Diagnostic ratios of individual polycyclic aromatic hydrocarbons for their identification in soils of power station

S Sushkova¹, T Minkina¹, A A Batukaev², T Dudnikova¹, A A Batukaev³, M V Shavanov², L K Adymkanov² and A Barakhov¹

¹ Southern Federal University, 105/42, Bolshaya Sadovaya Str., Rostov-on-Don, Russia
² Chechen State University, 32, Sheripov Street, Grozny, Russia
³ Chechen Agricultural Research Institute, 1, Lenin Street, Gikalo, Russia

E-mail: terra_rossa@mail.ru, tminkina@mail.ru, batukaevmalik@mail.ru, tyto98@yandex.ru, abuzar_batukaev@mail.ru, musa_vahaevich@mail.ru, adymhanov64@mail.ru, tolik.barakhov@mail.ru

Abstract. The article presents the study of the content of organic ecotoxins – polycyclic aromatic hydrocarbons in the soils of the impact zone of the energy industry enterprise of Novocherkasskaya power plant (NPP) – the largest producer of electricity in southern Russia. The study showed a high level of total PAH content in the soils of the studied territory, compared to the background territories. The degree of contamination of soils in the zone of influence of the energy industry enterprises with Benzo(a)pyrene is classified as highly contaminated soils. The diagnostic relationships of individual PAHs showed a significant effect of the NchGRES on the soils of sites located along the line of the prevailing wind from NPP. For these sites, the pyrogen-coal origin of PAHs was established.

1. Introduction

More than 35% of environmental emissions of various types of pollutants account for energy production [1]. According to the researchers [2], the share of the coal industry in the global energy market is 39%, and in Russia it is about 47% of GDP. The use of coal as a source of thermal energy is due, first of all, to savings on raw materials for energy production. Along with this, coal-fired power generating enterprises in the course of their work cause damage to all components of the biosphere in the emission zone. In the course of their work, coal-fired power plants emit various pollutants into the atmosphere in a gaseous, aerosol and solid state, which include hazardous pollutants — polycyclic aromatic hydrocarbons (PAHs) [3], most of which have carcinogenic, teratogenic, mutagenic properties [4].

PAHs are a group of macromolecular compounds the elementary unit of structure of which is benzene ring. Polyarenes are fat soluble and have a high melting point [5]. The subgroup of low molecular weight PAHs includes compounds with 2–3 condensed benzene rings, and the subgroup of high molecular weight PAHs includes compounds with 4 or more condensed benzene rings in their structure. The soil has the ability to accumulate these substances. The sorption potential of soils with respect to PAHs is primarily due to the properties of the soil itself (content and chemical composition of humus, pH, granulometric and mineralogical composition of the soil).

The list of priority pollutants of the United States includes 16 representatives of this class of compounds. In the Russian Federation, the norms are established for four substances of this class of compounds.
compounds, however, the maximum permissible concentration (MPC) for soils is developed for only one representative of PAHs – benzo(a)pyrene, carcinogen and mutagen of the first hazard class (20 ng/g) [6].

The purpose of the research was to establish the composition of individual PAHs in the soils of the energy complex enterprises by their diagnostic ratio.

2. Experimental area

The object of the study was the soils of the territories adjacent to the Second Generating Company of the Wholesale Electricity Market OGK-2 Novocherkasskaya Power Station (NPP). NPP is an enterprise with a capacity of more than 19 GW. In 2017, electricity generation amounted to 63.5 billion kWh, which is about 7% of the all-Russian electricity production. NPP takes the second place within the Russian Federation in terms of electricity generation, being second only to Surgut state district power station [7]. Power plants of 6000 kWh are classified as enterprises of the first hazard class [8].

Taking into account the above mentioned aspects, it can be concluded that NPP belongs to this type of enterprises and has a significant impact on the environmental situation, as in Novocherkassk itself, in the surroundings of which the enterprise is located (MPC of benzo(a)pyrene within the city averages 16.4 [9]), and the Rostov region and Russia as a whole.

