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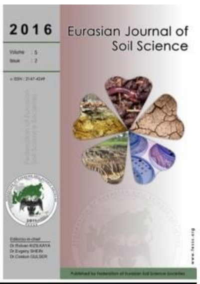

Benzo[a]pyrene contamination in Rostov Region of Russian Federation: A 10-year retrospective of soil monitoring under the effect of long-term technogenic pollution

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Abstract

The aim of the current work was to study the main tendencies in the accumulation and distribution of benzo[a]pyrene in soils of the affected zone of the Novocherkassk regional power plant. Studies were conducted on the soils of monitoring plots subjected to Novocherkassk regional power plant emissions. Monitoring plots were established at different distances from the Novocherkassk regional power plant (1.0–20.0 km). Regularities in the accumulation and distribution of benzo[a]pyrene in chernozemic, meadow-chernozemic, and alluvial soils under the effect of aerotechnogenic emissions from the Novocherkassk regional power plant have been revealed on the basis of long-term monitoring studies (from 2002 to 2011). The tendencies in the distribution and accumulation of BaP in the studied soils coincided during the 10 years of monitoring studies. It has been found the 5-km zone to the northwest from the power station, which coincides with the predominant wind direction, is most subjected to contamination by benzo[a]pyrene, with the maximum accumulation at a distance of about 1.6 km from the source. Dynamics of pollutant accumulation in soils depends on number of Novocherkassk regional power plant emissions. The content of benzo[a]pyrene in the soil is an indicator of the technogenic load impact on the areas, for which the combustion products of hydrocarbon fuel are the major pollutants. A gradual decrease of the pollutant content in the soils was revealed during the period from 2002 to 2011. It explained by the significant decrease in the volume of pollutant emissions from the plant and the self-purification capacity of soils and mechanisms of benzo[a]pyrene degradation.

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Introduction

The assessment of the environmental status of soils as a central link of ecosystems is an essential parameter in the system of environmental monitoring. The soil is the central ecosystem component depositing pollutants. The regular observation of the accumulation and distribution of anthropogenic pollutants in the

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soil is an essential problem of soil science. The improvement of the state of the environment under pollution is possible only after long-term monitoring studies for revealing the character and nature of pollution, the composition of pollutants, their diversity, and mechanisms for the accumulation and transformation of pollutants in the studied biogeocenosis (Cristale et al., 2012; Tobiszewski and Namiesnik, 2012). The most optimal methods for the restoration of the area subjected to technogenic contamination can be found only on the basis of large-scale monitoring studies and the investigation of the main tendencies in the accumulation of pollutants (Antizar-Ladislao et al., 2006; Augusto et al., 2013; Minkina et al., 2012; Oros et al., 2013).

Polycyclic aromatic hydrocarbons (PAHs) are among the most hazardous and widely distributed soil pollutants characterized by increased toxicity and carcinogenicity. The content of PAHs in all natural objects is subject to mandatory control throughout the world, which is regulated by legislations of different countries (GOST 17.4.1.02.-83, 2004; GOST 17.4.3.06-86, 1986; Jian et al., 2004; Wenzl et al., 2006).

Benzo[a]pyrene (BaP) is most frequently considered as the main marker of soil contamination by PAHs, because this is the most prevalent PAH characterized by a very high persistence in environmental objects and elevated carcinogenicity and mutagenicity (Jian et al.,, 2004). BaP is a compound of hazard class 1; it is included in the group of superecotoxicants, and its content in all objects of the ecosystem is subject of mandatory control (Tobiszewski and Namiesnik, 2012; Wenzl et al., 2006). In Russia, the maximum permissible concentration (MPC) of BaP is 0.02 mg/kg for all soils; in other countries, this value varies in the range of 0.1–2.7 mg/kg.

The monitoring studies of environmental pollution with PAHs has been performed in many countries over tens of years. A number of works well with the study of the state of the areas subjected to technogenic contamination with PAHs (Callén et al., 2013; Pereira et al., 2013; Singh et al., 2013; Sushkova et al., 2015; Sushkova et al., 2015; Witter et al., 2014; Li et al., 2006; Yam and Leung, 2013; Zhu et al., 2014). The contamination is of technogenic origin in all the cases.

Active sources of environmental pollution with PAHs include enterprises of energy industries, especially great thermal stations (DEFRA and EA 2002; Sushkova et al., 2015; Witter et al., 2014; Yam and Leung, 2013). The Novocherkassk Regional Power Plant (NRPP) is one of the greatest thermal power stations not only in Russia, but also in Europe. This is an enterprise of hazard class 1, which was set in operation in 1965–1971. At present, it includes eight working blocks and is the main source of electrical energy in Rostov oblast. Coal and natural gas are the major fuel types for the station. The height of the first chimneystack is 185 m; the three other stacks are 250 m high.

