Advances in Biology & Earth Sciences
Vol.3, No.3, 2018, pp.197-204

ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBON [PAH] LEVELS IN AIR OF ABSHERON PENINSULA, AZERBAIJAN, BY GAS CHROMATOGRAPHY OF MOSS TRANSPLANTS

S.R. Hajiyeva[1], Z.T. Veliyeva[1], A.A. Samadova[1], O.B. Hajiyev[1*]
M.V. Frontasyeva[2], A.I. Madadzada[2]

[1]Department of Ecological Chemistry, Faculty of Ecology and Soil Sciences, Baku State University, Baku, Azerbaijan
[2]Department of Neutron Activation Analysis and Applied Research, Division of Nuclear Physics, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Moscow, Russia

Abstract. For the first-time moss bags technique (active biomonitoring) was applied to assess levels of hydrocarbons in air of the Absheron peninsula, Azerbaijan. Our objective in this paper is to provide a brief, focused overview of what constitutes a PAHs found in mosses, highlight the harmful effects they may have on human population, make some comments on their environmental sources and analysis.

Keywords: *atmospheric pollution, PAHs, active moss biomonitoring, moss bag technique, Sphagnum girgensohnii, gas chromatography, urban environment, health risk ecology, chromatogram, environmental chemistry.*

Corresponding Author: *Orkhan Hajiyev, Department of Ecological Chemistry, Faculty of Ecology and Soil Sciences, Baku State University, Z. Khalilov str., 23, AZ1148, Baku, Azerbaijan,*
e-mail: orkhan.hajiyev9@gmail.com

***Received**: 12 September 2018;* ***Accepted**: 19 November 2018;* ***Published**: 11 December 2018.*

1. Introduction

In ten years, more than half the world's population will be living in cities. The United Nations (UN) has stated that this will threaten cities with social conflict, environmental degradation and the collapse of basic services. The economic, social, and environmental planning practices of societies embodying 'urban sustainability' have been proposed as antidotes to these negative urban trends (Basiago, 1999). One of the important problems of mankind is the threat to the stability of civilization and the environment, the dynamic growth of the economy in conditions of preserving the integrity of the environment, the growing threat of destruction of existing ecosystems. The entire world is concerned about the problems of ozone layer depletion (UNEP Assessment, 2016), global warming, the spread of desertification to wider areas, a significant decrease in biodiversity, and the spread of various diseases associated with environmental pollution (Vuković *et al*., 2015).

Worldwide annually approximately three million people die each year due to toxic pollution of the atmosphere. According to the World Health Organization, before 2040, polluted air can cause the death of six million people. In 2012, an estimated 6.5 million deaths (11.6% of all global deaths) were associated with indoor and outdoor air pollution together (WHO, 2012).

More than 55% of the population and 70% of the industrial potential of the Republic of Azerbaijan are concentrated on 4% of the country's territory (Absheron Peninsula). After the collapse of the USSR in result of the Karabakh conflict the population of Baku began to increase sharply at the expense of refugees and displaced persons from Nagorno-Karabakh and Armenia (about 1 million people). These factors, as well as the high density of the population, led to a strong anthropogenic load on the natural landscapes of the peninsula and especially the surrounding water area of the Caspian Sea (State Statistical Committee Report, 2017).

The Republic of Azerbaijan is in the southeast of the Caucasus, and borders on Russia, Georgia, Turkey, Iran, and Armenia. Throughout history, oil has been used as a leading mechanism in its political and economic life. Since Azerbaijan’s independence, oil has become the main political and economic factor for solving several national problems such as strengthening the country’s independence, defending its territorial integrity and especially providing economic development by attracting huge amounts of foreign investment (the Tehran Convention, 2006). Azerbaijan is one of the world’s oldest oil producers and the city of Baku and the Absheron Peninsula have long been known as historic sites for oil. The first oil well in the world was drilled in Absheron, Bibiheybat in 1847 using a primitive percussion drilling mechanism, also the first oil refinery was built in Baku in 1878. This refinery was connected to the Balakhani oil fields via a newly constructed pipeline 12 km long. The largest oil reserves of Absheron were located near the districts of Balakhani, Surakhani, Bibi-Heybat, Sabunchy, Ramana, and Binagadhi (located in Absheron peninsula) (Ciarreta *et al.*, 2011).

