Monitoring of the polycyclic aromatic hydrocarbons content in chernozem soils under longterm industrial pollution

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Abstract. Studies of polycyclic aromatic hydrocarbons (PAHs) content in soils adjacent to power plants is essential to determine the environmental risks. The monitoring was carried out over 3 years on the territory under the emissions of Novocherkassk Power Station (NPS). A significant excess in the PAHs content (up to 84–86%) in the soils under long-term industrial pollution was found compared to the background soil. The total PAHs content in the NPS emissions zone soils increased from 3553.1±25.4 to 4137.0±37.6 μg kg\(^{-1}\) at the most contaminated area located 2.1 km away from the enterprise in the prevailing wind direction. The increment was mostly observed in the content of high molecular weight (HMW) PAHs near the territories used for agricultural production. The LMW PAHs / HMW PAHs ratio of more than 1 indicates PAHs natural origin in the reference area soil. Moreover, it was found that in the NPS emissions zone soils the LMW PAHs / HMW PAHs ratio was 0.12–0.34 on the average, which is less than 1, that shows an anthropogenic origin of PAHs. The increase of this ratio with distance from NPS indicates lower anthropogenic pressure on the soil with longer distance from the emission source.

1. Introduction

The monitoring studies of sanitary soil conditions are primary in assessing food safety and carcinogenic risk and serve as the basis for engineering and survey work. This interest in soil quality is associated with its ability to accumulate hazardous chemical pollutants, including xenobiotics [1, 2].

Polycyclic aromatic hydrocarbons (PAHs) are a class of widespread carcinogenic pollutants. These compounds tend to accumulate in natural and technogenic landscapes due to imperfect technologies for the extraction, processing and operation of fuel [3, 4]. These substances are characterized by the presence in their structure of two or more condensed benzene rings. Compounds with 2 and 3 benzene rings are classified as low molecular PAHs (LMW PAHs), and those with 4, 5 and 6 benzene rings are referred to as high molecular weight PAHs (HMW PAHs).

Several studies have been published in the International Agency for Research on Cancer's annual reports have shown that high molecular weight PAHs are more carcinogenic than low molecular weight PAHs [5, 6]. The list of priority pollutants of the US Environmental Protection Agency is often used in assessing PAHs–contaminated soils. It includes 16 representatives of the PAH group. According to Maliszewska–Kordybach [7], the total contents in soils should not exceed 200 mg kg\(^{-1}\). However, as shown by a number of studies, in the soils of impact zones of industrial enterprises, the total PAHs content can reach 6000 mg kg\(^{-1}\) [8–13].
Fuel and energy enterprises are one of the most common sources of anthropogenic PAHs in the environment. According to the World Health Organization [14], the extraction and use of solid fuels increase the risk of death associated with upper respiratory tract diseases. Despite these risks, coal production over the past 10 years has increased by 5% in the world [14] and up to 10% in the Russian Federation [15]. By 2018, the share of coal in the fuel structure of the world's energy system was 38% [16], and in the Russian Federation, it was 64% [17]. Thermal power plants contribute to the country's unfavorable environmental situation, where 22% of the gross pollutant emission is accounted for the provision of electricity [18].

In the Rostov Region, more than 70% of all discharged wastewater is associated with electricity provision [12, 17, 18]. The Rostov Region territory has one of the largest power plants Novocherkasks Power Station (NPS), whose contribution is 1.4% of all power stations' total electricity production all over the Russian Federation [15, 16, 18].

Along with this, Rostov Region is a region with a highly developed agricultural production in the land fund structure, of which 87.8% of the area is occupied by agriculture with more than 51% being arable land [16, 17]. The adjacent location of agricultural land with industrial land poses a threat to the population's life and health, which necessitates monitoring of soils around industrial enterprises, including NPS.

The purpose of the present research was monitoring of the PAHs content in chernozem soils under long–term industrial pollution. In this regard, the dynamics of the PAHs content in the soils was investigated in the last 3 years during 2018–2020.

2. Object of study
The object of the study was the soils of the territories adjacent to NPS. NPS is an enterprise with an electric output of ≈ 19 GW. NPS occupies one of the leading places within the Russian Federation in terms of electricity generation [17]. According to sanitary rules of the Russian Federation (SanPiN 2.2.1/2.1.1.1200–03) [18], it belongs to the first hazard class enterprises.