Monitoring sites of the impact zone of NPP are located along the line of the prevailing wind rose [10] (No. 4, 8, 9, 10) at a distance of up to 20 km from the emission source, and around the enterprise (sites No. 1–3, 5–7, 11) at a distance of up to 3 km (Figure 1).

![Map of monitoring sites around Novocherkassk Power Station](image)

**Figure 1.** Map of monitoring sites around Novocherkassk Power Station

| №  | Site  | Direction and distance from NPP | Soil type | Physical clay, % | Slit, % | Humus, % | pH |
|----|-------|--------------------------------|-----------|-----------------|--------|----------|----|
| 1  | 1ne   | CH                             | 52        | 27              | 4.3    | 7.6      |    |
| 2  | 1.2e  | CH                             | 52        | 31              | 4.0    | 7.4      |    |
| 3  | 2.7sw | MC                             | 67        | 37              | 4.6    | 7.3      |    |
| 4  | 1.6nw | CH                             | 55        | 29              | 4.6    | 7.5      |    |
| 5  | 3sw   | FL                             | 7         | 3               | 3.1    | 7.5      |    |
| 6  | 2n    | MC                             | 55        | 30              | 4.1    | 7.7      |    |
| 7  | 1.5n  | CH                             | 51        | 27              | 4.1    | 7.6      |    |
| 8  | 5nw   | MC                             | 60        | 32              | 5.0    | 7.4      |    |
| 9  | 15nw  | CH                             | 52        | 30              | 4.2    | 7.6      |    |
| 10 | 20nw  | CH                             | 53        | 28              | 4.6    | 7.6      |    |
| 11 | 1.7 sw| CH                             | 53        | 30              | 3.5    | 7.6      |    |

Hoplic chernozem (CH) prevails in the soil cover of the study area, but fluvisols (FL) and meadow-chernozemic (MC) soils are also found (Table 1).
3. Methods and materials

Soil sampling was carried out by the envelope method from each monitoring site to a depth of 0–20 cm in July 2018 [11]. The transportation and storage of the samples were carried out in a portable device with a cooling element. The storage of samples, according to the guidelines, was carried out no more than a week from the moment of selection until the direct extraction of pollutants from soil samples. PAHs were extracted from soil samples by saponification, where the interfering fraction of soil lipids was removed by boiling the sample with a 2% alcohol solution of potassium hydroxide, followed by three times extraction of sample with hexane [12].

After the PAH extract in hexane was evaporated on a rotary evaporator and dissolved in 1 ml of acetonitrile, the acetonitrile solution of concentrated PAHs was transferred into vials. The concentration of PAHs in an acetonitrile solution was determined using high performance liquid chromatography on an Agilent 1260 chromatograph with fluorimetric detection no later than three days after the transfer of PAH concentrate to the vial [13]. Processing the results of mass concentrations of PAHs in the sample was performed using a computer in accordance with the calibration characteristic, taking into account concentration and losses during sample preparation.

In this study, PAHs such as naphthalene, biphenyl, anthracene, acenaphthene, acenaphthyline, phenanthrene, fluorene, which are low molecular weight and benzo(a)anthracene, fluoranthene, pyrene, chrysene, BaP, benz(k)fluorantene, benz(b)fluoranthene, dibenz(a)anthracene, benz(g, h, i) perylene, which are high molecular weight PAHs. All of the above PAHs, with the exception of biphenyl, are on the list of US priority pollutants [14].

4. Results and discussion

The total PAH content in the soils of the monitoring sites of NPP impact zone significantly exceeded the background (for Rostov region) total PAH content in the soils of the Persianovskaya Steppe specially protected natural area. The PAH content in the soils of the monitoring sites decreased with the distance from NPP in the NW direction (along the prevailing wind line) total, according to the following scheme: site No. 4 (1.6NW) – 3696.6 ± 180.0 ng / g > No. 8 (5NW) – 1420.1 ± 66.7 ng / g > No. 9 (15NW) – 1291.8 ± 58.2 ng / g > No. 10 (20NW) – 1157.1 ± 44.9 ng / g. The content of 3-ringed phenanthrene in the soils of monitoring sites located along the line of the prevailing wind prevailed quantitatively in the composition of individual low-molecular PAHs (table 2).