One more of important reasons of pollutions is an excessive population of the capital, around 9.9 million (52.9% of the population is urban, 47.1% t is rural residents, the population density per square kilometer is 114 persons (State Statistical Committee, 2007).

The main sources of technogenic pollution of PAHs are the burning of solid and liquid organic substances, including oil and oil products, wood, anthropogenic wastes. The migration and accumulation of benzopyrene are also played by its source, such as road transport. On the one hand, moving over long distances, cars contribute to a uniform separation of benzopyrene. On the other hand, sedimented benzopyrene accumulates in massive quantities along roads and on objects near them Homogenously, contaminants in sediments can release to the seawater through suspension of sediments. That means that sediments are not merely significant receivers but could also act as secondary sources of these persistent anthropogenic pollutants and greatly affect their fate in the environment (Jones *et al*., 1999; Palm *et al*., 2004).

Benzo[a]pyrene is a polycyclic aromatic hydrocarbon and the result of incomplete combustion of organic matter at temperatures between 300°C (572°F) and 600°C (1,112°F). The ubiquitous compound can be found in coal tar, tobacco smoke and many foods, especially grilled meats. The substance with the formula $C_{20}H_{12}$ is one of the benzopyrenes, formed by a benzene ring fused to pyrene. Its diol epoxide metabolites (more commonly known as BPDE) react and bind to DNA, resulting in mutations and eventually cancer. It is listed as a Group 1 carcinogen by the IARC (Definition from WIKI)

Benzopyrene belongs to the class of polycyclic aromatic hydrocarbons (PAHs). This group of organic compounds in the chemical structure of which there are benzene rings - groups of three rings and more.

Getting into the environment and accumulating in it, benzopyrene penetrates to plants, which in the future serve as fodder for livestock or used in human nutrition. The concentration of benzopyrene in plants is higher than its content in the soil, and in food (or feed) is even higher than in the raw material for their production (Kimberly et al., 2001).

Considering all this, it would be advisable to carry out measures to improve the ecological condition of the city, namely; to restrict the entry of cars into the city, to plant green spaces, which is currently being done. Air pollution leads to asthma, allergies, heart failure, chronic respiratory diseases, and other diseases (Kimberly et al., 2001).

The aim of this study was an assessment of the content of volatile organic compounds (VOCs) in the atmosphere of Baku and the Absheron peninsula.

2. Materials and methods

For this purpose, active biomonitoring using a moss transplant (moss bags) of *Sphagnum girgensohnii Russow* were 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 120m). This area is considered uncontaminated of airborne elements; materials from this area have been previously successfully used in several previous studies, for example, (Aničić et al. 2009b; Culicov et al. 2005). All samples exposed in plastic bags, at 21 sites of Absheron peninsula (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 Absheron peninsula. For this purpose, the moss-biomonitors (Aničić *et al*., 2009b) of the species *Sphagnum girgensohnii* were exposed for three months in 21 areas (refer to 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.

2.2. Moss sample collection, preparation of transplants and exposure

In order to better understand the used method of active moss biomonitoring, 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 (Aničić *et al*., 2009b). Firstly, moss samples (*Sphagnum girgensohnii*) were collected in appropriate amounts from relatively clean locations by the end of November 2016 from a pristine wetland area located near Dubna, Russian Federation (56°42′25.56″N 37°04′09.84″E, altitude 120 m). This area is considered uncontaminated of airborne elements; materials from this area have been previously successfully used in several previous studies, for example, (Aničić *et al*., 2009b; Culicov *et al*., 2005). 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 (Cao *et al*., 2009; Temple *et al*., 1981). 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 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.

