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SOIL POLLUTION AND REMEDIATION

New alternative method of benzo[a]pyrene extraction from soils and its approbation in soil under technogenic pressure

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Abstract
Purpose The optimization of benzo[a]pyrene extraction conditions by subcritical water extraction method from soils is the purpose of the research. The optimal conditions for benzo[a]pyrene recovery are 30-min extraction by water in a special steel cartridge at 250 °C and 100 atm.
Materials and methods Studies were conducted on the soils of monitoring plots subjected to Novocherkassk Power Station emissions. Monitoring plots were established at different distances from the Novocherkassk Power Station (NPS; 1.0–20.0 km).
Results and discussion It was shown that the use of water in subcritical state as a solvent for benzo[a]pyrene extraction from soil allows to avoid large volumes of organic solvents and to decrease the time of sample preparation. It is shown that the maximum benzo[a]pyrene maintenance was observed in soils of the monitoring plots located most close (to 5 km) to a pollution source in the area of the prevailing direction of a wind rose. Dynamics of pollutant accumulation in soils depend on number of Novocherkassk state district power station emissions.
Conclusions The method of benzo[a]pyrene subcritical water extraction from soil was developed and approbated during long-term monitoring researches of technogenic polluted territories. The optimum conditions for benzo[a]pyrene extraction from soil have been determined: the soil is treating by subcritical water at 250 °C and 100 atm of pressure for 30 min. Trends in the accumulation of benzo[a]pyrene in soil zones of the thermal power plant influence have been researched over a 5-year period of monitoring observations by subcritical water extraction method. Benzo[a]pyrene accumulation in soils depends on the technogenic emissions to the atmosphere from Novocherkassk power station and on the soil physical and chemical properties.

Keywords Benzo[a]pyrene · Extraction · Monitoring · Soil · Subcritical water

1 Introduction

The most significant contaminants group of the environment compounds which are the cancer-causing agents and mutagenic are polycyclic aromatic hydrocarbons (PAHs).

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Sixteen PAH compounds have been recommended as priority pollutants by the United States Environmental Protection Agency (USEPA) because of their carcinogenicity, mutagenicity, and toxicity (Jian 2004; Wenzl et al. 2006). 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 (Maliszewska-Kordybach et al. 2013). The assessment of soil contamination is one of the major indicators in the environmental monitoring system. The main marker of soil pollution by PAHs is benzo[a]pyrene (BaP) (Wenzl et al. 2006). Knowledge of soil contamination with BaP is needed to minimize the risk of human exposure and of environmental contamination (Mandzhieva et al. 2014). The BaP content in all environmental matrices and food is under obligatory regulations worldwide (Department for Environment, Food and Rural Affairs and the Environment Agency 2002; GOST 2004; Wenzl et al. 2006; Mandzhieva et al. 2014).

Common methodologies for PAH quantification in environmental samples include solvent extraction and analysis by high-performance liquid chromatography (HPLC) with fluorescence detection or by GC–MS. Solvent-based extraction methods of soil, sediments, or sludge samples are generally carried out using Soxhlet apparatus (Hawthorne et al. 2000), ultrasonication (Domeno et al. 2006), microwave-assisted extraction, pressurized liquid extraction, or accelerated solvent extraction (Smith 2002). Solvents include n-hexane, acetone, dichloromethane, toluene, and others. The extract volume is reduced under nitrogen or by rotary evaporation to a final volume less than 1 ml. The procedure may also include extract cleanup by solid phase extraction (typically using Florisil, aluminum oxide, or silica gel) before HPLC or GC–MS analysis. There are standardized United States Environmental Protection Agency (US EPA) methods for extracting organic pollutants, including PAHs, from environmental solids (soil, sediment, and sludge). For example, in method 3540C, PAHs are extracted for more than 8 h with a mixture of acetone and n-hexane in a Soxhlet extractor (US EPA 1996a). In method 3550C, solid samples are extracted with organic solvents combined with ultrasonic treatment (US EPA 2007a). US EPA PAH extraction methods 3545A and 3561 are based on extraction with organic solvents (US EPA 2007b) or organic solvents (dichloromethane in particular) in combination with supercritical carbon dioxide (31.2 °C, 72.8 atm) (US EPA 1996b). One of the widespread methods for the determination of PAHs in environmental samples is Soxhlet extraction, using 150 ml per sample by CH_2Cl_2–acetone extraction for a period of 18 h (Hawthorne et al. 2000, a).

