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Monitoring Researches of the Benzo[a]Pyrene Content in Soils Under The Influence of The Technogenic Zone

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Abstract: The regularities of benzo[a]pyrene accumulation and its distribution in the chernozemic soils being under the influence of aerotechnogenic emissions of the power complex enterprise were revealed on the basis of long-term monitoring researches for the first time. It is shown that the soils adjacent to a source of emission are polluted by benzo[a]pyrene at distance to 5 km. Trends in the accumulation of benzo[a]pyrene in soil zones of influence of the thermal power plant have been investigated over a 10-year period of monitoring observations. The assessment of soils pollution extent by benzo[a]pyrene is given in detail in the present manuscript.

Key words: Benzo[a]pyrene · Soils pollution · Aerotechnogenic emissions

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a typical class of persistent organic compounds derived from natural sources such as forest fires or/and anthropogenic processes such as urban and industrial activities and are prevalent in the environment. Sixteen PAHs compounds have been recommended as priority pollutants by the United States Environmental Protection Agency (USEPA) because of their carcinogenicity, mutagenicity and extreme toxicity [1-4]. These compounds are likely to accumulate in soils for many years because of their persistence and hydrophobicity. As a result, soils may be an important reservoir of PAHs [5-7]. The assessment of soils contamination is one of the major indicators in the environmental monitoring system. The main marker of soils pollution by PAHs is benzo[a]pyrene (BaP) [4]. Knowledge of soil contamination with BaP is needed to minimize the risk of human exposure and of environmental contamination [8, 9].

Enterprises of power energy are the active sources of polycyclic aromatic hydrocarbons (PAHs) environmental pollution. The most powerful enterprise of power complex in Rostov region is coal-fired Novocherkassk's power station (NPS). The total amount of emissions takes more than 90000 tons per year and about 10% from them are PAHs. Research shows us that individual heating systems represent more powerful source of PAHs environmental emissions than transport [10-12].

The research object was the soil in the emissions zone of NPS. Research about the environment of NPS emissions zone from 2001 to 2010 showed that this enterprise, one of the largest thermal power plants of Russia working since 1965-1971, is the main pollutant contribution in Rostov region [13-15]. An extremely negative influence on the environment in the city and adjacent territories also amplifies the fuel used at the enterprise, which don't conform to quality requirements [16]. The station annually consumes over 4.5 million tons of coal, 0,7 million tons of fuel oil and 380 million m^3 of gas. Coal arrives at the station without processing at concentrating factories. Actually NPS uses coal which has an ash-content and the sulfur content considerably exceeding projected. Coal is enriched with a wide range of heavy metals and toxic elements (Cu, Zn, Hg, Pb, Mn, As, etc.) and also radionuclides (Th, Sr, etc.) [16].

The main components of NPS's emissions are ashes, sulphurous anhydride, nitrogen oxides, soot (over 30 tons/year), vanadium pentoxide (about 8 tons/year), iron oxide (over 5 tons/year), chromic anhydride (about 0,1

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tons/year), fluoric hydrogen (7 kg/year), etc. Up to 85% of chemical elements containing in initial coal remains in ashes [14-17].

The purpose of research is the assessment of BaP content in soils of NPS emissions zone.

Research Tasks:

- Evaluate the content and distribution of BaP in soil monitoring plots of zone NPS influence.
- To study the trend of BaP accumulation in soils of investigated territories based on the results of long-term monitoring observations.
- Make a vote of the soil's chemical contamination under the influence of aerotechnogenic emissions of NPS.

MATERIALS AND METHODS

Studies were conducted on the soils of monitoring plots subjected to NPS emissions. In 2000, monitoring plots were established at different distances from the NPS (1.0-20.0 km). They coincided with the air sampling sites for the ecological certificate of the plant (plots 1, 2, 3, 5, 6, 7) (Fig. 1). The most attention was paid to the main wind direction from the contamination source to the northwest through the residential areas of Novocherkassk (zones 4, 8, 9, 10). The monitoring plots were located on virgin lands or fallow areas. Soil samples for the determination of soil properties and the contents of BaP were taken from a depth of 0-20 cm. The soil cover in the region under study consisted of ordinary chernozems, meadow-chernozemic soils and alluvial meadow soils (Table 1). The majority of the soils of monitoring plots were ordinary chernozems; the soils of plots 9 and 10 were used as control soils. The low-humus calcareous sandy alluvial meadow soil (plot 2), which had a light texture and a low cation exchange capacity (CEC) and the low-humus silty-clayey meadow-chernozemic floodplain soil (plot 3) with a high CEC that differed from the control soils. These differences are considered in the discussion of the results.

