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ACTIVE MOSS BIOMONITORING FOR EXTENSIVE SCREENING OF URBAN AIR POLLUTION IN BAKU, AZERBAIJAN. STUDY CASE: NARIMANOV, KHATAI DISTRICTS

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Abstract. Active biomonitoring of the air quality in Azerbaijan was performed using the moss Sphagnum girgensohnii. Moss bags were exposed for 3 months, at different sites. In this study, active biomonitoring of moss for air pollution and an assessment of polycyclic aromatic hydrocarbons (PAH's) were performed for the entire metropolitan areas of Baku, Azerbaijan. The Sphagnum girgensohnii (a species of the most recommended biomonitoring moss genus) is used. From November 2016 to February 2017, moss bags were exposed at 21 sampling sites, forming a dense network of sites. Moreover, new pollution hotspots, omitted by regulatory monitoring, were identified. Active moss biomonitoring could be applied as a pragmatic approach for optimizing the representativeness of regulatory monitoring networks. 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 in some areas of Absheron peninsula, make some comments on their environmental sources and analysis.

Keywords: *Environmental chemistry, active moss biomonitoring, gas chromatography, atmospheric pollution, PAH's, moss bag technique, Sphagnum girgensohnii, health risk ecology, chromatogram, urban environment.*

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1. Introduction

Human health research associated with polycyclic aromatic hydrocarbons (PAH's) has raised concerns because certain PAH's are classified as probable human carcinogens (IARC, 1983; WHO, 1998; Vestreng, 2002; Liu *et al*., 2007) and have shown tumorigenic activity and endocrine-disrupting activity in mammals (Cavalieri *et al*., 1978).

Urban air pollution is a major environmental and public health problem all over the world. Numerous studies have linked the synergic effects of particulate matter (PM) and the organic and inorganic chemicals adsorbed on the surfaces of PM to high numbers of deaths from cardiovascular and respiratory diseases and cancers (Curtis *et al*., 2006).

Polycyclic aromatic hydrocarbons (PAH's) are ubiquitous environmental contaminants originating from anthropogenic natural sources, primarily pyrogenic and petrogenic sources. Emissions from automotive vehicles are considered to be important contributors to the high concentrations of PAH's in atmospheric particulate materials and the gas phase of urban areas (Mastral & Callen, 2000).

Because of their thermally stable structure, PAH's generally exhibit a high melting point, a high boiling point, and a low vapor pressure. In the atmosphere, they are distributed between the gas and particle-bound phases (Gundel *et al.,* 1995; Kallio *et al*., 2003; Dzepina *et al.,* 2007; Ströher *et al*., 2007; Tasdemir & Esen, 2007; Machado *et al*., 2009). This phase partitioning is largely regulated by changes in atmospheric conditions (e.g., temperature and relative humidity), and the physical properties of the PAH's themselves (Baek *et al.,* 1991; Poor *et al.,* 2004; Vardar *et al*., 2004; Ravindra *et al*., 2006).

Pollutants originating from industry such as domestic heating and gasoline and diesel engines contain compound chemical components including proven and potential carcinogens and mutagens (Yamaguchi & Yamazaki, 2001; Zheng *et al.,* 2002). Current studies established that airborne particulates particularly diesel exhaust particles constitute an essential health threat factor. The harmful effect of diesel exhaust particles comprises acute irritation of eyes and respiratory tracts, annoyance reaction and protracted diseases such as allergic nasal catarrh, cancer, and asthma (Yamaguchi & Yamazaki, 2001; Rhead & Hardy, 2003).

Polycyclic aromatic hydrocarbons are a group of molecules that are composed of aromatic units, with the benzene ring as the central unit. PAH's can be subdivided into two different classes: the petrogenic classes and pyrogenic classes. The petrogenic group of PAH's derives from oil- and drilling activities, including oil disasters, spills, and pollution from industrial sites and refineries. The majority of the PAH's in the petrogenic class are small PAH's with 2–4 ring members, such as naphthalene, anthracene, phenanthrene, and chrysene (Kim *et al.,* 2009). Small PAH's are frequently associated with acute toxicity and genotoxicity but low carcinogenicity (IARC, 1987; NTP, 2011).

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's, the atmosphere, and aqueous environments (Kim *et al.,* 2009; Fu *et al.,* 2012; Kamens *et al*., 1988).

The purpose of air quality studies conducted locally is to recognize and characterize the emission sources responsible for the greatest inputs of certain pollutants and to assess air quality at a given location. This is essential at places where there are no air monitoring studies, nor control of the operation of industries, thereby increasing the degree of uncertainty present (WHO, 2010). In developing countries, atmospheric studies are expensive and difficult to implement, being necessary to focus on those sites where industrial parks are located, in order to be able to estimate the atmospheric conditions in nearby residential areas. Studies on atmospheric pollution have frequently been limited by the high cost of classical analytical methods and difficulties in carrying out extensive monitoring in time and space. Therefore, using alternative monitoring tools appears to be a suitable alternative (Aničić *et al*., 2009), with there being increasing interest in setting up monitoring networks using organisms that can act as bio accumulators.