All of the above-listed methods are characterized by long and multistage procedures for sample preparation using a large volume of toxic organic solvents, typically 50–450 ml per sample. Some prospective methods were recently developed for PAH extraction from various solid matrices using water or carbon dioxide under sub- or supercritical conditions. Subcritical water extraction is one of the most recent techniques developed for extracting organic compounds, including pollutants from environmental matrixes and food (Kocher et al. 1995; Hawthorne et al. 2000; Lagadec et al. 2000; Dadkhah et al. 2006; Latawiec et al. 2010; Islam et al. 2014;). This method is based on the use of superheated water (100 to 374 °C and 224 atm pressure) as a solvent in place of organic solvents. Subcritical water has unique characteristics; high temperature and pressure greatly reduce its dielectric constant, surface tension, and viscosity, thereby weakening the hydrogen bonding network of water molecules (Galkin and Lunin 2005; Carr et al. 2011). Increasing temperature from 25 to 350 °C at a pressure of 101 atm decreases the dielectric constant (ε) of water from 73 to 2. Therefore, the solubility of non-polar compounds increases as temperature increases in this range. For example, the dielectric constant of superheated water is 27 at 250 °C and 101 atm Pa pressure, which is between that of ethanol ($\varepsilon=24$ at 25 °C) and acetonitrile ($\varepsilon=36.2$ at 25 °C), one of the best solvents for BaP. Because superheated water acts as an organic solvent, subcritical water extraction could be categorized as a solvent extraction process (Islam et al. 2014). Moreover, superheated water is readily available, non-toxic, reusable, and very low in cost as well as environmentally benign. Thus, subcritical water extraction has been suggested as an alternative to organic solvents or toxic aqueous liquid media.

The present study is aimed at optimization of conditions for BaP extraction from soils and approbation of this method on long-term monitoring researches of technogenic territories. We determined the optimum conditions for subcritical water extraction of BaP. In this regard, we carried out the long-term monitoring analysis of BaP content by environmentally friendly method of subcritical water extraction instead of traditional methods for BaP determination using a large amount of organic solvents.

2 Materials and methods

Studies were conducted on the soils of monitoring plots subjected to Novocherkassk Power Station (NPS) emissions. Investigations of the ecological condition of the NPS zone showed us that the most dangerous pollutants are BaP and heavy metals (Sushkova et al. 2013; Minkina et al. 2014). The content of BaP in all objects of the ecosystem must be under obligatory control. However, monitoring researches of BaP content are conducted by the Committee of Environment and Natural Resources only within the settlement of Novocherkassk. It does not demonstrate an overall pollution extent of all NPS emissions area.

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

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 0–5 and 5–20 cm. Soil samples were selected and prepared for the chemical analysis according to GOST 17.4.4.02-84 (GOST 2004) requirements.

The most part of the territory is occupied by ordinary chernozems that revealed the following physical and chemical properties in 0–20 cm layer: a clay content of 265–286 g kg^{-1} and a physical clay content of 471–489 g kg^{-1}, pH of 7.3–7.5, organic C content of 23–24 g kg^{-1}, CaCO3 content of 1–1.5 g kg^{-1}, CEC of 35–37 mM kg^{-1} and exchangeable Ca, Mg, and Na contents of 27–29, 4–5, and 0.1 mM kg^{-1}, respectively. 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 flood plain soil (plot 3) with a high CEC that differed from the control soils. These differences are considered in the discussion of the results. The soil properties were determined by standard methods (Sokolov 1975).

Subcritical water extraction of BaP was used on the samples of soils of monitoring plots from year 2008 and optimization of conditions for BaP extraction. 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 Na_2SO_4. A BaP standard in acetonitrile (State Standard Sample of Russian Federation 7515–98) with concentration 200 mkg/cm^3 was used to prepare standards for HPLC analyses.

