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Monitoring the Content of Polycyclic Aromatic Hydrocarbons in Soils and Natural Herbal Vegetation of Technogeneously Polluted Territory

Andrey Barbashev[1], Svetlana Sushkova[1], Tamara Dudnikova[1], Tatiana Minkina[1], Vladislav Popov[1]

[1]Southern Federal University, Rostov-on-Don, Russia

* **Correspondence to:** Andrey Barbashev, Barbashev_andrei@mail.ru

Abstract: Currently, one of the most important problems is the pollution of natural systems by polycyclic aromatic hydrocarbons (PAHs) as a result of human industrial activity. In this connection, it is necessary to carry out monitoring of territories subjected to the anthropogenic impact. As a result of the monitoring study of the impact zone of the fuel and energy complex enterprises, it was found that polycyclic aromatic hydrocarbons (PAHs) in the soil of the impact zone accumulate mainly up to 2 km along the line of the prevailing wind rose from the enterprise. The group composition of PAHs is dominated by 4-ring compounds, exceeding the background values by 23 times. At the same time, plants growing on the territory of the impact zone mainly accumulate such compounds as fluoranthene, pyrene, benzo[a]anthracene and phenanthrene, which is 70–82% of the total content of polyarenes in various parts of plants.

Keywords: PAHs, benzo[a]pyrene, monitoring, soil-plants.

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Research Article

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1. Introduction

Studies of soil and vegetation cover through monitoring studies are primary in assessing food security and carcinogenic risk, and also serve as the basis for engineering and survey work [*Cristale et al.*, 2012; *Tobiszewski and Namieśnik*, 2012]. Polycyclic aromatic hydrocarbons (PAHs) are a class of widespread pollutants, many of which exhibit mutagenic, teratogenic, and carcinogenic effects on living organisms. Their prevalence in environmental objects is associated with the pyrolysis of hydrocarbon materials [*Tsibart and Gennadiev*, 2013; *Yunker et al.*, 2012]. The sources of formation and entry of these compounds into the environment are high-temperature and microbiological processes, as well as anthropogenic factors, which are mainly associated with the extraction, transportation and processing of fossil fuels, the impact of road and rail transport, energy, petrochemistry, and the production of building materials [*Kuppusamy et al.*, 2017; *Tsibart and Gennadiev*, 2013; *Yunker et al.*, 2012]. Emissions of pollutants into the atmosphere create technogenic halos around the emission source with an anomalous content of the pollutant for natural areas. Often, research on PAHs is focused on the study of 16 representatives of this group, included in the list of priority pollutants of the US Environmental Protection Agency [*US Environmental Protection Agency*, 2020]. In Russia, only benzo[a]pyrene (BaP) is subject to regulation for soils, the maximum permissible concentration (MPC) of which in soils is 20 µg/kg [*GN 2.1.7.2041-06*, 2006].

Since soils and plants are and function in close relationship, an integral system is formed that links the processes of accumulation and transformation of PAHs [*Yakovleva* *et al.*, 2008]. Therefore, one of the main tasks is to monitor the content of PAHs not only in the soils of impact zones, but also in wild vegetation. The aim of the work was to monitor the content of polycyclic aromatic hydrocarbons in soils and natural herbaceous vegetation of a technogenically polluted area.

2. Objects and methods

To conduct the study, 5 monitoring sites were laid and sampling was carried out [*GOST 17.4.3.01-2017*, 2019] on the territory of the Novocherkassk Power Station (NPS) impact zone, the largest enterprise of the fuel and energy complex and the main polluting enterprise in the south of Russia. Monitoring sites are located in the northwest (NW) direction from the enterprise (1n – 1.6 km NW, 2n – 6.9 km NW, 3n – 15.0 km NW, 4n – 20.0 km NW) are represented by Haplic chernozem and Gleyic Chernozems (site 2n) with similar physicochemical properties (Figure 1, Table 1). In the course of geobotanical expeditions, it was established that representatives of herbaceous plants, perennials, predominate on the monitoring sites of the NPS impact zone. Dominant species of natural herbaceous vegetation are represented by bluegrass (*Poa pratensis L.*), couch grass (*Elytrigia repens L.*) and sagebrush (*Artemisia austriaca Jacq.*). As a background, a monitoring site was laid on the territory of a specially protected natural area (SPNA) of the “Persianovsky reserved steppe” (Table 1).