Biomonitoring, in the general sense, may be defined as the use of organisms and biomaterials (biomonitors) to obtain information on certain characteristics of the environment, as long as they quantitatively reflect their ambient conditions (Wolterbeek, 2002).

In urban areas where naturally growing mosses are often scarce or absent, active biomonitoring using the ‘‘bags technique’’ has been developed in order to assess urban air pollution (Goodman & Roberts, 1971).

Sphagnum species have been considered to be especially suitable for the monitoring of heavy metal pollution due to the high cation-exchange capacity of their cell walls, large surface area in contact with the atmosphere (Clymo, 1963) and excellent water retention.

The moss bag technique provides information about the spatial and temporal deposition of air pollutants. In addition, mosses show how pollutant deposition interacts with living organisms through processes that depend on the environmental conditions in a particular study area (Aboal *et al*., 2010).

Azerbaijan is the largest agro-industrial country of the Caucasus with an extensively developed industry and a large agricultural sector with a dynamically developing economy, providing significant human impact on the environment. Baku is one of the most polluted cities on our planet. In the USSR period, it was considered as one of the cities with the highest level of atmospheric contamination (Samed-zade *et al.*, 1982) Strong air pollution in Baku has noted been in recently carried out foreign researches and agencies data (Kuliyev, 2004). Major factors of Baku air pollution are overflow of the urban population, placing of 60-65% of the country industry here, lack of the city planning structures, use of outdated equipment and technologies in manufacturing, popping of superfluous gas on offshore and coastal fields, car exhaust, etc. (Kahramanova & Namazov, 2009).

2. Materials and methods

Study Area

The study was conducted in Baku, the capital and the largest city of Azerbaijan with a population of about 3 million. Baku has a temperate semi-arid climate with hot and humid summers, cool and occasionally wet winters, and strong winds all year long. In winter, severe air pollution occurs frequently in here, particularly during meteorologically calm and stable conditions. Three representative locations- Nariman Narimanov, Khatai and Nizami districts-were chose for the investigation of pollutants` accumulation in moss bags. Sh. I. Khatai is the biggest district among the others.

Moss bags, containing 8-10 steams, were prepared and transplanted to the study area (n = 3 bags/site). These were placed 5-10 m above ground level and exposed for three months each, from November 2016 to February 2017. Once the exposure periods had been concluded, plants were collected, placed in paper bags and dried to constant weight in an oven.

Moss sampling, bag preparation, and exposure

An appropriate amount of *Sphagnum girgensohnii* was collected in February 2017. Moss bags were prepared by weighing about 3 g of air-dried moss and packing it loosely in 10 × 10 cm bags of nylon net with $1mm^2$ mesh size. The total 21 moss bags were suspended in the central zone of the Peninsula as shown in Fig. 1. After each exposure period moss bags were collected, transported to the laboratory in clean polyethylene bags and prepared for analysis. In the laboratory, the moss was air-dried and cleaned of soil particles and other foreign matter. Sampling and preparation of moss bags were carried out wearing disposable polyethylene gloves.