2.1 Subcritical water extraction

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

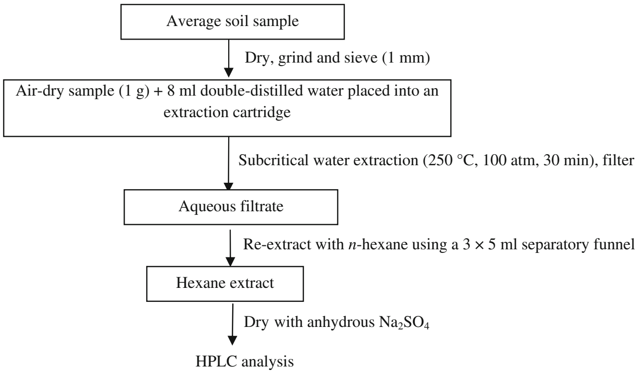

Fig. 2 Scheme of BaP analysis in soil material using subcritical water extraction and HPLC analyses of the extract

was placed into an oven connected to a temperature regulator (Lekar et al. 2013; Sushkova et al. 2014).

The process of BaP analyses in soils based on subcritical water extraction is schematically shown on Fig. 2. It consisted of the following step-by-step operations. An air-dried sample of the natural vegetation was ground in a porcelain mortar and passed through a 1 mm sieve. One gram of sample was placed into the extraction cartridge, and 8 ml of double-distilled water was added. The extraction cartridge was sealed from both sides with the screw caps. The cartridge was placed into an oven held at 230, 240, 250, 260, or 270 °C for 20, 30, or 40 min.

Subsequent extractions were conducted under optimum conditions (30 min at 250 °C and 100 atm) (Table 1). 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 was repeated two or three times, until the filtrate was clear. The aqueous extract was 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 Na_2SO_4 and evaporated to dryness in a pear-shaped flask on a vacuum evaporator in a 40 °C water bath. The residue was dissolved in 1 ml of acetonitrile by shaking for 30 min.

Liquid-liquid re-extraction of BaP from water extract is obligatory because BaP is 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. By shaking a mixture of BaP, microvolume extracted into the organic matrix directly emulsified 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 full BaP transition to extract.

Table 1 BaP concentration in ordinary chernozem depending on temperature and time extraction using subcritical water, ng/g (*n*=9)

Temperature of extraction, °C	Time of extraction, min		
	30	35	40
230	7.6 (0.1)*	6.3 (0.3)	5.8 (0.2)
240	9.4 (0.2)	8.5 (0.5)	7.6 (0.5)
250	11.9 (0.2)	11.1 (0.6)	10.4 (0.5)
260	8.2 (0.2)	7.9 (0.5)	7.2 (0.4)
270	5.4 (0.1)	4.7 (0.2)	3.9 (0.1)

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 (ISO 2005). Excitation wavelength of the FD is 263 nm, and emission wavelength of the FD is 408 nm. 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 was 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.

The efficiency of BaP extraction from soils was determined using a matrix spike (Procedure of Measurements 2008). The air-dried vegetation sample (1 g) was placed into a round-bottom flask, and BaP standard solution in acetonitrile was added to give BaP concentrations of 2, 4, 6, 8, 16, or 32 ng/g (Table 2). After evaporating the solvent for 30 min under a hood under ambient conditions, the BaP-spiked plant samples were incubated for 24 h at 7 °C. The samples were then analyzed by the subcritical extraction method described above.

The limit of BaP detection and quantification was 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. BaP concentrations in plant samples (A, ng/g) were calculated as follows:

$$A = k S_{\mathrm{I}} * C_{\mathrm{st}} * V / (S_{\mathrm{st}} * m) \qquad (1)$$

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

The results of the subcritical water extraction of BaP from soil showed that this method allows shortening the time extraction up to 30–40 min instead of 11–48 h requiring for those obtained by traditional methods (Table 1).