Ecological monitoring performed since 2000 showed that the NRPP is the main pollution source of the atmospheric air not only in the city of Novocherkassk, but also in the entire Rostov oblast, and makes the major contribution to the environmental pollution in this region. The aim of the current work was to study the main tendencies in the accumulation and distribution of BaP in soils of the affected zone of the NRPP.

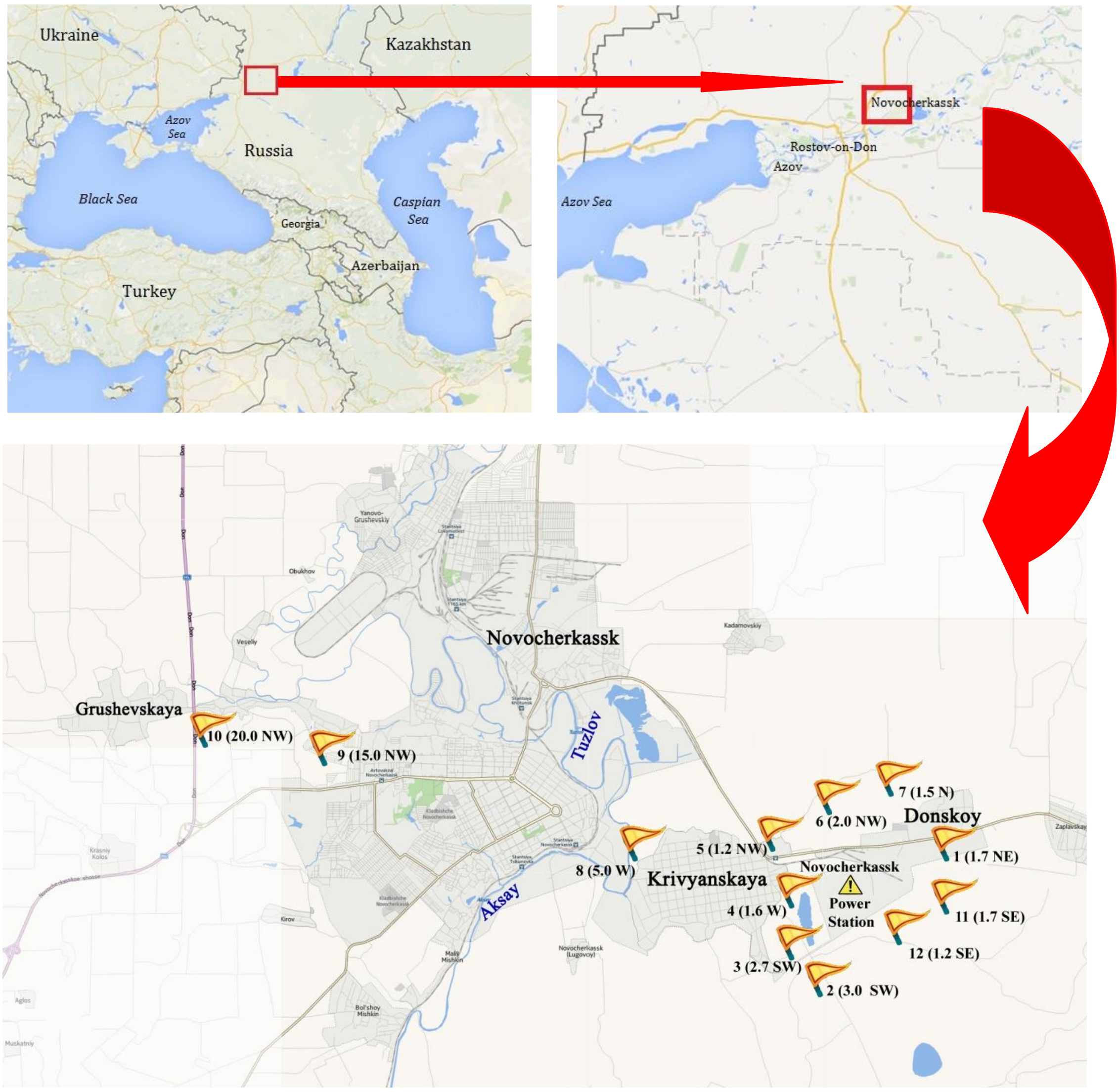
Material and Methods

The main objects of study were soils in the affected zone of the NRPP. The satellite images of the NRPP and its affected zone, as well as the locations of monitoring plots, are given in Figure 1. They coincided with the air sampling sites for the ecological certificate of the plant (plots 1, 2, 3, 5, 6, 7) (Figure 1). The most attention was paid to the main wind direction from the contamination source to the northwest through the residential areas of Novocherkassk (plots 4, 8, 9, 10) (Table 1). The monitoring plots were located on virgin lands or fallow areas. The soil cover in the region under study consisted of ordinary chernozems, meadow-chernozemic soils, and alluvial meadow soils.