According to the prevailing direction on the district of a wind rose the main direction of distribution of NPS atmospheric emissions was defined. It is a zone located on a straight line from a source of pollution through inhabited territories of Novocherkassk and Krivyanskii village. Samples were collected in soils of monitoring platforms No. 4, No. 8, No. 9, No. 10, in the area of the prevailing direction of a wind rose (Fig. 2). The requirement for the location of the monitoring platforms is the existence of a virgin soil cover or deposits (not subjected to technical processing).

The samples were collected layer-by-layer for the BaP content definition in soils. The soils cover of the monitoring territory is presented by ordinary carbonate heavy loamy chernozem, grassland-chernozem heavy and medium loamy, alluvial types of a flood plain of river Tuzlov (Table 1).

The most part of the territory is occupied by ordinary chernozem revealed the following physical and chemical properties: a clay content of 286 g kg^{-1} and a physical clay content of 471 g kg^{-1}, pH of 7.3, organic C content of 23 g kg^{-1}, $CaCO_3$ content of 1 g kg^{-1}, CEC of 37.1 mM kg^{-1} and exchangeable Ca^{2+}, Mg^{2+} and Na^{+} contents of 29.5, 5.5 and 0.1 mM kg^{-1}, respectively.

Soil samples were selected and prepared for the chemical analysis according to GOST 17.4.4.02-84 [2] requirements. BAP extraction from soils was carried out by a saponification method. The sequence of operations when carrying out the analysis is schematically shown in Fig. 2.

A 1-g aliquot of air-dried soil sample was placed in a conical flask and 30 ml of 2% solution of NaOH in ethanol was added. The mixture was boiled on a water bath for 3 h. After cooling, the liquid layer was decanted into another flask and 5 ml of double-distilled water and 15 ml of n-hexane were added. The flask was placed on a rotary shaker for 10 min, then transferred to a separatory funnel to collect the hexane layer. The hexane extraction was repeated twice. The combined hexane extract was transferred to a conical flask and washed with water until neutral reaction (using indicator paper), transferred to an amber flask containing 5 g anhydrous Na_2SO_4 and allowed to stand overnight at 5°C. The dehydrated extract was transferred to a round-bottom flask and evaporated to dryness by rotary evaporation in a 40°C water bath. The extract residue was dissolved in 1 ml of acetonitrile and analyzed by HPLC.

BaP in the extracts was quantified by HPLC (Model 2000, Thermo Separation Products, Waltham, MA, USA) with simultaneous ultraviolet (UV-1000) and fluorescence (FL-3000) detection following ISO 13877 requirements [18]. The BaP peak on chromatograms of soil sample extracts was identified by comparing retention time to that of the analytical standard sample using the two detectors. The limit of BaP detection and quantification were determined using standard solutions and calibration curves. A calibration standard was inserted after every six samples to correct for drift in retention time within a run.

Table 1: Properties of Novocherkassk's power station (NPS) emissions zone soils (an average for 2000-2011gg.)

Number of monitoring plot	Soil	Physical clay, %	Clay, %	C_{org}, %	pH	$CaCO_3$, %	CEC, mmol(+)/100g
1	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	52	27	4,3	7,6	0,5	35,0
2	Low-humus calcareous sandy alluvial meadow soil on alluvial deposits	7	3	3,1	7,5	0,4	10,9
3	Low-humus silty clayey flood-plain meadowchernozemic soil on alluvial deposits	67	37	4,6	7,3	0,2	44,8
4	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	55	29	4,6	7,5	0,7	31,2
5	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	53	27	4,3	7,5	1,0	35,7
6	Low-humus medium-thick clay loamy meadowchernozemic soil on loess-like loams	55	30	4,1	7,7	0,8	32,4
7	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	51	27	4,1	7,6	0,7	31,3
8	Low-humus medium-thick clay loamy meadowchernozemic soil on loess-like loams	60	32	5,0	7,4	0,4	47,6
9	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	52	30	4,2	7,6	0,6	31,4
10	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	53	28	4,6	7,6	0,5	36,0