The content of 4 ringed PAHs such as pyrene, chrysene, and fluoranthene, as well as 5 ringed BaPs and benz(b)fluoranthene in the soils of sites located along the line of the prevailing wind outnumbered in the composition of individual high molecular weight PAHs (table 3).

**Table 2. Content of low-molecular pah in the soils of monitoring sites located on the line of the prevailing wind**

| № site | Naphthalene | Diphenyl | Anthracene | Acenaphthene | Acenaphthyline | Fluorene | Phenanthrene |
|--------|-------------|----------|------------|--------------|---------------|----------|--------------|
| 4      | 144.2 ± 7.2 | 140.1 ± 6.8 | 61.4 ± 3.0 | 22.4 ± 1.1 | 55.1 ± 2.8 | 62.6 ± 3.0 | 453.0 ± 25.1 |
| 8      | 124.6 ± 5.9 | 24.6 ± 1.0 | 20.9 ± 1.1 | 10.7 ± 0.5 | 15.4 ± 0.8 | 14.9 ± 0.3 | 130.1 ± 6.5 |
| 9      | 113.1 ± 5.1 | 16.3 ± 0.8 | 18.6 ± 0.8 | 8.6 ± 0.4 | 12.9 ± 0.6 | 37.6 ± 1.7 | 93.2 ± 4.4 |
| 10     | 122.4 ± 5.7 | 13.6 ± 0.6 | 15.4 ± 0.7 | 8.9 ± 0.4 | 13.7 ± 0.6 | 50.5 ± 2.4 | 82.0 ± 3.9 |

In the soils of sites located around NPP, the total PAH content was within 716.3 ± 30 ng / g in the AL soil of site No. 5, up to 1083.1 ± 48 ng / g in the LF soil of site No. 3. The content of 3-ringed phenanthrene in the soils of monitoring sites located around NPP was quantitatively predominant in the composition of individual low-molecular PAHs (Table 4). The composition of high molecular weight PAHs was outnumbered by the content of 4 ringed PAHs: pyrene, chrysene, and fluoranthene, as well as 5 ringed benzo(b)fluoranthene and 6 ringed benzo(g, h, i) perylene in the soils of monitoring sites located around NPP (table 5).

**Table 3. Content of high-molecular pah in the soils of monitoring sites located on the line of the prevailing wind**

| № site | PAH, ng/g |
|--------|-----------|
| Naphthalene | Diphenyl | Anthracene | Acenaphthene | Acenaphthyline | Fluorene | Phenanthrene |
| 4      | 144.2 ± 7.2 | 140.1 ± 6.8 | 61.4 ± 3.0 | 22.4 ± 1.1 | 55.1 ± 2.8 | 62.6 ± 3.0 | 453.0 ± 25.1 |
| 8      | 124.6 ± 5.9 | 24.6 ± 1.0 | 20.9 ± 1.1 | 10.7 ± 0.5 | 15.4 ± 0.8 | 14.9 ± 0.3 | 130.1 ± 6.5 |
| 9      | 113.1 ± 5.1 | 16.3 ± 0.8 | 18.6 ± 0.8 | 8.6 ± 0.4 | 12.9 ± 0.6 | 37.6 ± 1.7 | 93.2 ± 4.4 |
| 10     | 122.4 ± 5.7 | 13.6 ± 0.6 | 15.4 ± 0.7 | 8.9 ± 0.4 | 13.7 ± 0.6 | 50.5 ± 2.4 | 82.0 ± 3.9 |
The MPC of BaP was exceeded in the soils of all monitoring sites located along the prevailing wind line from NPP, with a regular decrease with distance from the emission source in the following order: No. 4 (1.6 km NE) – 17.4 > No. 8 (5 km NE) – 4.5 > No. 9 (10 km NE) – 3.8 > No. 10 (20 km NE) – 3.4. The content of BaP for the soils of monitoring sites located around NPP ranged from 2.3 MPC in the soils of site No. 11 to 4.9 MPC in the soils of site No. 6. According to SanPiN 2.1.7.1287-03 "Sanitary and epidemiological quality requirements for Soils" [15], excesses of MPC of BaP in the soils of all monitoring sites make it possible to classify the soils of the study area as highly contaminated soils (Table 6).