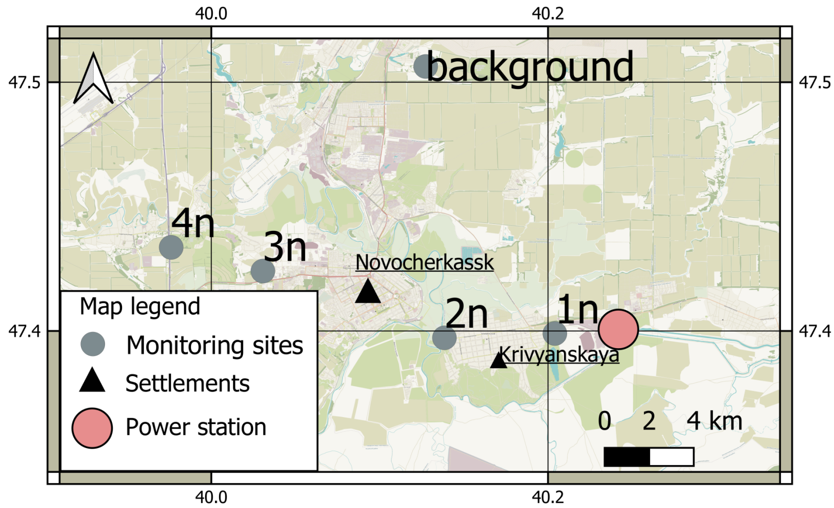

Figure 1. Location of monitoring sites.

Table 1. Soil properties of the monitoring sites of the study areas.

Site number	Physical clay, %	Silt, %	Humus content, %	pH	CaCO3, %	Soil texture	Soil type
			Persianovsky reserved steppe				
Background	57.4	31.3	4.4	7.8	0.9	Heavy loamy	Haplic Chernozem
			Impact zone NAS				
1n	58.4	31.2	4.4	7.4	0.9	Heavy loamy	Haplic Chernozem
2n	56.2	32.9	4.7	7.9	0.9		Gleyic Chernozems
3n	55.3	26.5	3.9	7.9	0.8		Haplic Chernozem
4n	53.5	26.7	3.9	7.7	0.7		Haplic Chernozem

Extraction of PAHs in soil and plant samples was performed using subcritical water [*Sushkova et al.*, 2014, 2015]. A portion of a specially prepared soil or plant sample weighing

1 g, sifted through a 1 mm sieve, was placed in a stainless-steel extraction cartridge and hermetically screwed on both sides. The cartridge was installed in a thermostat and heated to 250 °C and a pressure of 100 atm within 30 min. After cooling the system, the cartridge was unscrewed, the contents were filtered two or three times until the solution was transparent. The resulting aqueous extract was mixed with 5 ml of n-hexane (analytical grade) and placed on a mechanical shaker for 15 minutes. The layers were separated on a separating funnel with a volume of 50 ml sequentially in three stages with the next portion of hexane. The combined hexane extract was passed through a funnel with anhydrous sodium sulfate into a clean dry round bottom flask, evaporated on a rotary evaporator at a water bath temperature of 40 °C to dry residue. The obtained dry residue was dissolved in 1 ml of acetonitrile with stirring for 30 minutes. Quantitative determination of PAHs in extracts was carried out by high performance liquid chromatography (HPLC) on an AGILENT 1260 instrument.

3. Results and discussions

The total content of PAHs in the background soil, located at a distance from the impact zone, was 188 µg/kg (Table 2). At the same time, more than 50% of the total PAH content is accounted for by low molecular weight 2 and 3 ring compounds, mainly naphthalene and phenanthrene, which indicates the natural origin of PAHs in the soil of this area [*Abdel-Shafy and Mansour*, 2016; *Chai et al.*, 2017]. We can distinguish the following decreasing series according to the content of PAHs of different annularity in the studied soil: 3-x > 4-x > 2-x > 5-> 6-annular (Figure 2). Exceeding the MPC of BaP in the soil of the site was not detected, and, in general, the content of the most dangerous 5- and 6-ring PAH compounds does not exceed 20–25 µg/kg (Table 2).