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

2.3. Chemical analysis

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 ultrasonic bath with dichloromethane use. Extracts were filtered in a round-bottom flask and concentrated by means of a rotor evaporator at a temperature of 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.

During the analysis of the samples, dichloromethane solvents (Rathburn, Scotland) were used with chromatographic purity. Purposeful measures were taken to prevent contamination from glassware, teflon, steel materials. Deionized water and methylene chloride were used to clean the dishes.

Qualitative analysis was carried out on the Agilent 6890N device, 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 sample catcher. The analysis was carried out in the scanning mode (SCAN). WILLEY and NIST libraries were used as spectral databases.

3. Results and discussion

Below are the data (exit time) from the chromatogram for only two of the studied areas (the rest will be given in the following publications), given that the analysis was qualitative, not quantitative, only the exit time, the percentage of a single component (-%) in relation to all components (100%). This analysis does not provide any information on the quantitative content of the studied components.

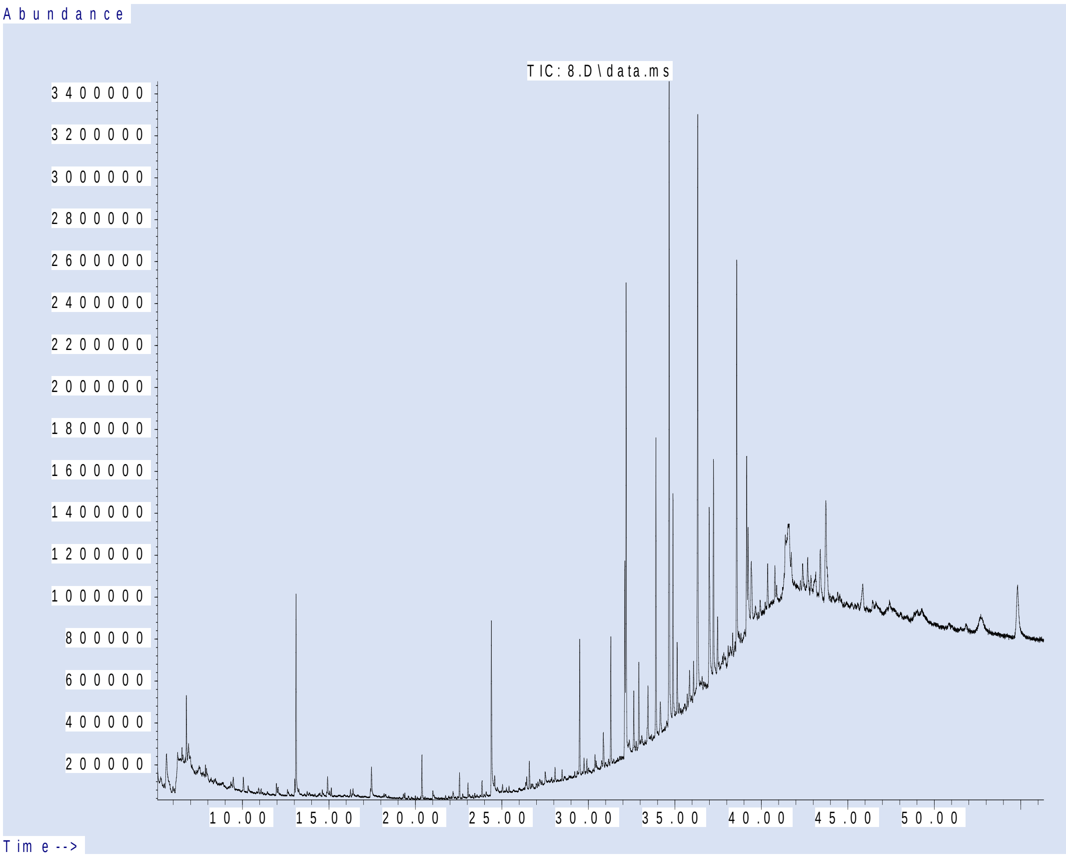

Fig. 2. Chromatogram of gases by means of the moss biomonitors taken from the territory of Fatmai No. 13 (GRFX+4H Fatmayı, Azerbaijan)