### Table 4. Content of low-molecular pah in the soils of monitoring areas around npp

| № | Site       | PAH, ng/g |
|---|------------|-----------|
|   |            | Naphthalene | Diphenyl | Anthracene | Phenanthrene |
| 1 | 36.1±1.6   | 19.3±0.9 | 13.0±1.0 | 11.3±0.5 | 32.9±1.6 | 16.3±0.8 | 213.2±10.1 |
| 2 | 44.0±2.2   | 22.5±1.0 | 7.5±0.3 | 9.5±0.4 | 20.2±1.0 | 12.8±0.6 | 69.6±3.4 |
| 3 | 42.1±2.1   | 23.6±1.1 | 8.5±0.4 | 32.8±1.6 | 16.2±1.0 | 12.8±0.6 | 69.6±3.4 |
| 5 | 59.3±2.9   | 18.7±0.9 | 8.5±0.4 | 32.8±1.6 | 16.2±1.0 | 12.8±0.6 | 69.6±3.4 |
| 6 | 66.3±3.3   | 44.3±2.2 | 10.2±0.5 | 16.2±1.0 | 26.1±1.3 | 16.6±0.8 | 265.5±26.2 |
| 7 | 25.5±1.1   | 23.1±1.1 | 21.3±1.0 | 11.2±0.5 | 15.4±0.7 | 10.3±0.5 | 106.4±5.0 |
| 11| 56.4±2.6   | 23.4±1.1 | 3.7±0.2 | 8.5±0.4 | 10.7±0.5 | 14.2±0.7 | 153.8±7.2 |

### Table 5. Content of high-molecular pahs in the soils of monitoring areas around npp

| № | Site       | PAH, ng/g |
|---|------------|-----------|
|   |            | Benz(a)anthracene | Pyrene | Fluoranthene | Chrysene | BaP | Benz (b) | Benz (k) | Dibenz (a, h)anthracene | Benz (g, h, i)perylene |
| 1 | 51.4±2.5   | 179.7±8.5 | 73.4±3.5 | 73.1±3.5 | 107.5±5.1 | 118.9±5.8 | 31.8±1.5 | 7.1±0.3 | 83.2±4.1 |
| 2 | 31.6±1.5   | 89.2±4.4 | 73.0±3.5 | 70.6±3.3 | 49.6±2.4 | 141.5±5.7 | 11.4±0.5 | 7.3±0.3 | 113.4±5.1 |
| 3 | 53.5±2.6   | 76.2±3.6 | 100.4±4.9 | 58.5±2.7 | 59.6±2.7 | 194.9±4.9 | 29.5±1.4 | 25.2±1.2 | 126.1±6.1 |
| 5 | 47.9±2.4   | 72.0±3.5 | 61.4±2.9 | 41.3±2.0 | 63.3±3.1 | 77.5±3.6 | 15.5±0.7 | 2.7±0.1 | 70.3±3.5 |
| 6 | 21.7±1.0   | 43.0±2.0 | 48.9±2.4 | 83.6±3.9 | 97.2±4.7 | 166.3±8.1 | 15.1±0.7 | 6.4±0.3 | 96.7±4.7 |
| 7 | 17.4±0.8   | 103.4±4.9 | 75.3±3.6 | 81.7±3.9 | 72.3±3.5 | 33.6±1.6 | 4.9±0.2 | 6.7±0.3 | 108.0±5.1 |
| 11| 52.2±2.5   | 82.0±4.1 | 70.0±3.5 | 43.9±2.1 | 46.4±2.2 | 74.6±3.2 | 15.8±0.7 | 4.0±0.2 | 81.1±4.0 |

The MPC of BaP was exceeded in the soils of all monitoring sites located along the prevailing wind line from NPP, with a regular decrease with distance from the emission source in the following order: No. 4 (1.6 km NE) – 17.4 > No. 8 (5 km NE) – 4.5 > No. 9 (10 km NE) – 3.8 > No. 10 (20 km NE) – 3.4. The content of BaP for the soils of monitoring sites located around NPP ranged from 2.3 MPC in the soils of site No. 11 to 4.9 MPC in the soils of site No. 6. According to SanPiN 2.1.7.1287-03 “Sanitary and epidemiological quality requirements for Soils”[15], excesses of MPC of BaP in the soils of all monitoring sites make it possible to classify the soils of the study area as highly contaminated soils (Table 6).