Table 1. Numbers of monitoring plots and their code including distance (km) and the direction from the Novocherkassk Regional Power Plant (NRPP), and also soil type on a plot

Plot No.	Code	Soil type	Plot No.	Code	Soil type
Group I			Group II		
5	1.2 NW	Co	1	1.0 NE	Co
4	1.6 NW	Co	7	1.5 N	Co
8	5.0 NW	MCS	6	2.0 N	MCS
9	15.0 NW	Co	3	2.7 SW	MCS
10	20.0 NW	Co	2	3.0 SW	AS

Co: Chernozem ordinary; MSC: Meadow chernozem soil; AS: Alluvial soil



Plot No.	The direction and distance from NRPP	Plot No.	The direction and distance from NRPP
1	1.0 km on the northeast (NE)	6	2.0 km on the northwest (NW)
2	3.0 km on the southwest (SW)	7	1.5 km to the north (N)
3	2.7 km on the southwest (SW)	8	5.0 km on the northwest (NW)
4	1.6 km on the northwest (NW)	9	15.0 km on the northwest (NW)
5	1.2 km on the northwest (NW)	10	20.0 km on the northwest (NW)

Figure 1. Schematic map of monitoring plots in the zone affected by the Novocherkassk Regional Power Plant (NRPP)

Most of the area in the affected zone of the NRPP is occupied by calcareous ordinary chernozem (Co); meadow-chernozemic soil (MCS) (plot 3SW) and alluvial soil (AS) also occur in the Tuzlov River floodplain of the studied zone (Table 2).

The Co and MCS have thick humus horizons (70–100 cm), relatively high content of humus (4.1–5.0%) and high cation exchange capacity (CEC) (31.2–47.6 cmol(+)/kg), including a high content of exchangeable calcium (76–90% of total exchangeable cations), and neutral or weakly alkaline reaction (pH_{water} 7.4–7.7) (GOST 26423-85, 1985). According to particle size distribution, they belong to heavy loamy and light clayey varieties developed on calcareous loess-like rocks. The climatic index of biological productivity (Bc) is 90–100 under natural conditions and 170–175 under optimum wetting conditions. The sufficient amount of heat and precipitation forms soils with high natural fertility, and the enrichment with carbonates from the parent rocks favors the development of high buffering properties. The alluvial soil has light texture, thinner humus horizon (40–60 cm), lower humus content (lower than 3.1%) and lower CEC (10.9 cmol(+)/kg) with a relatively high content of exchangeable calcium.

Table 2.Properties of the Novocherkassk Regional Power Plant (NRPP) emissions zone soils (an average for 2002-2011)

Number of montoring plot	Soil	Physical clay, %	Clay, %	C_{org}, %	pH	$CaCO_3$, %	CEC, cmol(+) kg^{-1}
1	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	52.0	27.0	4.3	7.6	0.5	35.0
2	Low-humus calcareous sandy alluvial meadow soil on alluvial deposits	7.0	3.0	3.1	7.5	0.4	10.9
3	Low-humus silty clayey flood-plain meadow chernozemic soil on alluvial deposits	67.0	37.0	4.6	7.3	0.2	44.8
4	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	55.0	29.0	4.6	7.5	0.7	31.2
5	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	53.0	27.0	4.3	7.5	1.0	35.7
6	Low-humus medium-thick clay loamy meadow chernozemic soil on loess-like loams	55.0	30.0	4.1	7.7	0.8	32.4
7	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	51.0	27.0	4.1	7.6	0.7	31.3
8	Low-humus medium-thick clay loamy meadow chernozemic soil on loess-like loams	60.0	32.0	5.0	7.4	0.4	47.6
9	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	52.0	30.0	4.2	7.6	0.6	31.4
10	Low-humus medium-thick calcareous clay loamy ordinary chernozem on loess-like loams	53.0	28.0	4.6	7.6	0.5	36.0

Soil samples were taken daily in June during 10 years from 2002 to 2011. The samples were taken by layers, from depths of 0 to 5 and 5 to 20 cm. Soil samples were selected and prepared for the chemical analysis according to GOST 17.4.4.02-84 (GOST 17.4.1.02.-83, 2004) requirements. The samples were used for the determination of soil texture by the Kachinskii method (Gabov and Beznosikov, 2014; Directive document 52.10.556-95, 2002).

Soil samples were taken annually and prepared for chemical analysis in accordance with the current requirements (Pikovskii, 1993; Sokolov, 1966; ISO, 2005). BaP was extracted from the soils of the objects under study by the standard method using for the removal of the interfering soil components by saponification (Directive document 52.10.556-95, 2002).