As can be seen from chromatograms 1 and 2 (corresponding to regions 1,2359 and 2,039) and based on the analysis in the air of the Surakhani district, benzo (e) pyrene, benzofuran, octadecane and other substances of different hazard classes are present in the air. The most hazardous is benzo (a) pyrene.

Thus, benzopyrene is hazardous not only as a background pollution of the environment but also as a substance that penetrates the body. According to Hygienic standards, 2.1.6.695-98 and 2.1.6.1338-03 (HYGIENE REGULATIONS), the maximum allowable average daily amount of benzopyrene in the air (MPCs) is 0.1 µg/100 m^3 or 10-9 g/m^3, and its maximum permissible concentration in soil according to

Hygienic standards 2.1.7.2041-06 - 0.02 mg/kg in total, considering the background level (Vuković *et al.*, 2014).

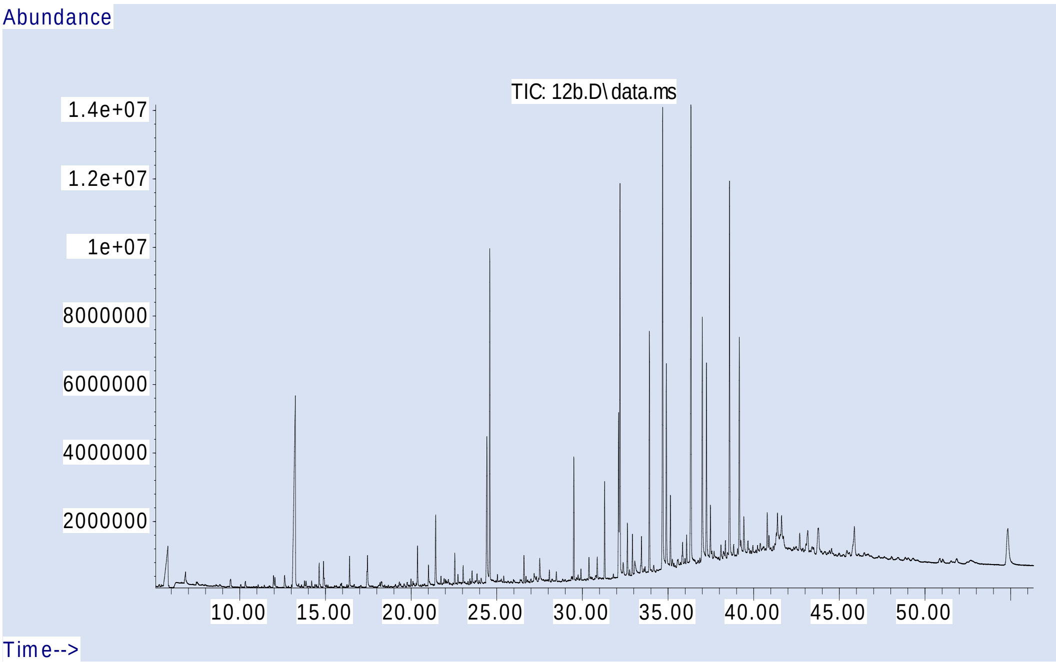

Fig. 3. Chromatogram of gases by means of the moss biomonitors taken from the territory of Surakhani No. 18. (C2JP+7R Baku, Azerbaijan)