The oxidation of the soil lipid fraction and the maximum transition of BaP into the water solution occur in a hermetic

Table 2 BaP extraction degree from ordinary chernozem using the extraction methods of saponification and subcritical water (*n*=9)

Initial BaP in sample (ng/g)		BaP content by method of extraction (ng/g)		Extraction efficiency of the method (% of initial)	
Background	Spike	Subcritical water	Saponification	Subcritical water	Saponification
11.9±0.7	2.0	10.3 (1.1)*	13.4 (0.9)	96.1	74.1
	8.0	14.7 (1.4)	19.2 (1.4)	96.4	73.8
	16.0	20.5 (2.9)	27.1 (2.5)	97.0	73.4
	32.0	32.4 (4.1)	42.2 (3.8)	96.2	73.8
	64.0	56.3 (3.9)	72.7 (4.4)	95.9	74.2

reactor at 230–270 °C and pressure of 100 atm for 30–40 min. Under these conditions, the water reveals a dielectric permeability equaled to ε=32.6–24.3 at 230–270 °C, respectively, what is comparable with ε=36.2 at 25 °C obtained for acetonitrile as an ideal BaP solvent, thus leading to a complete dissolution of BaP by the subcritical water. This is confirmed by the data presented in Table 1. The maximum of BaP extraction is observed at temperature of subcritical water 250 °C, and it consists 11.9 ng/g nearly 96 % BaP from its initial content in soil. This is more than 7 % higher than during 35–40 min extraction time result. During the experiment, it was found that if the water temperature is lowered to 230 °C, the degree of BaP extraction from the soil is reduced by 38 %. This can be explained by changes ε and determines that the behavior of water in these conditions as the organic solvent. By increasing the temperature to 260–270 °C, BaP recovery decreased to 50 % due to partial decomposition of BaP (Table 1). Based upon the obtained results, the optimum conditions of the BaP extraction from soil have been determined: the soil is treating by subcritical water at 250 °C and 100 atm of pressure for 30 min.

The results of the subcritical water extraction of BaP from soil were compared to those obtained by a standard method in modification permitting to remove limiting lipid macrocomponents from soil by the saponification method for increasing the efficiency of the pollutant extraction (Directive document 2002).

The saponification method has been elaborated with the view of determining the BaP in bottom deposits, but it was used and approbated for soils. The given method involves treating the soil samples with a boiling mixture of 1 g soil and 100 ml of alkali and ethyl alcohol (96 %) for 3 h, further on, the re-extraction of BaP in 15 ml of the hexane solution three times. Subsequent stages in analyzing the obtained extracts are identical to those described for the extraction method using the subcritical water.

3 Results and discussion

The main trends in pollution by NPS emissions were identified in such important components as the impact zone of the soil by results of monitoring researches of BaP content in soils from 2008 to 2012 (Table 3). Data analysis within 5 years established that the number of defined compound in soils vary widely (Cachada et al. 2014) (Table 3). The main reason for the variation of the absolute values of BaP contents in soils adjacent to NPS can serve as a different load on the power plant energy units, which worked at various power in different years of observations. Every year, emissions to the atmosphere changed. 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.

The accumulation of BaP in the investigated steppe ecosystem 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 (Minkina et al. 2013). 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 3).

The main accumulation of pollutant in 20 cm layer of soils is noted directly in affected zone (Gabov and Beznosikov 2014). These are soils from the territory where plots No. 4, 5, 8, 9, and 10 (Table 3) are located. 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 (Tsibart and Gennadiev 2013).

The maximum quantity of a pollutant was founded in the soil of plot No. 4 located mostly close to a source of pollution in the direction of prevailing winds. Value from 2008 to 2009 reached to 275.6 ng/g in 5 cm soil layer and 117.8 ng/g in 5–20 cm soil layer that exceeded the BaP maximum concentration limit level in the soil up to 14 times (Table 3). The BaP