A 1-g of the prepared soil was put into a pear-shaped flask for rotary evaporator; 20 mL of 2% KOH solution in ethanol was added, and the mixture was refluxed on a water bath for 3 h. The saponificaiton of lipids and gummy soil components occurred during the refluxing, which increased the recovery of PAHs and reduced the amount of coextracted substances in the extract. The supernatant was decanted into an Erlenmeyer flask, and 15 mL of n-hexane and 5 mL of distilled water were added for the better separation of the layers. The mixture was shaken on a rotary shaker for 10 min and transferred into a dividing funnel. The hexane layer was poured into a separate vessel. The residue in the flask was extracted twice more in a similar way. The combined hexane extract was washed with distilled water to neutral pH (using litmus as an indicator), transferred into a dark vessel with a close lid, and desiccated by adding 5 g of anhydrous Na_2SO_4. After exposure at +5°C for 8 h, the desiccated extract was decanted into a dry round-bottomed flask and evaporated to dry on a rotary evaporator at a bath temperature of 40°C. The dry residue was dissolved in 1 mL of acetonitrile.

The content of BaP in the test samples was determined by the external standard method (Anonymous, 2008). The content of BaP in the soil was calculated from the equation

$$C_s = k\, S_i \times S_{st} \times V/(C_{st} \times m) \quad (1)$$

where Cs is the content of BaP in the soil sample (μg/kg); Sst and Si are the BaP peak areas for the standard solution and the sample, respectively; Cst is the concentration of the standard BaP solution (μg/kg); k is the recovery factor of BaP from the sample; V is the volume of the acetonitrile extract (mL); and m is the mass of the sample (g).

From the results of determining BaP concentrations in the upper and lower soil layers (C_{0-5} and C_{5-20}, μg/kg, respectively), the weighted average concentrations of BaP in the 0- to 20-cm layer (C_{0-20}, μg/kg) were calculated from the equation

$$C_{0-20}=(5C_{0-5}+15C_{5-20})/20 \quad (2)$$

The vertical distribution coefficients of BaP between the upper and lower layers (Kd) were calculated from the equation

$$K_p=15*C_{5-20}/5*C_{0-5} \quad (3)$$

The averaged BaP distribution coefficients between the soil layers were also determined for each monitoring plot during the period from 2008 to 2010 (the period of the maximum stabilization of fallouts), and a correlation between these values and different physicochemical and agrochemical parameters of soils was established. The obtained results were processed by mathematical statistics methods using Microsoft EXEL and SigmaPlot 2011 software.

Results

Dynamics of solid emission products and the composition of pollutants

In the later 1990s, the total volume of emissions from the NRPP reached 139 thousand tons. Due to the re-equipment of the NRPP, which started in 2000, the proportion of gas in the fuel exceeded 40% in 2004. This resulted in a reduction of solid emissions into the atmosphere down to 54 thousand tons, i.e., more than twice (Figure 2). In the following two years, the annual volume of solid emissions increased and remained within the range of 83–101 thousand tons during the next five years (up to 2011) (Ecological messenger of Don…, 2012).

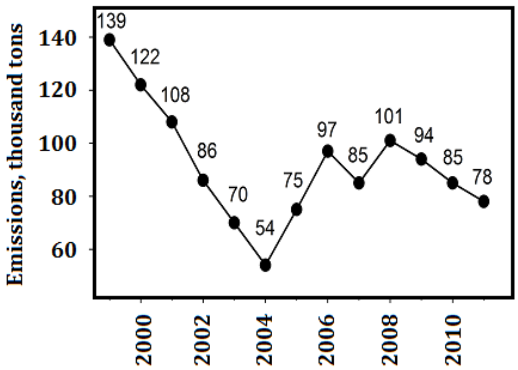


Figure 2. Dynamics of average pollutant emissions value from the Novocherkassk Regional Power Plant (NRPP) between 1999 and 2011 (according to Ecological Messenger of Don, 2012)

The emissions from the NRPP mainly consist of processed coal ash. The coals furnished to the NRPP are enriched with a wide range of organic and inorganic toxic substances (Mandzhieva et al., 2014). The main components of the NRPP emissions are ash, sulfur monoxide, nitrogen oxides, soot (more than 30 t/year), vanadium pentoxide (about 8 t/year), iron oxide (more than 5 t/year), chromic anhydride (about 0.1 t/year), hydrogen fluoride (7 kg/year), etc. Ash retains up to 85% of the chemical elements that were present in the original coal (Gorobtsova et al., 2005; GOST 14.4.3.06-86, 1986; Hybholt et al., 2011; Gennadiev et al., 2004). It was calculated that PAHs make up about 10% of the total annual emission from the NRPP (about 90 thousand tons) (Antizar-Ladislao et al., 2006). Some authors indicate that ash can contain up to 60% PAHs (Gorobtsova et al., 2005), and BaP composes up to 10% of them (Gennadiev et al., 1989).