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

No	Industrial enterprises	Pk (peak)	minute	absorption region, %	Name of substance	Percent of peak's credibility
1	**Surakhani district 18** - brick plant, oil and gas wells, construction of buildings, enterprises to produce concrete, stone pit	81	35.8	0.46	Hexadecane,1 Iodine-	95
		88	37.1	0.10	Benzo[e]pyrene	38
		102	39.1	2.69	Octadecane, 1-iodo-	97
		122	42.6	0.90	Benzofuran, 2,4,5,6,7,7a-hexahydro-2,4,4,7a-tetramethyl-2-(1-methylethenyl)-	25
2	**Fatmai district 13** - enterprises for the smelting of cast iron, a workshop to produce iron doors and gratings	41	41.4	0.47	Benzofuran,3-(4-chlorophenyl)-2,6-dimethyl-	37

Benzopyrene is easily "included" in the cycle of substances in nature: with atmospheric precipitation, it is recorded even in the territory removed from the main source of PAHs, enters the reservoirs, however, during the evaporation processes, again rises into the air. This ability of benzopyrene to migrate that leads to the fact that its content can be high in places where there is no power source of this substance.

Octadecane is an organic chemical compound of the alkane class. This substance is not classified as hazardous according to the legislation of the European Union.

Benzofuran can be regarded as a furan ring, condensed in *α*- position with benzene; it is an oxygen analog of indole. To be able to make broad generalizations the chemistry of benzofuran and its derivatives, in general, has not been sufficiently studied.

4. Conclusion

This pilot study is a small part in the framework of a big project to quantify the extent of air pollution in Absheron peninsula using the moss bag technique. Analysis and investigation of organic wastes released to the environment show that the entry of these substances into the environment is related to the activities of cast iron workshops, enterprises to produce iron doors and windows, and shops engaged in the production of gypsum. 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.

Acknowledgment

This paper was realized as a part of the project No 4574-4-16/16 financed by the grant from Ministry of Education and Science of the Republic of Azerbaijan, as well as in the frame of bilateral cooperation with Frank Laboratory of Neutron Physics, JINR, Dubna, Russia. Also, on the side, study was conducted on the results of the multi-element NAA at the IBR-2 reactor which were reported at the International Conference ISINN-25 (http://isinn.jinr.ru/, May 2017, Dubna, Russia). The work is accomplished with the immense help and support of Leyla Sadikhova.

References

Aničić, M., Tomašević, M., Tasić, M., Rajšić, S., Popović, A., Frontasyeva, M.V., ... & Steinnes, E. (2009). Monitoring of trace element atmospheric deposition using dry and wet moss bags: accumulation capacity versus exposure time. *Journal of Hazardous Materials*, *171*(1-3), 182-188.

Basiago, A.D. (1998). Economic, social, and environmental sustainability in development theory and urban planning practice. *Environmentalist*, *19*(2), 145-161.

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.

Caspian Sea state of the environment: Changes in environmental quality (Tehran convention report, 2006) http://www.tehranconvention.org/IMG/pdf/Caspian_SoE_Eng_fin.pdf

Ciarreta, A. & Nasirov, S. (2010). Analysis of Azerbaijan oil and gas sector. *United States Association for Energy Economics Research Paper Series*, 43-46.

Countries by Population Density 2015 - List of Countries by Population Density http://statisticstimes.com/demographics/countries-by-population-density.php

Culicov, O.A., Mocanu, R., Frontasyeva, M.V., 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*(1-3), 229-240.

Ecology of Azerbaijan: 2010 was declared the Year of Ecology in Azerbaijan http://eco.preslib.az/index_en.html

Elderfield R.N. Heterocyclic compounds. *Benzofuran and its Derivatives*, 2, 16.

Frontasyeva, M.V., Steinnes, E., Harmens H. (2016). Monitoring long-term and large-scale deposition of air pollutants based on moss analysis. In: *Biomonitoring of Air Pollution Using Mosses and Lichens: Passive and Active Approach – State of the Art and Perspectives*, Edts. M. Aničić Urošević, G. Vuković, M. Tomašević, Nova Science Publishers, New-York, USA.