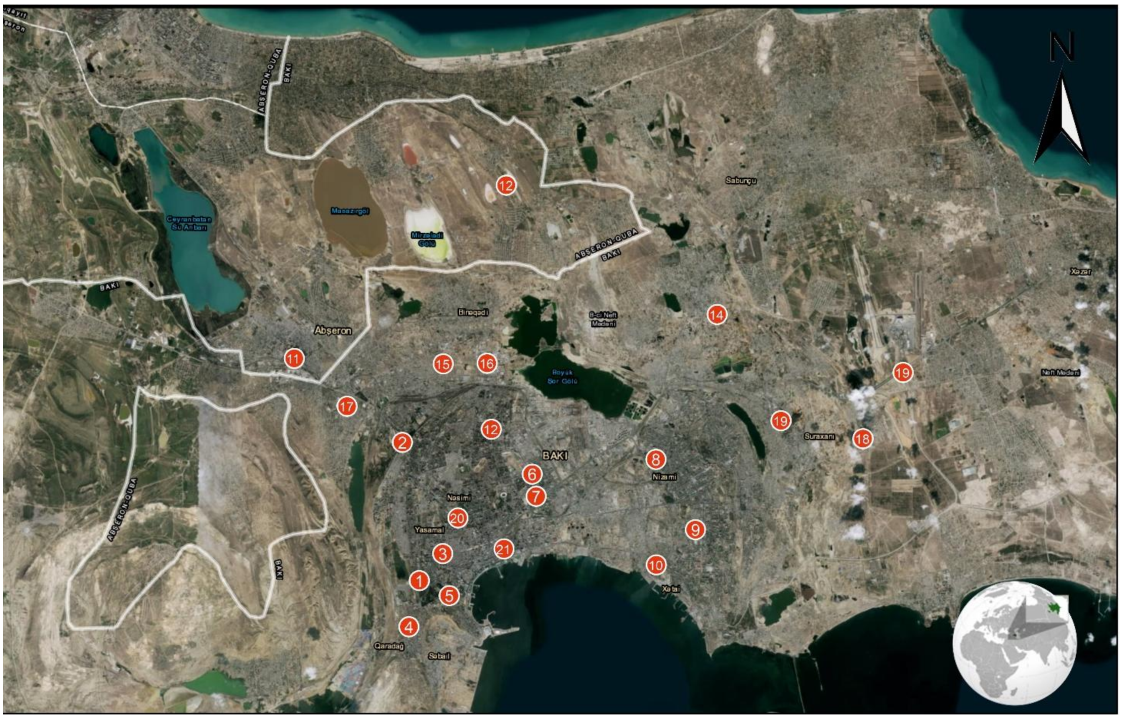


Fig. 1. Map of the location of moss-biomonitors in the territory of Baku and Absheron peninsula, Azerbaijan Republic.

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.

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.

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.

3. Results and discussion

The qualitative results of 3 months of biomonitoring for two districts are shown in the below table (Table 1).

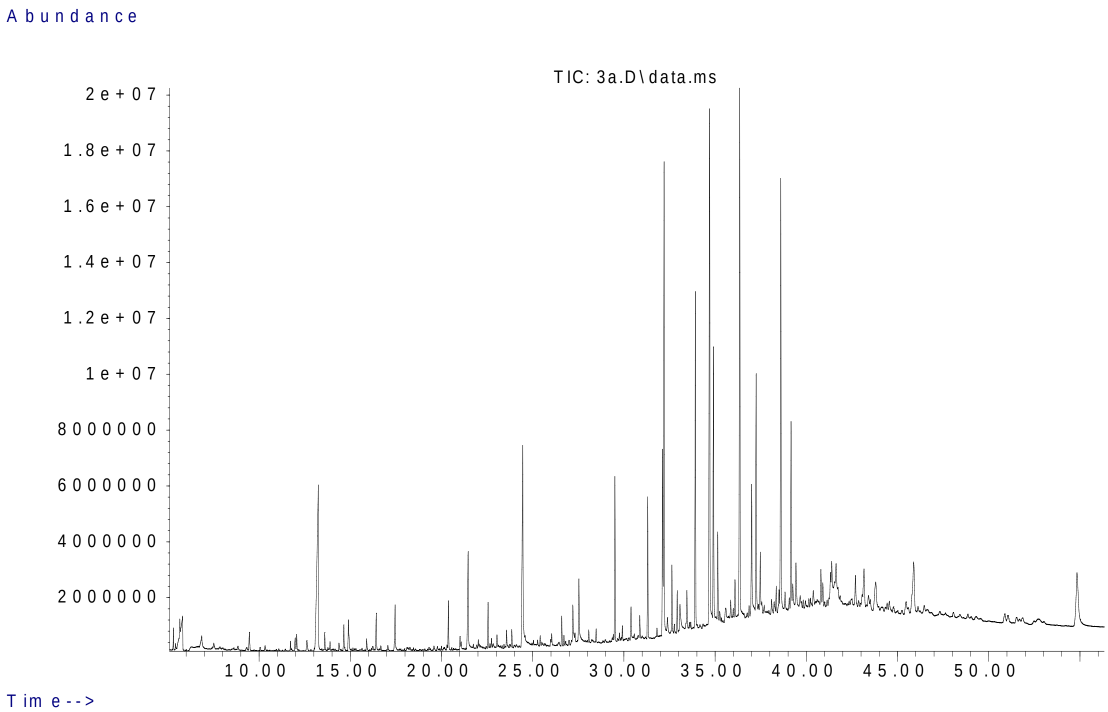
Table 1. The results of the chromatogram by using moss biomonitors in the territory of Narimanov and Khatai districts