Table 3 The BaP content in soils of monitoring plots for years 2008–2012

Number of monitoring plots, direction, and distance from NPS	Selection depth, sm	BaP content, ng/g				
		2008	2009	2010	2011	2012
1. 1,0 Northeast	0–5	62.7±3.4	72.3±1.7	54.9±1.4	24.0±0.9	28.4±2.7
	5–20	24.8±1.1	23.9±1.7	26.6±0.9	17.1±2.1	6.9±0.7
2. 3,0 Southwest	0–5	28.0±1.3	18.2±1.4	18.4±1.6	22.7±0.1	7.7±1.1
	5–20	27.3±2.1	26.3±2.1	24.7±2.4	19.4±1.8	18.4±1.8
3. 2,7 Southwest	0–5	69.5±3.3	123.9±6.7	57.3±4.7	24.5±2.7	17.0±1.5
	5–20	18.4±0.6	62.8±5.4	19.8±1.5	8.6±1.2	12.5±0.8
4. 1,6 Northwest	0–5	182.5±3.5	275.6±9.2	84.2±6.8	62.4±5.8	46.2±5.9
	5–20	113.9±16.4	117.8±7.6	47.8±3.8	37.1±2.6	34.0±3.7
5. 1,2 Northwest	0–5	118.5±4.0	138.1±8.6	65.4±3.4	45.4±4.3	16.9±0.6
	5–20	72.8±8.2	92.1±3.7	45.3±2.0	35.9±2.8	21.3±1.3
6. 2,0 Northwest	0–5	46.6±2.8	67.4±2.8	32.4±1.4	34.3±2.6	28.5±2.6
	5–20	25.7±1.5	36.7±2.2	16.2±1.5	8.1±0.5	13.1±0.5
7. 1,5 North	0–5	38.5±2.1	87.6±3.7	39.5±2.4	36.4±2.3	35.2±3.4
	5–20	17.3±1.7	35.9±2.1	14.4±1.5	16.3±0.4	12.8±0.8
8. 5,0 Northwest	0–5	60.3±3.4	82.4±3.6	47.8±3.0	35.9±1.6	33.2±2.9
	5–20	41.7±1.7	28.4±1.7	28.6±2.7	24.6±2.1	19.1±1.4
9. 15,0 Northwest	0–5	27.4±0.9	25.6±2.6	18.4±1.2	13.0±0.7	27.5±2.2
	5–20	11.8±0.3	18.4±0.7	11.9±0.7	11.9±0.4	18.2±1.1
10. 20,0 Northwest	0–5	26.9±1.5	48.0±4.2	28.6±2.2	12.1±0.8	36.4±1.7
	5–20	17.4±0.7	32.5±3.2	14.1±0.7	7.5±0.6	19.2±1.0

level in a 5 cm soil layer gradually decreased since 2011; the quantity of a pollutant in the soil of the most polluted platform decreased 62.4 ng/g, and in 2012, it consists 46.2 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 3). However, in the majority of soils, their concentration in an underlying layer was lower (Sushkova et al. 2015). Superficial accumulation of BaP prevails in soils of researched 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 (Antizar-Ladislao et al. 2006; Gennadiev and Tsibart 2013). The exception is made by the sandy alluvial soil of plot No. 2 situated at distance 3.0 km to the Southwest that points to the increased migratory ability of BaP to underlying layers of this plot soil.

4 Conclusions

The method of BaP determination in soils by subcritical water extraction under the optimum conditions was used for long-term monitoring researches of technogenic polluted territories. The efficiency of the given method involves the use of subcritical water as an environmentally friendly solvent, a shorter time for analysis. BaP distribution and accumulation tendencies were investigated during the 5 years of monitoring researches in studied soils. The main factor of technogenic influence on the soil of the investigated area are toxic emissions of the enterprise of a power complex—NPS. Gradual decrease in the pollutant content in soils of the studied territory was established for 5 years period of supervision. It was explained by considerable reduction of volumes of polluting substances emission by the enterprise. Despite the environmental activities of the enterprise, the impact of emissions on the environment location nearby today is still primary one. Benzo[a]pyrene accumulation and distribution in soils depends on their physical and chemical properties. In the sandy alluvial soil, the compound can migrate in the soil profile, in the low-humus calcareous sandy alluvial meadow soil provide the mobility for benzo[a]pyrene because of light texture and a low cation exchange capacity, but accumulation of this pollutant in the low-humus silty-clayey meadow-chernozemic flood plain soil with a high CEC differed by low mobility down the soil profile and accumulation the most part in the 5 cm layer of the soil.

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