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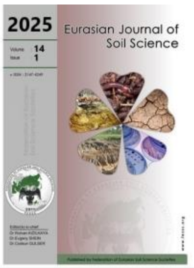

Development and adaptation of methods for PAHs extraction from bottom sediments using subcritical water extraction, saponification, and ultrasound extraction

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that pose significant environmental and health risks due to their widespread distribution and carcinogenic properties. Developing efficient and environmentally friendly extraction methods for PAHs from complex matrices like bottom sediments is essential for advancing pollution monitoring and mitigation efforts. The influence of temperature and time parameters of water in a subcritical state on the extraction of widespread, contrasting in physicochemical properties polycyclic aromatic hydrocarbons (PAHs) from bottom sediment samples of the Lena River with varying initial pollutant content was studied. It was shown that the optimal extraction parameters for naphthalene are 240°C for 20 minutes, for phenanthrene and fluoranthene – 240°C for 30 minutes, for benzo(a)pyrene – 250°C for 30 minutes, and for benzo(g,h,i)perylene – 260°C for 40 minutes. Under these conditions, the proportion of extracted PAHs varies from 76% to 85%. A comparison was conducted of widely used PAH extraction methods based on the use of toxic solvents from standard techniques. It was established that the efficiency of extraction methods can be ranked as follows: ultrasound extraction > subcritical extraction > saponification method. In this case, the value of the PAH extraction coefficient during subcritical extraction was 1.23-1.29, during saponification - 1.35 and 1.34, and during the ultrasonic extraction method - 1.10 and 1.08.

Keywords: Polycyclic aromatic hydrocarbons, organic pollutants, bottom sediments, pollution, naphthalene, phenanthrene, benzo(a)pyrene, extraction method, high-performance liquid chromatography.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of high-molecular compounds that exhibit carcinogenic and mutagenic properties (IARC, 2020; Fedorenko et al., 2021; Sushkova et al., 2021). These substances are part of hydrocarbon fossils, are formed during fires, and are products of incomplete combustion of carbon-containing materials (Tsibart and Gennadiev, 2013). Due to the wide variety of sources of their intake, PAHs are ubiquitous in the environment (Dudnikova et al., 2023a,b). From point sources of emission, PAHs in carrier particles can migrate for hundreds of kilometers, accumulating in natural environments of background territories (Chaplygin et al., 2023). At the same time, up to 98% of PAHs accumulate in depositing environments - soils and bottom sediments (Macdonald et al., 1996; Sojinu et al., 2010).

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To date, there is no unified concept for assessing the ecological state of depositing environments contaminated with PAHs. Despite the fact that the International Agency for Research on Cancer annually publishes a list of substances and factors that contribute to carcinogenesis. In this list, more than 30 PAHs are noted as substances that likely contribute to the formation of cancer (IARC, 2020). In world practice, when assessing and predicting the ecological state of soils, the content of 16 PAHs from the list of priority pollutants of the US Environmental Protection Agency is often determined (US EPA, 2020). In this regard, the use of reliable methods for analyzing and monitoring the content of PAHs in bottom sediments is required. However, at present, the quality of the assessment and forecast is limited by a number of factors, including the relevance of generally accepted methods for determining the mass fraction of pollutants in bottom sediments. Existing methods for extracting PAHs from natural environments are based on the use of various toxic organic solvents (Lau et al., 2010; Wu et al., 2019). The disadvantages of such methods include the duration of the sample preparation process, high consumption of organic solvents, which subsequently require specialized disposal (Song et al., 2002). An alternative extractant for organic pollutants from natural environments is subcritical water. Subcritical water is water in a liquid state at a temperature above 100°C and a pressure above the saturated vapor pressure (Zhang et al., 2020). By increasing the temperature of water in sealed conditions, it changes its physical and chemical properties, primarily the value of dialectical permeability, acquiring the characteristics of organic solvents. By varying the parameters of water temperature and time of exposure to the sample, it is possible to achieve conditions under which the yield of PAHs in the extract will be comparable to generally accepted methods of extracting pollutants (Sushkova 2014, 2024). In this regard, the aim of the study was to determine the optimal parameters of temperature and time of exposure to bottom sediment samples to determine the PAH content.