№	Industrial enterprises	Peak	Min.	Absorption, %	Name of substance	Percent of peak's credibility
1	**Narimanov district 7.** (3a) building construction, vehicle intensity, wood processing, granite marble enterprise	185	464,678	0,2869	4a(2H)-Phenanthrenemethanol, 1,3,4,9,10,10a-hexahydro-6-methoxy-1,1-dimethyl-7-(1-methylethyl)-, (4aR-trans)-	44
		190	493,193	0,0259	10,11-Dihydro-7,12-bis-dihydroxymethylbenz[a]anthracene-trans-10,11-diol	64
		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	**Khatai district 9**. (5a) bakery, oil, and gasprocessing plant, motor traffic	189	373,336	0,5895	2-Methyloxycarbonyl-6-methoxyanthracene	11
		203	387,083	0,4257	Naphthalene, 1-(phenylmethyl)-	58
		232	422,794	0,3225	2,2'-Binaphthalene, 6,6'-dihexyl-	43

The investigation with the use of mosses for biomonitoring of ambient air has mainly been focused on PAH’s. The present study, however, deals with active monitoring and has been devoted to PAH’s exclusively. It shows that, in addition to studies on passive monitoring, active monitoring with mosses collected from clean areas is a powerful instrument in tracing elevated concentrations of PAH’s in air.

According to the results from the gas chromatography, in the air of the N. Narimanov and Sh.I. Khatai districts, different derivatives of PAH’s, are present in the air.

Outdoor naphthalene sources mainly originate from fugitive emissions and motor vehicle exhaust. Spills to land and water during the storage, transport, and disposal of fuel oil and coal tar are released to the atmosphere by volatilization, photolysis, adsorption, and biodegradation. Naphthalene can enter through the air into your lungs, through the skin. In large amounts, naphthalene may damage some of the red blood cells.



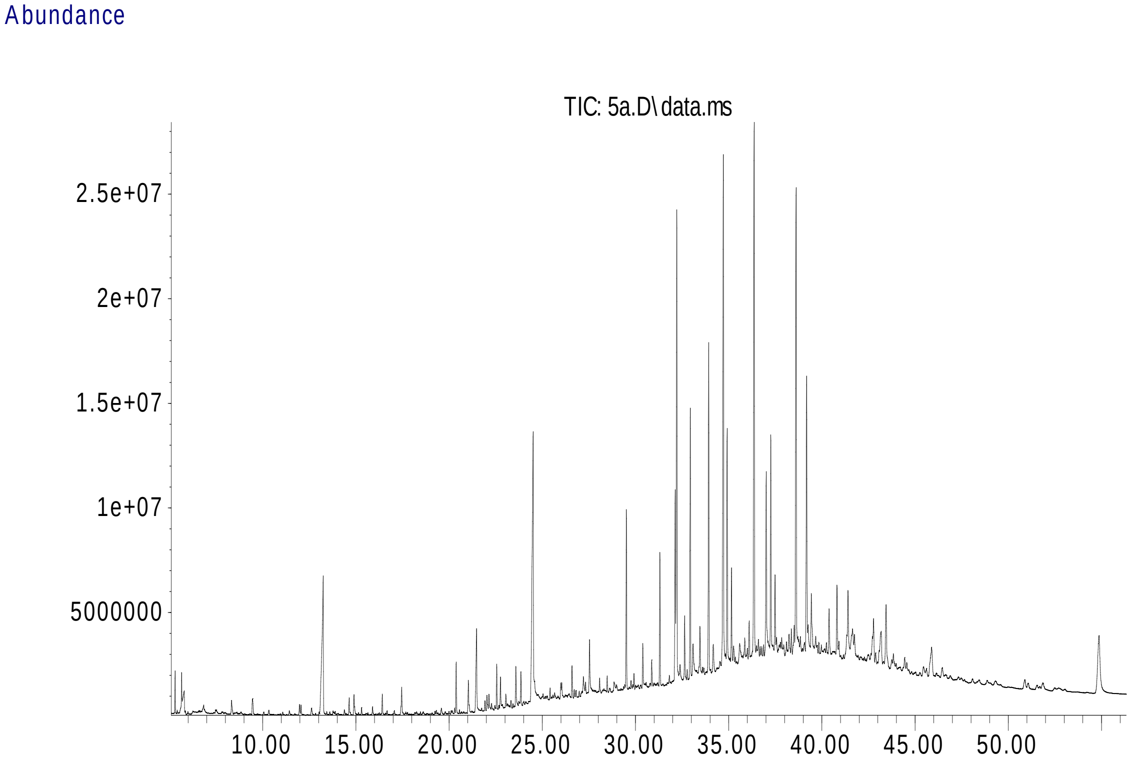


Fig. 2. Chromatograms of moss samples taken from the territory of N. Narimanov (3a) and Sh. I Khatai (5a)

4. Conclusion

In conclusion, this article notes that many studies have been done to evaluate various aspects concerning the PAH's in the atmosphere. In spite of, this fact and observation, PAH's are still major topic and proposes more and in-depth studies especially concerning the assessment of the effectiveness of emission control technologies as well as of emission standards set by various bodies around the world.

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