The monitoring of soils in the NPS emissions zone has been carried out for more than 18 years. The study area's monitoring sites were located around the enterprise at a distance up to 3 km and along the line of the prevailing wind in the north–western direction at a distance of up to 20 km. The soil of the specially protected natural area “Persianovskaya reserved steppe” situated at the opposite side of the prevailing wind direction was used as a background (table 1).

| Monitoring plot no. | Distance from NPS, km | Soil type       | Soil assignment        |
|---------------------|----------------------|-----------------|------------------------|
| 1                   | 2.1                  | Haplic Chernozem | agricultural production|
| 2                   | 7.0                  | Haplic Chernozem | undefined              |
| 3                   | 15.4                 | Haplic Chernozem | undefined              |
| 4                   | 19.7                 | Haplic Chernozem | undefined              |
| background           | 10.0                 | Haplic Chernozem | protected natural area |

This study presents the total content of 16 PAHs in the soils of four the most contaminated monitoring sites located in the north–western direction. The study area soil cover is represented by Haplic Chernozem with the soil properties presented in table 2.

The physical and chemical characteristics of the study area soils indicate their high sorption potential in relation to PAH [19–21].

3. Method of research
Sampling was carried out annually during 3 years from the depth of 0–20 cm. The extraction of pollutants from soil samples was carried out in accordance with the GOST 28268–89 method [22].
Table 2. Physics and chemical soil properties.

| Monitoring plot no. | Physical clay content, % | C<sub>org</sub>, % | CaCO<sub>3</sub>, % | pH<sub>water</sub> |
|---------------------|--------------------------|-------------------|-------------------|-----------------|
| 1                   | 56.4                     | 31.2              | 2.6               | 7.4             |
| 2                   | 58.8                     | 32.9              | 3.5               | 7.9             |
| 3                   | 55.3                     | 26.5              | 2.3               | 7.9             |
| 4                   | 53.5                     | 26.7              | 2.3               | 7.7             |
| background           | 52.2                     | 30.0              | 2.5               | 7.5             |

Briefly, a weighed portion of 1 g of the sample was boiled in a 2% alcohol solution of potassium hydroxide for 3 hours to remove interfering lipid components of the soil. Then, the pollutants were extracted with hexane in triplicate. The total PAHs contents in the extract were quantified by high-performance liquid chromatography (HPLC) on an Agilent 1260 chromatography with fluorometric detection. Acetonitrile was used as the liquid phase, and silica gel was used as the solid phase.

The calculation of PAHs' total content in the extract was carried out, taking into account the moisture content of soil samples, determined according to methodological requirements [23].

It should be noted that before the injection of the main sample, the HPLC was calibrated. A standard sample with a fixed concentration was injected into the HPLC to detect release time of each component.

The calculation of the results was carried out according to the standard external method:

\[
X = \frac{S_XV_3100}{AK_pM(100-W)} \cdot 1000, \tag{1}
\]

where:

- \(X\) – mass concentration of individual PAHs in the extract, µg kg\(^{-1}\);
- \(S_X\) – peak area of the determined PAH, mV×s;
- \(V_3\) – extract volume, cm\(^3\);
- \(A\) – relative calibration factor, mV×s×cm\(^3\) µg\(^{-1}\);
- \(K_p\) – correction factor for sample preparation losses;
- \(M\) – mass of the sample taken for analysis, g;
- \(W\) – sample moisture, %.

\[
W = \frac{m_1-m_2}{m_1} \cdot 100, \tag{2}
\]

where:

- \(m_1\) – weight of weighing bottle before drying, g;
- \(m_2\) – weight of weighing bottle after drying, g;
- \(m\) – weight of empty bottle, g.

4. Results and discussion

The excess of the PAHs total content in the soils of the monitoring sites in the impact zone was established over a 3-year study period compared to the background territory soil. The result showed a 14–16% increase on average over 3 years. The maximum load falls on the soil of site 1 (2.1 km northwest), where the total PAHs content on average over 3 years of research was 20 times higher than in the soil of the background area. This observation was accounted for 3826.9±35.4 µg kg\(^{-1}\) on average over 3 years (figure 1).

The total PAHs content in the background area soil was observed to be in the averaged value of 258.7±12.6 µg kg\(^{-1}\).
It was established that the total PAHs content decreased in soils with increasing distance from the emissions source. In the soil of monitoring site no. 1 (2.1 km northwest) it was $3826.9\pm35.4 \mu g \ kg^{-1}$ and decreased in the soil of site no. 4 (19.7 km northwest) up to $1099.1\pm26.8 \mu g \ kg^{-1}$ on average over 3 years of research. Comparing with the data of Maliszewska–Kordybach [7], it can be noted that the soils of the monitoring sites located in the northwest direction from the NPS for the entire study period were highly polluted (table 3).