Material and Methods

The Lena River is located in Eastern Siberia, flowing across the entire territory of Russia. Its length reaches 4400 km, the basin area is 2.49 million km2, the average long-term flow is about 530.2 km^3/year. It flows into the Laptev Sea of the Arctic Ocean, forming the largest delta in the Arctic. Samples were collected from the bottom sediments of the Lena River delta using Van Veen Grab sampler in August 2024. Samples were packed in hermetically sealed bags and frozen at temperature -10 Celsius degree. Transportation to the laboratory was carried out under frozen conditions. To develop and adapt the method for PAH extraction using subcritical water, two samples of bottom sediments were selected, representing varying hydrological conditions at a distance from direct sources of pollutants with contrasting levels: d12 (72.572352°N; 126.435160°E) and d21 (72.563507°N; 126.452868°E). According to preliminary studies, the total content of priority PAHs in the bottom sediments of sample d12 was 169 ng g^{-1}, d21 – 407 ng g^{-1}. In general, the level of PAH content in the samples does not exceed international standards and concentrations established for bottom sediments from different regions of the world (Buchman, 2008; Rabodonirina et al., 2015; Marvin et al., 2021; Dudnikova et al. 2023a,b). However, the bottom sediment sample with the lowest PAH content (d12) was considered as an uncontaminated sample, d21 – as contaminated. The method was developed using the example of widespread pollutants included in the list of priority pollutants, contrasting in physicochemical properties and toxicity to representatives of the PAH group: 2-ring naphthalene (Sigma Aldrich, CAS: 91-20-3, 98%), 3-ring phenanthrene (Sigma Aldrich, CAS: 85-01-8, 98%), 4-ring -fluorene (Sigma Aldrich, CAS: 86-73-7, 98%), 5-ring benzo(a)pyrene (Sigma Aldrich, CAS: 50-32-8, 98%), 6-ring benzo(g,h,i)perylene (Sigma Aldrich, CAS: 191-24-2, 98%) (US EPA, 2020; IARC, 2020; ATSDR, 1995, 2020; Dudnikova et al., 2023a,b) (Table 1).

Table 1. Limits of detection (LOD) and limits of quantification (LOQ) of PAHs

№	PAHs	Formula	Number of benzene rings	Molar Mass, g/mol	Solubility in water, mg/l at 200˚C	LOD	LOQ	Retention time, min
1	Naphthalene	$C_{10}H_8$	2	128.2	30.00	0.11	0.05	5.2
2	Phenanthrene	$C_{14}H_{10}$	3	178.2	1.18	0.12	0.08	8.4
3	Fluoranthene	$C_{16}H_{10}$	4	202.3	0.28	0.09	0.05	10.5
4	Benzo(a)pyrene	$C_{16}H_{12}$	5	252.3	0.001	0.15	0.10	25.1
5	Benz(g,h,i)perylene	$C_{22}H_{12}$	6	276.3	0.000003	0.12	0.10	39.7

Methods

Selection of conditions for PAH extraction from bottom sediments using subcritical water

To select the conditions for PAH extraction in a subcritical water environment, we used the author's laboratory cartridge made of stainless steel with a metal thickness of 0.5 cm. The studied temperature parameters were in the range of 230-270°C, time - 10-50 minutes. These parameter ranges are most often encountered when studying the possibility of using subcritical technologies for the extraction of organic pollutants from bio-bone systems, plant and animal tissue (Latawiec and Reid, 2010; Sushkova, 2014, 2024; Yabalak et al., 2024). When determining the optimal conditions for PAH extraction, the analytical repetition in the experiment was ninefold. A 1 g sample of the analyzed substance from bottom sediments with a particle size of 1 mm, selected and prepared in accordance with GOST (MU 1424076, 1976; GOST 17.4.4.02-84, 1986) was placed in an extraction cartridge filled with broken Pyrex glass with a particle size of 1 mm and 0.5 mm of 0.5 g each. The cartridge was then connected to a laboratory setup, where the sample was heated to 230-270°C with a constant flow of bidistilled water passing through the cartridge under pressure. at a rate of 1 mL/min for 10-50 minutes. 5 mL of n-hexane (Sigma Aldrich, CAS 110-54-3, 97%) were added to the resulting aqueous extract and the mixture was shaken for 15 min. on a shaker at 135 rpm. The layers were separated in a 50 mL separatory funnel in three stages with the next portion of hexane. The hexane extracts were combined, passed through a funnel with anhydrous sodium sulfate (Sigma Aldrich, CAS 7757-82-6, 99%) into a clean dry rotary flask and evaporated to dryness on a rotary evaporator at a water bath temperature of 49°C. 1 mL of acetonitrile (Sigma Aldrich, CAS 75-05-8, 99%) was added to the dry residue and thoroughly mixed for 30 minutes. The scheme of the laboratory setup is shown in Figure 1.