### Table 6. Soil contamination categories

| Substance hazard class | The 1st class | The 2nd class | The 3rd class |
|------------------------|--------------|--------------|--------------|
| > 5 MPC                | Very high    | Very high    | High         |
| From 2 to 5 MPC        | Very high    | High         | Average      |
| From 1 MPC to 2 MPC    | Low          | Low          | Low          |

It is necessary to note that the soils of monitoring sites located along the prevailing wind line are located near settlements (the village of Grushevskaya, the village of Kushchevskaya, Novocherkassk) (Figure 1), which may have the effect of additional pollution factors on the content of PAHs in the soils of this region due to mass use of vehicles.

In order to assess the contribution of NPP directly to the PAH content in the soils of monitoring sites located along the prevailing wind line from the enterprise, we calculated the ratios of individual PAHs. This calculation method is based on theoretical knowledge of the conditions for the formation...
of PAHs. First of all, PAHs are formed during the burning of organogenic fuel under conditions of oxygen deficiency. Toxicants can be formed as a result of anthropogenic activities, as well as as a result of natural processes.

Figure 2. PAHs diagnostic ratios for soils of monitoring sites situated through the prevailing wind direction

However, PAHs are not formed singly they always present a mixture [16]. The ratio of some PAHs contained in the soil will depend on the material from which they are formed, for example, the chemical composition of oil or coal; kind of burnt wood, etc. [17], and from the conditions of formation: temperature, oxygen access. Diagnostic ratios determine the origin of pollution by comparing the relative concentrations of individual PAHs according to the following indicators (table 7) [18].

Table 7. PAH diagnostic ratios of individual pah. Pah source identification coefficients

| Ratios                                              | Range of values | Source            |
|-----------------------------------------------------|-----------------|-------------------|
| ∑ Low molecular weight PAHs / ∑ High molecular weight PAHs | < 1             | Pyrogenic         |
| ∑ High molecular weight PAHs                        | > 1             | Petrogenic        |
| Benz (a) anthracene / (Benz (a) anthracene + Chrysene) | < 0.2           | Petrogenic        |
|                                                     | 0.2–0.45        | Coal pyrolysis    |
|                                                     | > 0.45          | Car emissions     |

The highlighted area in Figure 2 indicates the pyrogenic-coal origin of PAHs in the soils of monitoring sites located along the line of the prevailing wind from NPP. Since these diagnostic ratios are characteristic of soils of all monitoring sites located along the line of the prevailing wind rose from NPP, this may indicate the direct effect of the enterprise on the content of PAHs in the soils of the studied territory.

5. Conclusion

Thus, a significant excess of the content of hazardous ecotoxicants – PAHs in the soils of the impact zone of NPP was revealed, compared to the soil in the background regions. The maximum technogenic load is experienced by the soil of monitoring site No. 4 (1.6 km NW), where PAH content is exceeded by 17 times compared to PAH content in the background areas. It was established that in the soils of monitoring sites located along the line of the prevailing wind, the total PAH content decreases with distance from the emission source. In the soils of the monitoring sites located around NPP, the accumulation of PAHs depended more on the soil properties than on the distance and location of the soil of the monitoring site relative to the NPP.

The excess of MPC of BaP in soils of all monitoring sites located along the line of prevailing winds was recorded. The maximum value of MPC of BaP was found in the soils of site No. 4 (17.4 MPC). Sanitary status of soils according to BaP classifies the soils of the study area as highly contaminated soils.
The diagnostic ratios of individual PAHs to each other and the total content of low molecular weight PAHs to the total content of high molecular weight PAHs have confirmed the significant effect of NPP on the soil adjacent to the emission source. The pyrogenic-coal origin of PAHs in soils most susceptible to the influence of NPP monitoring sites is established.