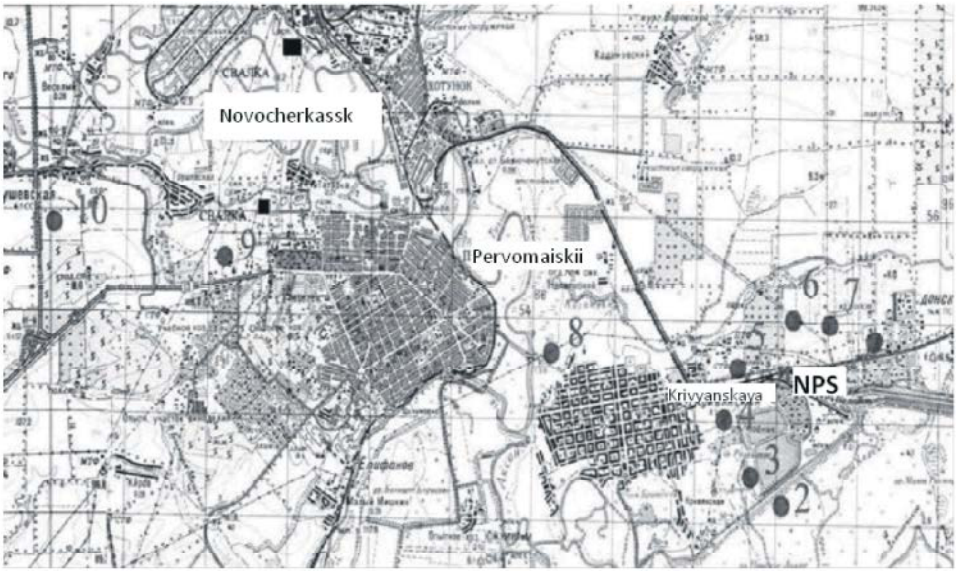

Fig. 1: Schematic map of monitoring plots in the zone affected by the Novocherkassk power station:
Plot No. The direction and distance from NPS:
1 1 km on the northeast;
2 3 km on the southwest;
3 2,7 km on the southwest;
4 1,6 km on the northwest;
5 1,2 km on the northwest;
6 2,0 km on the northwest;
7 1,5 km to the north;
8 5 km on the northwest;
9 15 km on the northwest.
10 20 km on the northwest

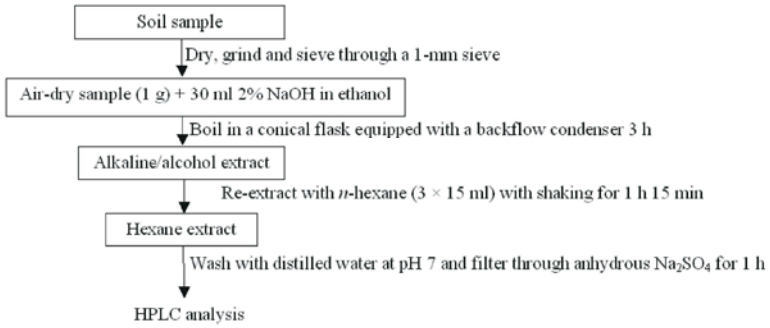

Fig. 2: Scheme for determination of BaP in soils by saponification followed by hexane extraction and HPLC analysis

BaP concentrations in nanogram for gram of soil sample (A, ng/g) were calculated as follows:

$$A = k\ SI \times Cst \times V/(Sst \times m)$$

where Sst and SI = respective areas of BaP peaks in chromatograms of standard and sample solutions; Cst = BaP concentration in standard solution (ng/ml); k = coefficient of BaP recovery from a sample; V = volume of acetonitrile extract used for HPLC (ml); m = mass of the sample (g). Data handling and statistical analyses were conducted using Microsoft EXEL.

Soil properties were analyzed using Russian standard methods [19] (Table 1). Soil organic carbon was measured using 0.4 N potassium bichromate (the Tyurin method modified by Simakov). Soil particle size distribution (silt and clay content) was determined by the pipette method after the pyrophosphate treatment. Cation exchange capacity (CEC) of the soil was determined using 1M ammonium chloride (the Bobko-Askinazi method). The exchangeable potassium was determined by the Machigin (molybdenum blue) method. Adsorbed Na^+ was analyzed by flame atomic adsorption spectrophotometery. Soil pH was measured with a pH electrode using a 1:5 suspension of a soil to water ratio. Exchangeable calcium and magnesium were measured by the titration at pH 12.5-13 and 10 respectively. Carbonates were measured by the Kudrin method using 0.005 NH_2SO_4 and then an excess of the acid was titrated with alkali.

RESULTS AND DISCUSSION

An early research of the ecological condition of the NSP zone showed us that the most dangerous pollutants are BaP and heavy metals [13-16]. The content of BaP in all objects of the ecosystem must be under obligatory control. However, monitoring researches of BaP content are conducted by Committee of environment and natural resources only within the settlement of Novocherkassk. It doesn't demonstrate an overall pollution extent of all NPS emissions area [14, 15].