**Table 3. Soil pollution classification [7].**

| Soil pollution class      | $\Sigma16$ PAHs, mkg kg$^{-1}$ |
|--------------------------|---------------------------------|
| Not contaminated         | $< 200$                         |
| Slightly contaminated    | 200–600                         |
| Contaminated             | 600–1000                        |
| Highly contaminated      | $> 1000$                        |

Comparing with the data of Maliszewska–Kordybach [7], it can be noted that the soils of the monitoring sites located in the northwest direction from the NPS for the entire study period were highly polluted (table 3).

**Figure 1.** The total PAHs content in the soils of the study area.

**Figure 2.** The total PAHs content in the soils of the Novocherkassk Power Station impact zone.

* The figure shows average values.
The LMW PAHs / HMW PAHs ratio of less than 1 indicates an anthropogenic source of PAHs origin in the soil, according to a number of reports [24–26]. In addition, this indicator reflects the predominant composition of PAHs in soils, and the LMW PAHs / HMW PAHs ratio is less than 1. With a high total PAHs content in the soil, serious concerns are raised, primarily associated with the carcinogenic activity of HMW PAHs. It was found that in the soils of the NPS impact zone the LMW PAHs / HMW PAHs ratio was less than 1.

Figure 3. Total PAHs content in the soils of the Novocherkassk Power Station impact zone.

In general, it increased from the soil of the monitoring site with the maximum load from NPS (no. 1 – 1 km northwest) to the soil of the monitoring site located 19.7 km northwest (no. 4 – 2.1 km northwest). This circumstance indicates a decrease in the technogenic load on soils with increasing distance from the emission source (table 4).

The exception was the soil of monitoring site No. 2, in which this indicator was lower than in the soils of other monitoring sites. This circumstance is most likely due to the specific features of the properties with an alkaline pH, the highest organic carbon content, and the largest number of particles with a size of < 0.01 mm. The most favorable conditions for the PAHs sorption can be created in the soil of monitoring site no. 2 compared to the soils of the rest of the study area. This assumption is confirmed by many studies of effect of the soil properties on the accumulation of PAHs in soil [19–21]. The LMW PAHs / HMW PAHs ratio of more than 1 indicates the natural origin of PAHs in the
background territory soil, despite a slight excess, according to the Maliszewska–Kordybach classification [7].

**Table 4.** Average values of LMW PAHs / HMW PAHs ratio for different monitoring plots.

| Monitoring plot no. | 1     | 2     | 3     | 4     |
|---------------------|-------|-------|-------|-------|
| Background          | 1.05  | 0.25  | 0.12  | 0.31  |

Figure 3 shows the dependence of the increase in the LMW PAHs and HMW PAHs content on the increase in the total content of pollutants in the soil. In general, the increase in total content of PAHs in the NPS emissions soils zone over a period of three years of research is primarily due to the accumulation of HMW PAHs in the soil.

The share of the increase in the most dangerous HMW PAHs is clearly expressed for the soils of monitoring sites no. 2 (increase by 22.9%) and no. 3 (increase by 24.6%) (figure 3). This may indicate that soils located at a distance of up to 15.4 km in the northwest direction from NPS are mostly exposed to the HMW PAHs input.

5. **Conclusion**

Thus, the study showed an excess of the total PAHs content in the soils of the NPS emission monitoring sites compared to the soils of the background territory of up to 84–86% on average. According to the classification of total PAHs content in contaminated soils exposed to the NPS impact, the soils were classified as heavily contaminated during all observation periods. The maximum technogenic load from the enterprise was set for the soil of monitoring site no. 1, located closest to the NPS in the prevailing wind direction (2.1 km northwest). Further, with distance from the emission source, the total PAHs content in soils decreased from 3826.9±35.4 μg kg⁻¹ in the soil of site no. 1 (2.1 km northwest) to on average 1099.1±26.8 μg kg⁻¹ in the soil of site no. 4 (19.7 km northwest) over 3 years of research. The LMW PAHs / HMW ratio established for all monitoring sites around NPS of less than 1 indicates the anthropogenic origin of pollutants in the soil. During the period of three years of research, an increase in the total PAHs content in the studied NPS emissions zone soils was established. In this case, the content of HMW PAHs increased to a greater extent than LMW PAHs. In general, this effect in the soils of the impact zone monitoring sites was observed at a distance of up to 15.4 km (no. 3 northwest) from the emission source and weakens in the soil of site no. 4 (19.7 km northwest).

**Acknowledgments**

The research was carried out with the financial support of the RFBR project no. 19-29-05265 mk, 19-34-90185.

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