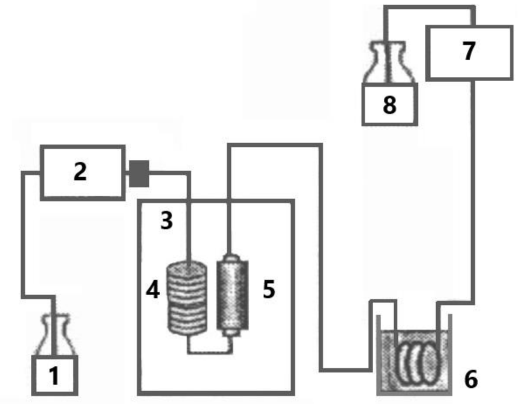

Figure 1. Schematic diagram of the setup for PAH extraction with subcritical water: 1. Tank for bidistilled water; 2. Pump "Elilex LABS, INC. MENLO PARK, CA" (model AA-100-S-2); 3. Thermostat (electric oven, model HRHK C-242 - 100/179/2150W, 230V); 4. Thermostat spiral (system communications L=3.5 m, folded in the form of a spiral L=12 cm); 5. Cartridge (stainless steel L=150 mm and internal diameter 4.5mm); 6. Ice bath; 7. Restrictor (pressure limiter); 8. Tank for collecting extracts

To establish the completeness of PAH extraction from river bottom sediments by the methods under consideration, a blank experiment was additionally conducted with the introduction of solutions of a given concentration into river bottom sediments (additive method). In this case, the additive is introduced as an acetonitrile solution of each PAH into a 1 g sample of river bottom sediments placed in a flask for a rotary evaporator. After evaporation of acetonitrile (at room temperature), the sample with the introduced additive is processed in accordance with the proposed method. The experiment is repeated nine times. The correction factor (k) was calculated using equations (1, 2):

$$k = \frac{C1}{C2} \tag{1}$$

$$C1 = Cst + \mathrm{C}p, \tag{2}$$

where C1 is the total concentration of each PAH in the river bottom sediment sample, ng g^{-1}; C2 is the concentration of each PAH in the river bottom sediment determined by the saponification method, ng g^{-1}. Cst is the concentration of each PAH in the river bottom sediment due to the addition of its standard solution, ng g^{-1}; Sp is the average concentration of each PAH in the river bottom sediment sample, ng g^{-1};

For the developed method for determining PAH in river bottom sediments, the random component of the measurement error was estimated, which for the concentration range of 1–500 ng g^{-1} was 0.5–1.5%.

To assess the efficiency of the method, the results obtained by means of PAH extraction in a subcritical water environment were compared with widely used methods based on the use of a large number of toxic organic solvents.

Extraction of PAHs using saponification method

The analysis was carried out in accordance with the requirements (RD 52.10.556-95), allowing the removal of interfering matrix components (Sushkova et al., 2024). This method is the most adapted to the analysis of bottom sediment components, therefore it was chosen as the main method for the analysis in this project.

Briefly. The selected bottom samples were crushed and sieved through a 1 mm diameter sieve. For further analysis, the interfering lipid fraction was removed by saponification of 1 g of bottom sediments with a 2% alcohol solution of KOH (Sigma Aldrich, CAS 1310-58-3, 99%) in a water bath in round-bottomed flasks attached to reflux water condensers for 3 hours. During boiling, saponification of lipids and resinous components and the aliphatic fraction of PAHs in bottom sediments occurred, which increased the recovery of PAHs and decreased the amount of extracted substances in the extract (Poole et al., 1990). The resulting percalate was poured into 100 mL conical flasks, 5 mL of distilled water and 15 mL of hexane were added. Then, extraction was carried out on a mechanical shaker for 10 minutes at a frequency of 135 shakes per minute in triplicate. The resulting hexane extracts were combined in a separatory funnel, transferred to a clean dry rotary flask, evaporated on a rotary evaporator with a water-jet pump at a water bath temperature of 49°C until a dry residue was obtained (Figure 4). 1 mL of acetonitrile was added to the resulting dry residue and left for 30 minutes.