Dynamics of the content and distribution of BaP in soils of the affected zone of the NRPP

It was found that the concentration of BaP in soils of the affected zone of the NRPP varied in a wide range: from 11 to 423 μg/kg in the 0- to 5-cm layer and from 5 to 249 μg/kg in the 5 to 20-cm layer (i.e., in the ranges of 0.6–21 and 0.3–11 MPC, respectively). On most of the plots, the concentrations of BaP in the both soil layers varied synchronously.

The weighted average BaP concentrations in the 0- to 20-cm layer of soils on the monitoring plots during the period from 2002 to 2011 are shown in Figure 3. The results for the soils located along the predominant wind direction (to the northwest) and within a radius of 1–3 km from the plant in the northern, northeastern, and southwestern directions are shown separately (Figure 3A–3C).

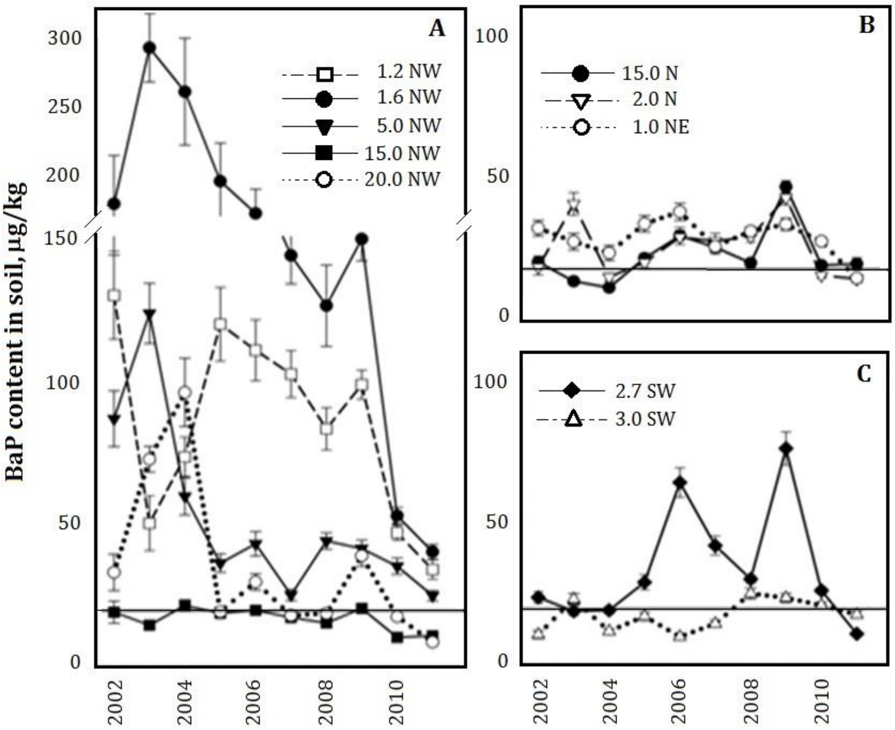


Figure 3. Dynamics of BaP average concentrations in 20-cm layer of soil monitoring plots in the Novocherkassk Regional Power Plant (NRPP) emission zone on the north-west - through the prevailing direction of the wind rose (A), as well as around NRPP on north / northeast (B) and southwest (C) directions. The line indicates the level of MPC in the soil.

The analysis of the results shows that the accumulation of BaP in the soils of the studied area depends on the distance of the controlled plots from the emission source and their location with respect to it. The major part of pollutants accumulates in the soils of the northwestern direction from the NRPP, which coincides with the main direction of winds (Figure 3A). The most significant pollution of soils in this direction is observed within a radius of 5 km, with a maximum at 1.6 km, where $C_{0\text{-}20}$ reached 125–300 µg/kg (6–15 MPC) and $C_{0\text{-}5}$ reached 423 µg/kg (22 MPC) in 2002–2003. When the distance from the emission source increases, the level of contamination with BaP gradually decreases to a minimum at 15 km from the plant, where $C_{0\text{-}20}$ varies in the range of 1–2 MPC and $C_{0\text{-}5}$ does not exceed 2.6 MPC.

In all the soils located along the predominant wind direction, an active decrease of BaP content in the entire 0- to 20-cm layer was observed during the 10-year-long period of observations. This tendency is most manifested in the soil of plot 4 with the maximum level of contamination (Figure 3A), where the concentration of BaP decreased by more than 7 times: from 290 to 40 µg/kg. An almost similar decrease of $C_{0\text{-}20}$ (from 125–130 to 25–25 µg/kg, i.e., by 4–5 times) was observed on plots 1,2nw and 5nw.

