: Accumulation capacity versus exposure time. Journal of Hazardous Materials 171:182-188

[27] Culicov OA, Mocanu R, Frontasyeva MV, Yurukova L, Steinnes E (2005) Active Moss Biomonitoring Applied to an Industrial Site in Romania: Relative Accumulation of 36 Elements in Moss-Bags Environmental Monitoring and Assessment 108:229-240

[28] Cao, T., Wang, M., An, L., Yu, Y., Lou, Y., Guo, S., Zhu, Z. (2009). Air quality for metals and sulfur in Shanghai, China, determined with moss bags. Environmental Pollution, 157(4), 1270-1278.

[29] Temple PJ, McLaughlin DL, Linzon SN, Wills R (1981) Moss Bags as Monitors of Atmospheric Deposition Journal of the Air Pollution Control Association 31:668-670

[30] Nilmara de Oliveira Alves, Alexandre Teixeira Vessoni, Annabel Quinet, Rodrigo Soares Fortunato, Gustavo Satoru Kajitani, Milena Simões Peixoto, Sandra de Souza Hacon, Paulo Artaxo, Paulo Saldiva, Carlos Frederico Martins Menck, Silvia Regina Batistuzzo de Medeiros (September 7, 2017). "Biomass burning in the Amazon region causes DNA damage and cell death in human lung cells". Scientific Reports. 7.