Monitoring research of BaP content in soils from 2002 to 2011 allow identifying the main trends in pollution by NPS emissions in such important components as the impact zone of the soil. Data analysis within 10 years established that the number of defined compound in soils vary widely (Table 2). The main reason for the variation of the absolute values of heavy metal contents in soils adjacent to NPS can serve as a different load on the power plant energy units, which worked at various powers in different years of observations. Every year emissions to the atmosphere changed (Fig. 3). Two from nine NPS power units were transferred to natural gas from 2007 to 2008. It reduced emissions of BaP in the atmosphere practically twice. Since 2010 the enterprise has been actively working on installing purification filters for catching emissions, also the amount of anthracite coal which used as fuel at the power plant is reduced, transition to natural gas is occurring [14].

The dynamics changes of NPS emissions from 1999 to 2011 are shown in Fig. 3. The accumulation of BaP in the investigated steppe biocenosis occurred as a result of precipitation of solid emissions of NPS in the neighborhood and was dependent on the prevailing wind direction and consumption of vegetation. Should be noted the similar regularities by years in BaP accumulation in the test soils which were taken from the zone of greatest technogenic NPS emissions (Table 2).

The main accumulation of pollutant in 20 cm layer of soils is noted directly in affected zone. These are soils from the territory where plots No. 4, 5, 8, 9 and 10 are located (Table 2). At the same time, some increasing of the BaP content is observed in soils at distance of 20 km from state district power station that is connected with proximity of a site to the highway.

Thus within the observation period in the area there is an active reduction of BaP content in the surface layer of the soil, especially in nearby soils to the enterprise. It can be caused by decrease of emissions of polluting components from enterprise.

The maximum quantity of a pollutant was founded in the soil of the plot No. 4 located mostly close to a source of pollution in the direction of prevailing winds. Value from 2002 to 2004 reached to 423 ng/g in 5 cm soil layer and 249 ng/g in 5-20 cm soil layer that exceeded the BaP maximum concentration limit level in the soil up to 20 times (Table 2). The BaP level in a 5 cm soil layer gradually decreased more than 100 ng/g and made from 173 to 278 ng/g from 2005 to 2009. The same tendencies are observed in underlying layers of soil. Since 2010 the quantity of a pollutant in the soil of the most polluted platform decreased to 78 ng/g and in 2011 it is 56 ng/g in a 5-cm layer.

Similar regularities are observed in changes of pollutant concentrations that proceeded almost synchronously in the soil in 0-5 and 5-20 cm layers (Table 2). However, in the majority of soils their concentration in an underlying layer was lower.

Table 2: The Benzo[a]pyrene content in soils of monitoring plots for 2002-2011 years