In the most remote point of group I (20NW), as well as in almost all soils of group II (Figure 3B, 3C), the content of BaP remained low (at 0.5–2 MPC); only on plot 2,7nw, it reached 3–4 MPC in some years. In points 20NW and 1ne, a tendency of slow decrease in the concentration of BaP (by about 2 times for 10 years) was observed; on the other plots, the most significant decrease in BaP concentration was observed only in the last years (from 2009 to 2011).

The revealed tendencies in the decrease of BaP concentration in the soils of monitoring plots are analogous to those observed for the decrease in the volume of solid emissions from the plant during the period from 1999 to 2004. In most of the curves, the peaks of increasing and decreasing BaP concentration coincide with each others and with the peaks of soot emission but are delayed from the emission dynamics by about a year. After 2004, the decrease of BaP concentration in the soil continued, in spite of the relative stabilization of emissions from the NRPP, and accelerated during the period of the last decrease in the volume of solid emissions beginning from 2008.

From the data shown Figure 3, the period of half-decrease of BaP concentration in the soils (T_{50}) could be estimated. In points 1.2NW, 1.6NW, 5.0NW, and 15.0NW, where the weighted average concentration of BaP in the 0- to 20-cm layer increased to 100–300 µg/kg, the value of T_{50} varies in the range of 1–5 years. In the two points with low contamination levels (20NW and 1.0NE), where the maximum BaP concentration did not exceed 20–40 µg/kg, this value was about 10 years. In the other soils subjected to slight contamination, the rate of decrease in BaP concentration could not be determined.

The concentrations of BaP in the 0- to 5- and 5- to 20-cm layers of soils on the monitoring plots averaged for the period of 2005–2011, when the annual emissions from the power plant were stabilized at a level of 75–101 thousand tons. In all the sampling points on chernozemic and meadow-chernozemic soils, the averaged concentrations of BaP in the upper soil layer exceed its contents in the lower layer by 1.5–2 times. An exception is point 2 on sandy alluvial soil located in the Tuzlov River floodplain, where the concentrations of BaP in the both layers are similar and do not exceed the MPC.

Discussion

It was established that the vertical distribution coefficients of BaP between the 5- to 20- and 0- to 5-cm layers (with account for their thicknesses) in different sampling points vary during the observation period from 0.7 to 5.2 and significantly depend on the soil properties. The highest values of Kd are typical for the sandy soil, and the lowest values are typical for the light clayey soil. The former vary among the years in the range of 1.6–5.2, and the latter vary in the range of 0.8–2.1; in the most common group of loamy soils, Kd varies in the range of 0.7–2.9.

The closest correlations are found between the average coefficients of vertical distribution and the properties of soil during the period of 2008–2010, when the volume of solid emissions was stabilized on the level of 78–101 thousand tons (Figure 4). For this period, close inverse correlations between the Kd values and the contents of physical clay and humus and CEC with the correlation coefficients (R) of 0.93, 0.91, 0.74, and 0.80, respectively (for this data set, the critical R value is 0.632 at p = 0.05) were observed. Analogous, although looser, correlations are traced between these values during other observation periods. For the other properties, correlations with Kd are loose or absent.

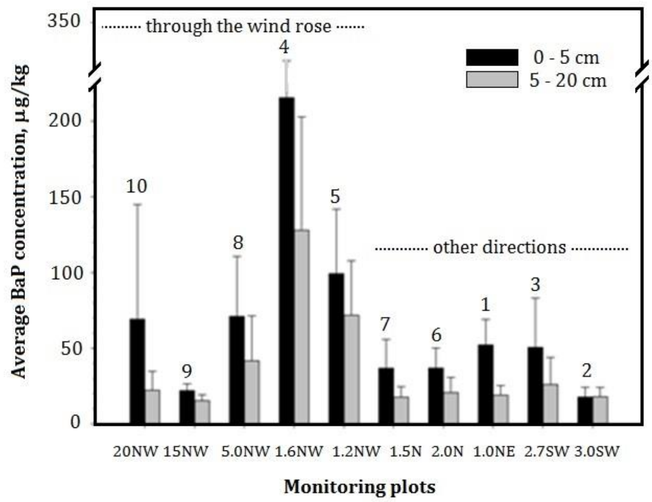


Figure 4. Average BaP concentration in 0-5 and 5-20 cm soil layers of monitoring plots in the Novocherkassk Regional Power Plant (NRPP) emission zone during 2005-2011: in Group I - through the prevailing direction of the wind rose (plots 20NW, 15NW, 5NW, 1.6NW and 1.2NW) and in Group II – around NRPP (plots 1.5N, 2.0N, 1.0NE, 2.7SW and 3.0SW).