The total content of PAHs in soils of the NPS impact zone is 6–20 times higher than in the soil of protected areas and forms the following decreasing series: 3840 µg/kg (1n 1.6 km NW) > 1729 µg/kg (2n 6.9 km NW) > 1515 µg/kg (3n 15.0 km NW) > 1056 µg/kg (4n 20.0 km NW) (Table 2). The distribution pattern of PAHs in soils corresponds to the pyrogen-coal association of pollutants, since compounds with 4 benzene rings predominate in the composition of PAHs – 409–1355 µg/kg, the content of which decreases with distance from NPS (Figure 2) [*Kołtowski et al.*, 2016; *Medunić et al.*, 2016]. In addition to 4-ring PAH compounds, benzo[b]fluoranthene, benzo[g,h,i]perylene, and phenanthrene make a significant contribution to the total content of polyarenes (Table 2). The content of other PAH compounds does not exceed 80 µg/kg. An exception was BaP, the content of which in the soil of the monitoring site 1n is 355 µg/kg, which exceeds the MPC by 18 times. With the distance from the source of pollution, the content of BaP in the soil decreases and corresponds to 7.7, 3.5, and 2.5 MPC of BaP, respectively (Table 2).

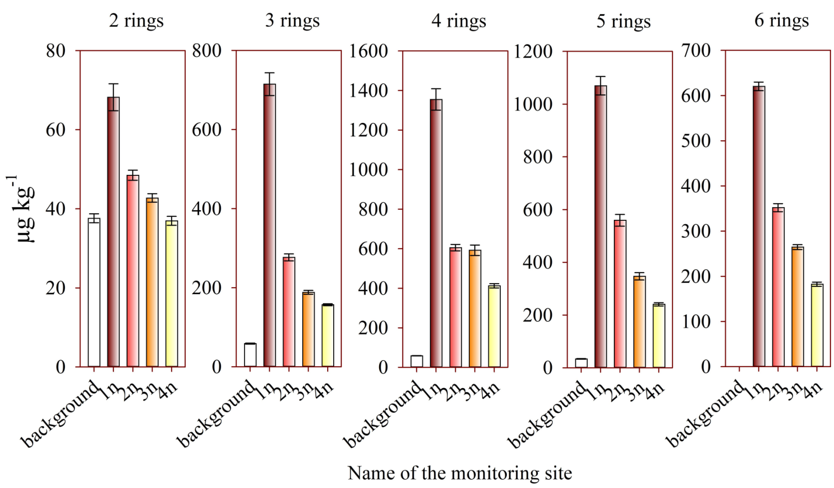

Figure 2. The total content of PAHs with the same number of rings in the soils of the monitoring sites of the NPS impact zone.

Table 2. Content of individual PAH compounds in the soils of the monitoring sites of the NchGRES impact zone.

Number of benzene rings	PAH representative	Name of the monitoring site				
		Background	1n	2n	3n	4n
2	Naphthalene	24.0±0.7	25.0±1.3	30.0±1.2	26.0±1.8	25.7±1.5
3	Anthracene	0.4±0.03	28.9±1.7	32.7±1.6	22.6±0.9	24.5±1.2
	Fluorene	8.8±0.4	13.7±0.6	23.0±1.4	15.9±0.6	8.5±0.5
	Phenanthrene	49.4±1.9	667.4±40.0	217.4±13.0	150.5±9.0	123.5±6.2
4	Benzo[a]anthracene	3.6±0,2	311.2±18.7	164.7±11.5	91.3±5.4	63.2±4.1
	Pyrene	30.3±1.2	470.4±23.5	198.6±14.7	253.0±19.2	175.2±9.9
	Fluoranthene	24.3±1.2	573.4±37.4	248.2±16.2	245.8±13.3	170.2±9.2
5	Benzo[b]fluoranthene	10.2±0.6	401.6±21.9	263.8±14.4	181.6±11.8	125.7±7.8
	Benzo[k]fluoranthene	5.7±0.5	138.4±7.5	70.9±4,6	56.1±3.0	38.8±1.9
	Benzo[a]pyrene	17.6±1.5	354.9±20.6	154.1±9.1	69.9±6.1	48.4±2.3
	Dibenzo[a,h]anthracene	0.2±0.02	189.2±12.9	70.5±4.8	37.0±2.6	25.6±1.9
6	Benzo[g,h,i]perylene	0.3±0.03	622.3±47.7	353.2±26.4	264.6±17.8	183.2±8.8

The content of pollutants in plants growing on the background plot is observed mainly in their root part. Accumulation of 2-ring PAHs, mainly naphthalene (20–23 µg/kg), and 3-ring polyarenes, mainly phenanthrene (5–18 µg/kg) is typical for various parts of plants. The content of 4-ring PAHs did not exceed 7 µg/kg, while that of 5- and 6-ring PAHs did not exceed 1 µg/kg (Figure 3).