Acknowledgment
The present study was done with the financial support of the Ministry of Education and Science of the Russian Federation for applied scientific research and experimental development as part of the implementation of the Federal Targeted Program “Research and Development in Priority Areas of the Development of the Scientific and Technological Complex of Russia for 2014-2020”, Agreement No. 14.577.21.0292 from 04.12.2018; Project of the President of Russian Federation no. MK-2973.2019.4; RFBR no. 19-29-05265 MK and 19-34-90185.

References
[1] Lazarev G E and Shapovalov A B March 2017 The formation of dominant emissions during energy generation Ecological and environmental problems of modern society and their solutions XIII Int. sci. Conf. (Moscow) pp 53–66
[2] Corrigenda to OECD Publications Retrieved from: http://www.oecd.org/about/publishing/corrigenda.htm Electricity information 2018.
[3] Kumar V, Kothiyal N C, Saruchi P V and Sharma R Jul 2016 Sources, distribution, and health effect of carcinogenic polycyclic aromatic hydrocarbons (PAHs)--current knowledge and future directions J. of the Chinese advan. Mater. society 4(4) 302–21
[4] Abdel-Shafy H I and Mansour M S December 2018 Phytoremediation for the Elimination of Metals, Pesticides, PAHs, and Other Pollutants from Wastewater and Soil (Singapore: Springer) pp 101–36
[5] Rovinsky F Ya, Teplitskaya T A and Alekseeva T A 1988 Background monitoring of polycyclic aromatic hydrocarbons p 44
[6] GN 2.1.7.2041-06 Maximum permissible concentration (MPC) of chemicals in the soil 2006 (Moscow)
[7] Sushkova S N, Minkina T M, Deryabkina I G et al Mach 2019 Environmental pollution of soil with PAHs in energy producing plants zone Sci. of the Total Environ. 655 232–41
[8] SanPiN 2.2.1/2.1.1.1200-03 Sanitary and epidemiological rules and standards SanPiN 2.2.1/2.1.1.1200-03 Sanitary protection zones and sanitary classification of enterprises, structures and other objects 2003 (Moscow)
[9] Don’s Ecological Bull. On the State of the Environ. and Natural Resour. of the Rostov Reg. in 2017 2018 10–18
[10] Sushkova S N, Deryabkina I G, Antonenko E M et al August 2018 Benzo[a]pyrene degradation and bioaccumulation in soil-plant system under artificial contamination Sci. of the Total Environ. 633 1386–91
[11] GOST (State Standard) 17.4.4.02-84 Nature Protection. Soils. Methods for Sampling and Preparation of Soil for Chemical, Bacteriological, and Helminthological Analysis 1984 (Moscow: Izd. Standartov)
[12] Sushkova S N, Minkina T M, Mandzhieva S S et al April 2015 New alternative method of benzo[a]pyrene extraction from soils and its approbation in soil under technogenic pressure J. of soils and sediments 16(4) 1323–9
[13] ISO 13877-2005 Soil quality-determination of polynuclear aromatic hydrocarbons – Method using high-performance liquid chromatography 2005
[14] Wenzl T, Simon R, Anklam E and Kleiner J Analytical methods for polycyclic aromatic hydrocarbons (PAHs) in food and the environment needed for new food legislation in the European Union. Trend. Anal. Chem. 25(7) 716–25
[15] SanPiN (sanitary and epidemiological rules) 2.1.7.1287-03 Sanitary and epidemiological requirements for soil quality Decree of the Chief State Sanitary Doctor of the Russ. Fed. of April 2007 no 20

[16] Tobiszewski M and Namieśnik J Mach 2012 PAH diagnostic ratios for the identification of pollution emission sources Environ. Pollut. 162 110–9

[17] Gennadiev A N, Pikovsky Yu I, Smirnova M A et al Mach 2016 Hydrocarbon state of soils of background taiga landscapes (south-western part of the Ustyansky plateau) Vest. Moskovsky Univer. 5(3) 90–7

[18] Chunhui W A N G, Shaohua W U, Shenglu Z H O U et al February 2017 Characteristics and source identification of polycyclic aromatic hydrocarbons (PAHs) in urban soils: a review Pedosphere 27(1) 17–26