Earlier studies showed that the accumulation of BaP in the studied steppe biocenosis is due to the deposition of solid emission products from the NRPP in adjacent areas and depends on the predominant wind direction, which confirms the earlier conclusions (Sushkova et al., 2012, 2015; Gorobtsova et al., 2005; Minkina et al., 2011; Nazarenko et al., 2007). In the current work, the migration and transformation of BaP are considered in more detail.

Our studies showed that, beginning from 2002–2003, the reduction of environmental load is accompanied by a simultaneous decrease in the content of BaP in the both layers of soils on the monitoring plots in the affected zone of the NRPP, especially along the predominant wind direction, where its weighted average concentration reached high values of 100–300 µg/kg. The content of BaP in the both layers remained above the MPC during the entire period of observations. However, in 2011, the concentration of BaP in the soils of most plots decreased to the MPC level; only along the predominant wind direction (within the radius of 5 km), it still exceeded this level by 1.2−2 times.

The abrupt decrease in the content of BaP in the soil of monitoring plot 5nw compared to plot 1,6nw (by more than 3.5 times) indicates that the distribution area of the densest plume containing the maximum amount of pollutant is about 5 km to the northwest, and the maximum fallouts are observed at a distance of about 1.6 km (Sushkova et al., 2012). The areas located around the NRPP up to 3 km in the northern/northeastern and southwestern directions are less contaminated. An exception is the soil on plot 2.7SW, which is the closest to group I, where the concentrations of BaP in the 0- to 20-cm layer reached 60−70 μg/kg in 2006 and 2009.

It should be noted that the soils of the plots located at 1−2 km to the north and northeast of the plant are almost not subjected to the impact of polluting emissions. During the entire period of observations, the content of BaP in the 0- to 20-cm layer of soils on these plots located at a short distance from the plant (1−2 km) exceeded the MPC by no more than 2.5 times (Figure 3C).

The soils on the most remote monitoring plot 10 (20NW) occupy a special place in the description of the affected zone of NRPP. The obtained data indicate the presence of additional sources of pollutant emission near the plot: exhausts from motor vehicles on the M-4 Don highway, which passes at 350m from the sampling site. The plot is located within the V-shaped area enclosed by two highways (the Rostov−Moscow road from the northwest and the Rostov−Novocherkassk road from the southeast), which results in the contamination of soils with vehicle exhausts containing BaP. In addition, this plot is apparently subjected to the plumes from the Novocherkassk dumps, as well as combustion products formed at the stove heating of houses in the village of Grushevskaya. Nonetheless, the accumulation of the pollutant in the soil due to the additional emission sources is significantly lower than that caused by the NRPP.

The period of half-decrease of the pollutant concentration in the most contaminated soils varies in the range of 1−5 years; during the period of 2009−2011, the process was accelerated and T_{50} decreased to 0.1−1 years. On the slightly contaminated soils, T_{50} did not exceed 10 years or could not be determined at all.

The almost simultaneous decrease of BaP concentrations in the upper and lower layers of soil, as well as the acceleration of this process to 2011, indicates the leading role of the microbial degradation of the pollutant in the entire soil layer under study. Although the photo-oxidation of BaP on the soil surface also cannot be excluded (Shabad, 1982), its contribution to the decomposition is apparently minimum because of the shielding of molecules sorbed by soil and soot particles.

It is known that BaP belongs to the persistent pollutants, because microorganisms are incapable of using 4−5-ring PAHs as the only source of carbon and energy. Nonetheless, the microbial degradation of BaP occurs in oxidative conditions under the effect of microorganisms utilizing 2−3-ring PAHs, which usually accumulate in the contaminated soils because of the adaptation of soil microflora (Shabad, 1982). The accelerated degradation of BaP, which is observed in the most contaminated soils, is due to the faster adaptation of microorganisms in the presence of the selective factor (Gabov et al., 2007; Galiulin et al., 2002). The slower decrease of BaP concentration in the slightly contaminated soils can be related to their low availability to biodestructors due to the strong sorption by soil humus or pyrogenic particles (Augusto et al., 2013). However, the absence of appreciable BaP accumulation in the soil, in spite of the continuing input of soot fallouts in the affected zone of the NRPP, can also argue for the degradation of the pollutant.

The analysis of the physicochemical and agrochemical properties of soils in the studied areas (Table 2) suggests that, in spite of the intensive long-term technogenic load and the high contents of BaP and heavy metals in soils of the studied areas, the high level of fertility still remains in the affected zone of the NRPP, which sustains the ecological balance and forms the basis for the stability and balanced functioning of the ecosystem (Nazarenko et al., 2007; Sushkova et al., 2014; Page et al., 2006).

