New approaches and methods for technologically polluted territories remediation

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) have been a major concern because of their carcinogenicity, mutagenicity, teratogenicity and wide distribution in the environment. Over 90% of PAHs in the environment exist on soil surface/sediment. Thus, it is critically important to understand the patterns of BaP accumulation and transformation peculiarities in soil for the technologically polluted territories remediation. It was studied the soils contaminated by power energy enterprise working on the burning coal with over 70% emissions containing PAHs. The territory adjoined to the Novocherkassk Power Station showed an intensive accumulation of polyarenes increased from 2012 up to 2019. With increasing distance from the plant, the PAHs accumulation in soils gradually decreases. The maximum of the PAHs content in the soil was found on the monitoring site located at 1.6 km from the enterprise 4185.4 ± 167.4 ng/g, the lowest level of PAHs was found at 20 km (1185.5 ± 45.0 ng/g PAHs). PAHs extraction from collected soil samples was performed using new ecologically clean express-method of subcritical water extraction without organic solvents use. The approaches for improving the contaminated territory ecological situation have been proposed including biological remediation by biochar, activated carbon.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most significant environmental contaminants with mutagenic and carcinogenic properties to all living organisms [1]. Sixteen PAHs compounds are obligatory controlled all over the world that regulated by legislation because of their carcinogenicity, mutagenicity and toxicity [2], [3]. These compounds are very persistence and hydrophobicity in environmental objects especially during soil contamination because of complicated soil matrix structure [4]. Soil has a high ability to PAHs accumulation that cause a high availability of these compounds to plants [5], [6], [7]. The assessment of regularities of biogeochemistry PAHs in soil-plant system is one of the major indicators in the environmental monitoring system [8].

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Benzo[a]pyrene (BaP) is the main marker of pollution of soil-plant system by PAHs [2], [9]. Knowledge of soil contamination with BaP needed to minimize the risk of human exposure and of environmental contamination [10], [11]. The BaP content in all environmental matrices and food is under obligatory regulations worldwide [2], [12], [13].

The present study was aimed to research the new approaches and methods for technologically polluted territories remediation. The content of PAHs in contaminated soil was determined using new ecologically friendly method of subcritical water extraction instead of traditional methods for PAHs determination using a large amount of organic solvents. The developed method was approbated during ecological monitoring performed in the area of the Novocherkassk power station (NPS), which was the main pollution source of the atmospheric air not only in the city of Novocherkassk, but also in the entire Rostov Region, and makes the major contribution to the environmental pollution in this region.

2 Methods

Studies were carried out with the soil sample collected from the upper (0-20 cm) layer of carbonate heavy loamy chernozem (virgin) on the territory of the NPS emission zone located in Rostov Region (South of Russian Federation). This soil has the next characteristics: Corg 3.4%, pH 7.3, cation exchange capacity (CEC) 37.1 mMol(+)/100g; content of CaCO3 0.1%, physical clay 53.1% and clay 32.4% [13]. The monitoring plots were situated at distance 1,6nw, 5nw, 15nw, 20nw of the NPS along the prevailing wind direction rose.

A new method was used for extraction of BaP from soil and plant samples, which is based on extraction of pollutants with subcritical water [14], [15]. Subcritical water extraction of BaP from soil samples was conducted in a specially developed extraction cartridge made of stainless steel and equipped with screw-on caps at both ends. The extraction cartridge containing a sample and water was placed into an oven equipped with a temperature regulator [16]. The process of BaP analyses in soils based on subcritical water extraction consisted of the following step by step operations. An air-dried sample of the soil/plant sample ground in a porcelain mortar and passed through a 1 mm sieve. One gram of sample placed into the extraction cartridge and 8 ml of double-distilled water added.

Extraction conducted under optimum conditions (30 min at 250°C and 50 atm). After cooling, the content of the cartridge was filtered (Whatman no. 1) into a conical glass flask and washed with 2 ml of double-distilled water. This operation repeated two or three times, until the filtrate was clear. The aqueous solution re-extracted three times with 5 ml of n-hexane by shaking for 15 min in a separatory funnel. The hexane extracts were combined and filtered through anhydrous Na2SO4 and evaporated to dryness in a pear-shaped flask on a vacuum evaporator in a 40 °C water bath. The residue dissolved in 1 ml of acetonitrile by shaking for 30 min.

Liquid-liquid re-extraction of BaP from water extract is obligatory because BaP does not dissolved in the water. Concentrating the extract, if necessary, its purification by column chromatography and determination of BaP by HPLC using fluorimetric detection are required steps BaP detection in water and other objects. The process of shaking a mixture of BaP microvolume extracted into the organic matrix helps directly emulsify in the aqueous solution. The amount of organic solvent (matrix) must be sufficiently high for the extraction of molecules of BaP, but at the same time sufficiently small for the concentration of the impurity (for the most intense luminescence), but needs to obtain the
structure in the luminescence spectra HPLC. Shaking during 30 min required for BaP entirely transition to extract.

BaP in the extracts was quantified by HPLC (Agilent 1260) with simultaneous ultraviolet and fluorescence detection following ISO 13877 requirements [17]. The results were used to determine correlation coefficients between the initial BaP concentrations in the chernozemic soil and spring barley plants, as well as to estimates equation coefficients of linear dependence of K, T50 and Kp from Co. The parameters calculated with the help of Sigma-Plot software. Solvents and reagents were HPLC grade and included ethanol (96%, analytical grade), n-hexane (99%, analytical grade), potassium hydrate (98%, analytical grade), acetonitrile (99.9%, analytical grade), NaOH (97%, analytical grade), and anhydrous Na2SO4. A BaP standard in acetonitrile (Sigma-Aldrich CAS Number 50-32-8) with concentration 200 mkg/cm3 used to prepare standards for HPLC analyses.