Harmful substances in diesel fuel cause health issues: Quality of SOCAR diesel in Azerbaijan 21 times lower than European standards https://stratasadvisors.com/Newsroom/In-The-News

How Does Oil Impact the Environment: Emissions and Byproducts Are Produced from Burning Petroleum Products http://environment-ecology.com/energy-and-environment/92-how-does-oil-impact-the-environment.html

Jones, K.C., & De Voogt, P. (1999). Persistent organic pollutants (POPs): state of the science. *Environmental pollution*, *100*(1-3), 209-221.

Mammadova, Sh. (2013). Assessment of Pollution of the Atmospheric Air in the Cities of Azerbaijan, *International Journal of Humanities and Social Science*, 3(18).

Miller, K.P., & Ramos, K.S. (2001). Impact of cellular metabolism on the biological effects of benzo [a] pyrene and related hydrocarbons. *Drug Metabolism Reviews*, *33*(1), 1-35.

Palm, A., Cousins, I., Gustafsson, Ö., Axelman, J., Grunder, K., Broman, D., & Brorström-Lundén, E. (2004). Evaluation of sequentially-coupled POP fluxes estimated from simultaneous measurements in multiple compartments of an air–water–sediment system. *Environmental Pollution*, *128*(1-2), 85-97.

Temple, P. J., McLaughlin, D. L., Linzon, S. N., & Wills, R. (1981). Moss bags as monitors of atmospheric deposition. *Journal of the Air Pollution Control Association*, *31*(6), 668-670.

The State Statistical Committee of the Republic of Azerbaijan: Motorways, road transport and number of motor vehicles (2017) https://www.stat.gov.az/source/transport/?lang=en

The State Statistical Committee of the Republic of Azerbaijan: Political division, population size, and structure (2017) https://www.stat.gov.az/source/demoqraphy/?lang=en

The State Statistical Committee of the Republic of Azerbaijan: The demographic situation in Azerbaijan (2017) https://www.stat.gov.az/news/index.php?id=3759?lang=en

UNEP Assessment 2016: Rate of Environmental Damage Increasing Across Planet but Still Time to Reverse Worst Impacts. https://www.un.org/sustainabledevelopment/blog/2016/05/rate-of-environmental-damage-increasing-across-planet-but-still-time-to-reverse-worst-impacts/

Vergel, K.N, Goryainova, Z.I, Vikhrova, I.V, Frontasyaeva, M.V. (2014) Method of moss-biomonitors and GIS-technology in the estimation of air pollution by industrial enterprises of the Tikhvinsky district of the Leningrad region, *Journal of Ecology of Urbanized Territories*, 2.

Vuković, G. et al. (2016). Active moss biomonitoring: Short-term and small-scale deposition of air pollutants in urban areas based using moss bags. In: *Biomonitoring of Air Pollution Using Mosses and Lichens: Passive and Active Approach – State of the Art and Perspectives*, Edts. M. Aničić Urošević, G. Vuković, M. Tomašević, Nova Science Publishers, New-York, USA.

Vuković, G., Urošević, M.A., Goryainova, Z., Pergal, M., Škrivanj, S., Samson, R., & Popović, A. (2015). Active moss biomonitoring for extensive screening of urban air pollution: Magnetic and chemical analyses. *Science of the Total Environment*, *521*, 200-210.

Vuković, G., Urošević, M.A., Razumenić, I., Kuzmanoski, M., Pergal, M., Škrivanj, S., & Popović, A. (2014). Air quality in urban parking garages (PM10, major and trace elements, PAHs): Instrumental measurements vs. active moss biomonitoring. *Atmospheric environment*, *85*, 31-40.

World Health Organization (WHO) (2012) - WHO releases country estimates on air pollution exposure and health impact http://www.who.int/news-room/detail/27-09-2016-who-releases-country-estimates-on-air-pollution-exposure-and-health-impact