The content of PAHs in plants growing on the territory of the impact zone is higher than in plants of the background territory. In general, under the condition of a similar level of soil pollution, according to the ability to accumulate pollutants, plants are located in the following descending order: sagebrush > wheatgrass > bluegrass.

The total content of PAHs in the root part of the plants of the impact zone of the NAS is 3.1–7.0 times higher than in the plants of the background territory and varies from 256–429 µg/kg for sagebrush, 167–255 µg/kg for cereals (bluegrass and wheatgrass) (Figure 3). The content of pollutants in the aerial parts of plants is lower than in the root part, it is 157–300 µg/kg for sagebrush, 48–115 µg/kg for bluegrass and wheatgrass (Figure 3). The highest values of PAH content were established for plants from monitoring site 1n (1.6 km NW), and the minimum values were found for site 4n (20.0 km NW). In general, for all plant species of the impact zone of the NAS, the nature of the accumulation of polyarenes corresponds to the following decreasing series: 4-x > 3-x > 2-x > 5-> 6-annulate (Figure 3). At the same time, 70–82% of the total content of polyarenes in various parts of plants falls on fluoranthene, pyrene, benzo[a]anthracene, and phenanthrene. The accumulation of other PAHs in the root part of plants does not reach 30 µg/kg, and in the aerial part it is less than 10 µg/kg (Figure 3).

Among all the studied species of steppe plants, the lowest content of PAHs in the root part is noted for bluegrass. Most likely, this is due to the physiological characteristics of its root system. The presence of a knotty rhizome and numerous adventitious roots contributes to a greater formation of root exudates compared to other species, which stimulates the growth in the number of PAH-degrading microorganisms in the rhizosphere [*Kumar et al.*, 2017; *Sasse et al.*, 2018; *Wood et al.*, 2016].

4. Conclusion

Thus, it was established that in the soils and plants of the background territory of the protected area, mainly low-molecular compounds accumulate, among which 2-ring naphthalene and 3-ring phenanthrene predominate. With pollution, an increase in the content of pollutants in soils and plants, especially high-molecular 4-ring PAHs, is

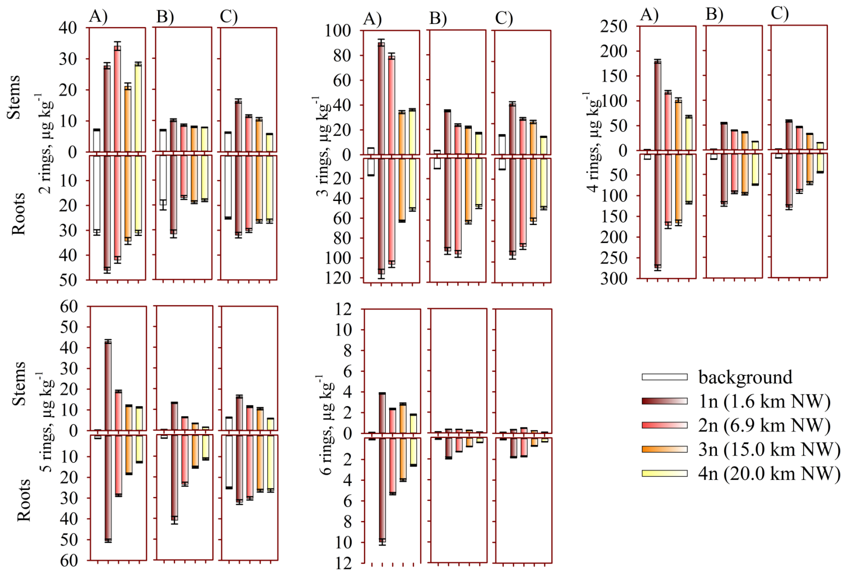

Figure 3. The content of PAHs with the same number of rings in different parts of herbaceous plants on the monitoring sites of the NAS impact zone.

observed. MPC BaP in the most polluted soil of monitoring site 1n, located 1.6 km in the NW direction, reaches a value of 18. An increase in the content of pollutants in the soil increases their accumulation in plants, which is especially pronounced for fluoranthene, pyrene, benzo[a]anthracene and phenanthrene, especially for bluegrass. At the same time, pollutants in the soil and plants of the impact zone accumulate mainly up to 2 km from the enterprise.

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