Data handling and statistical analyses conducted using STATISTICA 11.0.

3 Results and Discussion

The dynamics of changes in the PAHs content and distribution in the soils of the NPS emission zone, the largest condensation power plant in the region, has been studied for a 9-year period of monitoring studies. Generalization of the long-term monitoring data showed that the accumulation of PAHs in soils depended on the distance and location of the sites in relation to the emission source, as well as on the volume of the enterprise's emissions. Emissions from NPS are mainly represented by ash from processed coal. A feature of the coals supplied to NPS is their enrichment with a wide range of toxic elements with organic and inorganic nature [14]. At the end of the 90s, the total volume of emissions from NPS reached 139 thousand tons. As a result of re-equipment of NPS, which began in 2000, the share of gas in fuel by 2004 amounted to more than 40%. This led to a decrease in solid emissions into the atmosphere to 54 thousand tons, i.e. more than doubled. Over the next 10 years, the annual volume of solid emissions increased and remained in the range of 75-117 thousand tons until 2014, and in recent years the volume of emissions has reached 220 thousand tons (Fig. 1).

![Fig. 1. Novocherkassk Power Station total volume of emissions.](image-url)

It was found that in the soils of all sites located along the prevailing wind direction, during the 9-year observation period, there was a tendency to an increase in the PAHs content. The steady trend of an increase in the total PAHs content in the soil over time was established on the soil with the highest aerotechnogenic load. At the same time, the
curve of the dynamics of the PAHs total accumulation in the soil was characterized by significant fluctuations. Since 2012, an increase of the PAHs concentration in soils has been observed, due to an increase in the volume of emissions from the enterprise. This tendency is especially character for the soil of site No. 4 with the maximum level of contamination.

The results of long-term monitoring made it possible to identify general patterns in their accumulation in soils. The main mass of pollutants accumulates in the soils of the north-western direction from the NPS, which coincides with the main direction of the winds in this area. The greatest pollution in this direction was observed within a radius of up to 5 km with a maximum at a distance of 1.2-1.6 km. With increasing distance from the plant, the accumulation of PAHs in soils gradually decreases. A decrease in the total content of PAHs in the soil of the monitoring site located 5 km from the enterprise (No. 8) in comparison with the soil of site No. 4 (more than 1.5 times), indicates that the area of the densest smoke plume distribution is about 5 km, and the maximum fallout occurs at a distance of about 1.6 km (4185.4 ± 167.4 ng/g PAHs) and decrease at a distance of 20 km (1185.5 ± 45.0 ng/g PAHs) (Fig. 2).

**Fig. 2.** PAHs content in soils of monitoring plots situated along the prevailing wind direction from emission source.

Due to the fact that at the current level of industrial development it is impossible to exclude the impact of pollutants on the environment, it is necessary to develop new and improve existing technologies for the restoration of PAHs environmental objects. One of the most effective methods for the restoration of PAHs contaminated soils under conditions of technogenic pollution is the method of sorption bioremediation, which, during the purification process, leads to the complete decomposition of organic pollutants to biophilic substances and allows for in situ soil cleaning. The most important requirements for modern sorbents are as follows: environmental safety, high capacity and high binding constants of toxicants.

At present, in terms of the development and implementation of "green" technologies, the issue of using environmentally friendly natural compounds for detoxification of contaminated soils is becoming more and more urgent. In the domestic literature, there are a number of works devoted to the bioremediation of contaminated soils through the use of natural sorbents, as well as the cultivation of hyperaccumulator plants of certain chemical elements on them [18]. Most of the research in this area belongs to foreign authors [19]. In this regard, interest in organic sorbents is growing. Using organic sorbents is a cost-effective way to improve environmental conditions. Such technologies of soil reclamation not only contribute to the effective restoration of all its properties, but also do not pose a threat of secondary pollution, and are also inexpensive.
Activated carbon is one of the most effective sorbents removing pollutants from the soil. As the most powerful adsorbent, it can handle a wide variety of pollutants. In the branched pore system of activated carbons, there are centers that bind the molecules of pollutants. At the same time, the porous structure of coals is very diverse. Small molecules, such as phenol and chloroform, are sorbed in the smallest pores, while larger molecules are sorbed in medium-sized pores. Large macropores serve as transport tunnels through which pollutant molecules diffuse.

Among carbon sorbents, the use of biochar is becoming more and more popular, which has sorption properties similar to that of activated carbon, but much cheaper [20]. Biochar (biochar) is a fine-grained, highly porous material with a large surface area. The high specific surface area and cation exchange capacity, which is largely determined by the source material and the pyrolysis temperature, makes possible an increased sorption of both organic and inorganic pollutants on the surface of a substance and a decrease in their mobility in contaminated soils.

4 Conclusions

The tendencies in the distribution and accumulation of BaP in the studied soils coincided during the 8 years of monitoring studies. The toxic emissions from the NPS are the main factor of technogenic impact on the soils in the region under study; vehicle exhausts can be sources of additional PAHs emission. A gradual increase of the pollutant content in the soils of the studied areas was revealed during the period from 2012 to 2019, which was related to the significant increase in the volume of pollutant emissions from the plant. In spite of the conservation measures undertaken at the power plant, the atmospheric emissions from the NPS have still the predominant effect on the environmental situation in the adjacent areas at present. The new approaches for improving the contaminated territory ecological situation have been proposed including biological remediation by biochar, activated carbon and other sorbents.

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