The comparison of the concentrations of BaP in the 0- to 5- and 5- to 20-cm layers showed that the surface accumulation of BaP prevails in the chernozemic soils of heavy texture occurring in the affected zone of the NRPP. However, the relatively high vertical distribution coefficients of the pollutant between these layers, which exceed 1 in most cases and reach 2.9, indicate the migration of BaP throughout the soil profile, at least within the 0- to 20-cm layer. The most intense migration of BaP proceeds in the floodplain soil of the Tuzla River floodplain, where the value of Kd reaches 5.2. A close correlation is found between the vertical migration coefficient of BaP and the contents of physical clay, clay, and humus and CEC in soils of the all monitoring plots (Figure 5).

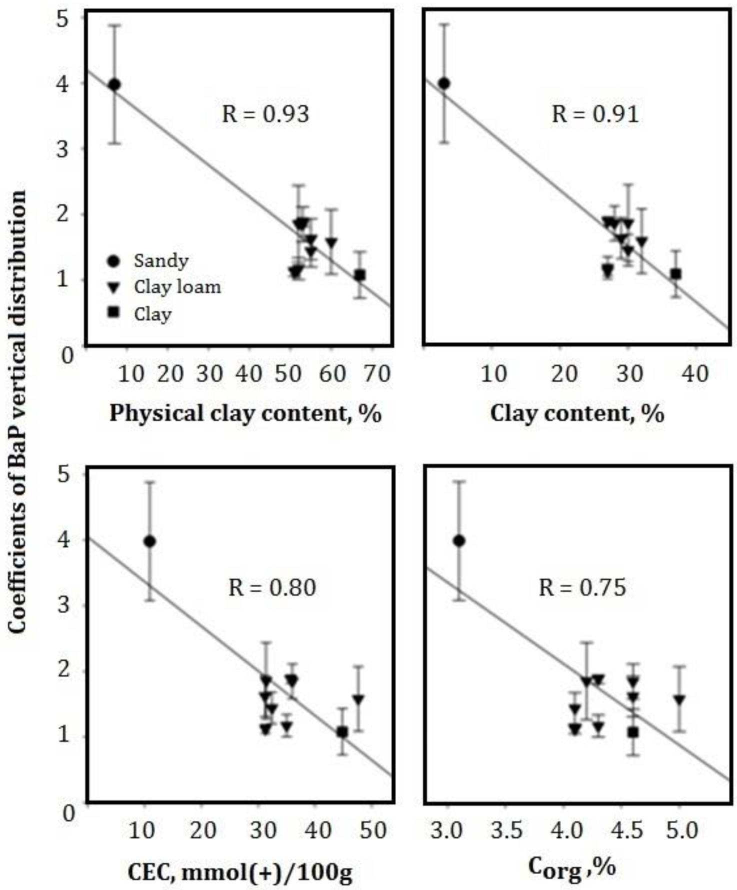


Figure 5. Correlations between the average coefficients of BaP vertical distribution in the 5-20 cm soil layer and 0-5 cm soil layer and the properties of monitoring plots soil

The low mobility of BaP in the zonal chernozemic soils is due to its low solubility in water, high lipophilicity, and increased capacity of being sorbed by soil organic matter, whose content is maximum in the fine fraction of soil and depends on the content of fine particles. In the less humified soil of light texture, the migration of BaP is appreciably enhanced.

The obtained data agree with the results of studies (Gabov et al., 2007; Sushkova et al., 2012, 2015; Gorobtsova et al., 2005; Minkina et al., 2011; Nazarenko et al., 2007), which indicate the effect of soil texture on the migration of BaP in the soils of natural and technogenic landscapes.

Conclusion

The tendencies in the distribution and accumulation of BaP in the studied soils coincided during the 10 years of monitoring studies. The toxic emissions from the NRPP are the main factor of technogenic impact on the soils in the region under study; vehicle exhausts can be sources of additional BaP emission. A gradual decrease of the pollutant content in the soils of the studied areas was revealed during the period from 2002 to 2011, which was related to the significant decrease in the volume of pollutant emissions from the plant and the self-purification capacity of soils due to the microbiological and other mechanisms of BaP degradation. In spite of the conservation measures undertaken at the power plant, the atmospheric emissions from the NRPP have still the predominant effect on the environmental situation in the adjacent areas at present.

The particle size distribution in the soils significantly affects the accumulation and differentiation of BaP in the soil profile. A positive correlation of the vertical distribution coefficients of BaP between the 0- to 5- and 5- to 20-cm layers of soil with the contents of physical clay, clay, and humus and CEC is revealed. The elevated values of Kd in the sandy floodplain soil of the Tuzlov River floodplain indicate the possible migration of the hazardous pollutant to the ground and surface waters of the studied region.

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