Ultrasonic extraction

To determine the efficiency of the methods used in the work, an assessment of the conformity of the developed and adapted methods to the international level and standards was carried out. To solve the problem, PAH extraction from bottom sediments was carried out according to the international method of ultrasonic extraction US EPA 3550c (US EPA Method 3550C, 2007).

Briefly. A 1 g sample of a solid object is placed in a 50 cm3 conical flask with a ground glass stopper. 15 mL of a hexane / dichloromethane = 1/1 mixture are used as an extractant. The extraction procedure was carried out for 5 minutes on a Branson 5510 ultrasonic bath in triplicate. The resulting extract is placed in a glass column pre-filled with 2 g of aluminum oxide. After the precipitation of aluminum oxide, 0.5 g of anhydrous sodium sulfate was added. The column was then washed with 20 mL of hexane, discarding the eluate coming out of the column. Then the PAH was eluted with 30 mL of a mixture of dichloromethane/hexane = 1/4. The entire eluate was collected in a flask for evaporation and evaporated on a rotary evaporator at a temperature of 49°C. The dry residue was dissolved in 2 cm3 of acetonitrile.

Chromatographic analysis

The PAH content in the extracts obtained using different methods of samples was determined by high-performance liquid chromatography using an Agilent Technologies chromatograph (Santa Clara, CA, USA) with a fluorescence (FL-3000) detector. A mixture of acetonitrile and deionized water (4:1) was used as the mobile phase at a flow rate of 0.5 mL/min and a temperature of 20°C. The volume of the injected solution was 20 µl. The PAH content in the analyzed samples was calculated using the external standard method (absolute calibration). The detection limits (LOD) and quantification limits (LOQ) are given in Table 1.

The PAH content in river bottom sediments was calculated using the equation:

$$a = k\,SI \times C\text{ст} \times \frac{V}{S\text{ст} \times m}, \qquad (3)$$

where a is the PAH content in river bottom sediments (ng g^{-1}); Sst and SI are the peak areas of the PAH standard solution and sample; Cst is the concentration of the PAH standard solution (ng/mL); k is the coefficient of PAH extraction from the sample; V is the volume of acetonitrile extract (mL); m is the mass of the sample (g).

Results and Discussion

It was found that for unpolluted soil, the highest yield of naphthalene in the extract is observed at 240°C for 20 minutes, phenanthrene and fluoranthene - at 240°C for 30 minutes, benzo(a)pyrene - at 250°C for 30 minutes and benzo(g,h,i)perylene - at 260°C for 40 minutes. With an increase in the extraction temperature and exposure time above the listed values, a significant decrease in the yield of PAHs in the extract is observed. The effect is enhanced with a decrease in the dimension and molecular weight of the substance, which is due to the degradation of PAH molecules in the subcritical water environment (Islam et al., 2015). For contaminated bottom sediments, the optimal conditions for PAH extraction are similar, but the proportion of extracted compounds is 2-6% higher compared to unpolluted bottom sediments (Figure 2).