Number of monitoring plots,direction and distance from NPS	Selection depth, cm	Benzo[a]pyrene content, ng/g 2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
1. 1,0 Northeast	0-5	69,4±4,3	66,0±7,1	34,7±4,3	62,5±4,8	68,2±4,9	48,4±3,7	56,4±2,4	68,1±2,7	48,1±2,4	23,9±1,8
	5-20	20,1±2,2	14,9±1,5	20,0±2,1	24,5±2,2	28,3±2,4	18,5±1,4	23,0±1,2	22,4±1,9	21,0±0,9	11,7±1,1
2. 3,0 Southwest	0-5	26,2±1,8	33,7±2,7	17,8±1,7	25,4±2,3	15,0±1,3	16,7±1,5	27,8±1,3	15,3±1,3	16,2±0,8	18,5±1,1
	5-20	5,3±1,3	19,6±1,7	9,7±0,5	14,2±1,1	8,0±0,5	13,6±1,1	24,2±2,1	26,3 ±1,7	22,5±1,2	17,3±1,2
3. 2,7 Southwest	0-5	36,4±4,8	27,3±2,2	24,5±2,1	42,3±3,7	89,1±7,8	53,6±4,7	67,4±3,0	123,9±7,4	53,1±2,7	21,4±0,7
	5-20	19,5±1,1	16,0±1,4	17,4±1,1	24,7±2,4	56,3±4,4	38,3±2,9	17,8±0,8	60,8±5,4	17,2±0,7	7,3±0,2
4. 1,6 Northwest	0-5	328,4±57,4	423,1±74,5	303,2±44,8	278,9±34,7	223,5±27,5	198,4±14,6	173,3±4,5	260,4±11,9	78,7±6,3	56,0±4,7
	5-20	129,0±28,0	249,2±37,6	246,4±37,1	167,5±25,4	154,7±14,3	125,1±8,4	110,1±17,4	112,1±6,3	43,9±1,8	34,7±1,9
5. 1,2 Northwest	0-5	144,1±14,5	80,6±22,4	117,1±14,5	138,0±15,7	127,5±12,4	113,2±9,3	113,4±4,9	135,1±8,6	66,5±4,5	41,2±5,6
	5-20	124,6±15,6	39,8±5,3	58,5±4,4	113,2±11,9	104,6±10,1	98,3±7,8	72,8±8,2	86,1±3,9	40,1±2,0	31,4±2,6
6. 2,0 Northwest	0-5	19,2±2,9	48,7±2,9	28,2±2,4	26,1±2,4	35,3±3,4	42,0±3,6	45,8±2,8	66,7±3,2	29,1±2,4	35,9±3,2
	5-20	18,3±2,5	38,5±4,4	10,8±1,0	18,3±1,7	27,2±2,2	23,2±2,4	23,9±1,5	35,4±2,4	11,3±0,5	7,3±0,7
7. 1,5 North	0-5	31,4±2,8	16,6±1,1	11,2±1,1	36,3±3,3	41,4±4,8	35,5±2,9	37,4±2,1	86,9±5,1	37,8±3,2	35,1±4,7
	5-20	16,8±1,9	12,7±0,8	11,5±1,2	17,0±1,1	25,9±2,5	22,4±2,2	14,4±1,1	33,8±1,2	13,2±0,6	14,7±1,3
8. 5,0 Northwest	0-5	152,5±12,4	138,9±12,1	57,7±6,3	58,5±5,6	69,0±5,7	48,3±3,7	59,1±3,9	81,2±4,8	50,9±4,8	32,3±2,7
	5-20	64,4±8,9	118,0±10,0	60,0±6,6	28,6±2,4	34,1±3,8	17,2±1,4	38,7±2,5	27,8±2,4	29,7±2,2	22,2±1,5
9. 15,0 Northwest	0-5	26,2±5,3	17,6±1,5	26,3±2,8	21,7±2,1	23,5±1,8	23,4±2,3	22,4±1,4	23,2±2,2	17,3±1,3	12,4±0,9
	5-20	16,6±3,4	13,4±1,1	19,6±1,7	17,6±1,1	18,3±1,1	15,0±1,1	12,8±1,3	19,3±1,1	7,8±0,4	10,2±1,0
10. 20,0 Northwest	0-5	67,4±18,1	215,3±12,4	223,4±25,6	28,1±2,6	45,4±4,2	29,3±2,1	24,9±1,5	51,1±5,0	27,4±2,0	13,4±0,4
	5-20	21,3±2,4	24,6±1,8	53,0±7,4	16,1±1,4	24,2±2,4	14,0±1,0	16,4±1,4	34,5±3,2	14,1±0,7	6,9±0,5

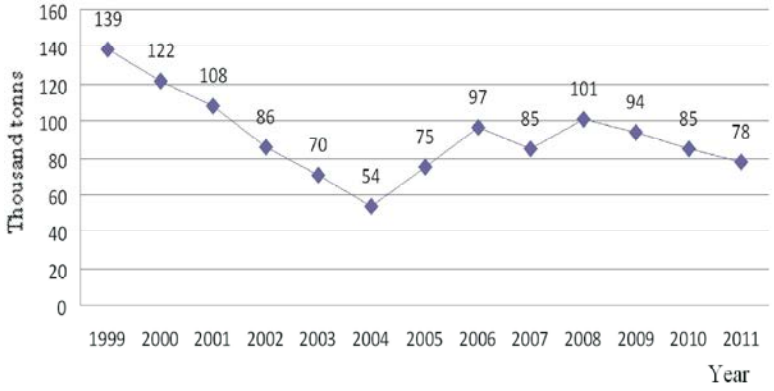

Fig. 3: Total emissions of pollutants of branch Novocherkassk's power station, thousand tons/year

Decreasing in BaP content in 5-20 cm layer of soil was recorded in soils of all monitoring plots for the entire period of research. Superficial accumulation of BaP prevails in soils of investigated territories. Decrease in BaP concentration in a layer of 5-20 cm on the average was caused by low solubility in water of studied carcinogen and its weak mobility [10, 11, 17]. The exception is made by the sandy alluvial soil of plot No. 2 that points to the increased migratory ability of BaP to underlying layers of this plot soil.

CONCLUSIONS

BaP distribution and accumulation tendencies coincide for 10 years of monitoring researches in studied soils. The main factor of technogenic influence on the soil the investigated area is: toxic emissions of the enterprise of a power complex-NPS; transport exhausts can be sources of BaP additional issue. Gradual decrease in the pollutant content in soils of the studied territory was established for 10 years period of supervision. It was explained by considerable reduction of volumes of polluting substances emission by the enterprise. Despite the environmental activities of in the enterprise, the impact of emissions on the environment location nearby today is still primary one.

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