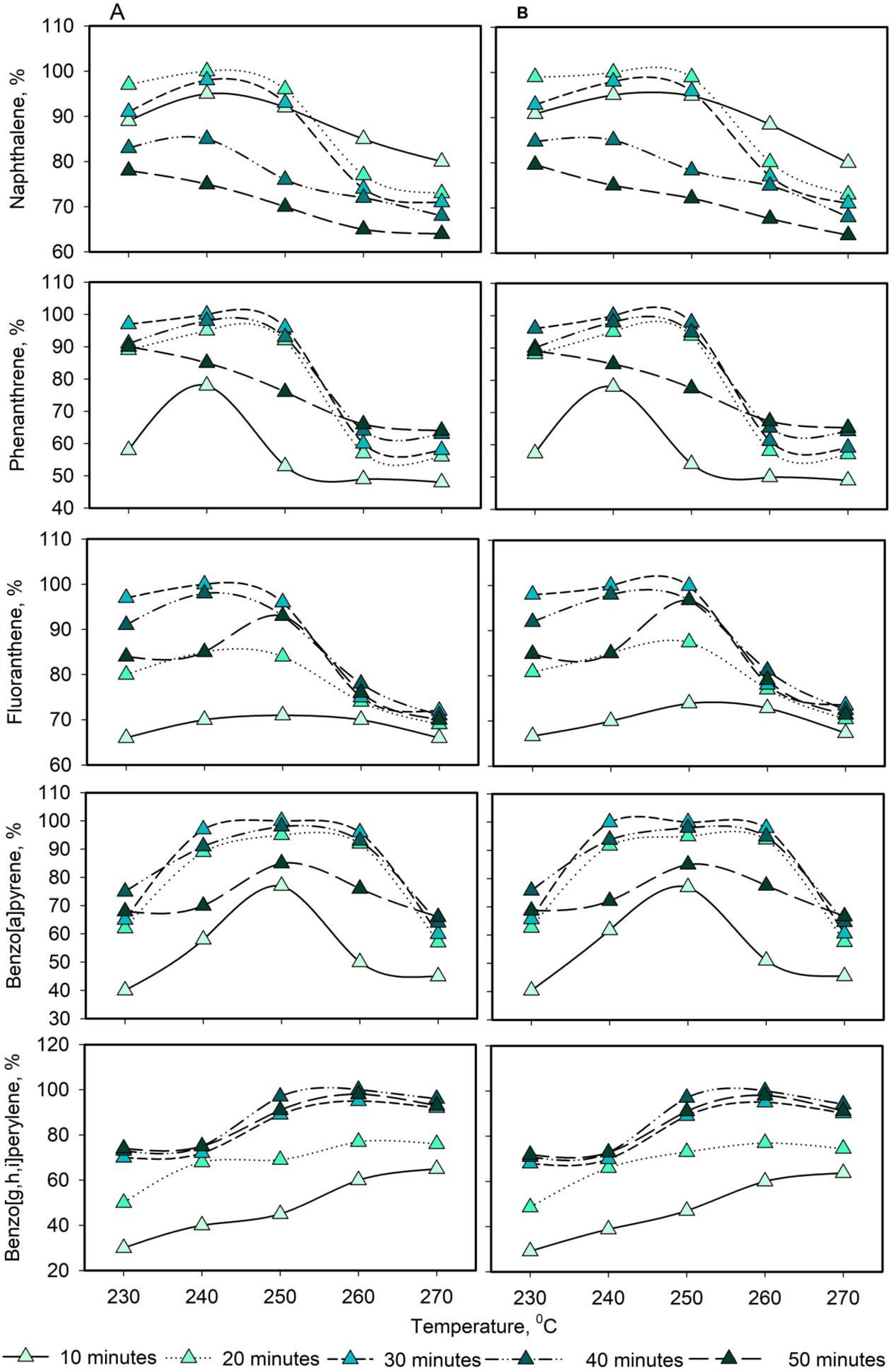

Figure 2. The proportion of PAH extraction from contaminated and uncontaminated bottom sediments depending on the temperature and time of extraction in a subcritical water environment

With increasing pollutant content in the deposition media, especially for low-carbon bio-based systems, PAH molecules are concentrated at low-affinity reaction sites (Xu et al., 2014). Therefore, the energy spent on pollutant desorption is lower, which leads to more complete extraction during subcritical extraction (Liang et al., 2016). In the unpolluted sample, PAH molecules are most likely concentrated in the pool of aromatic structures of organic matter and the energy spent on their extraction increases (Xu et al., 2014; Diagboya et al., 2018). Under optimal extraction conditions, the naphthalene content in the samples of uncontaminated and contaminated bottom sediments was 0.9 ng $g^{-1}$and 13.2 ng g^{-1}, phenanthrene – 72.6 ng $g^{-1}$and 233.2 ng g^{-1}, fluoranthene – 18.8 ng g^{-1} and 30.1 ng g^{-1}, benzo(a)pyrene 6.0 ng g^{-1} and 14.8 ng g^{-1}, benzo(g,h,i)perylene – 6.2 ng g^{-1} and 19.2 ng g^{-1}, respectively (Table 2).

Table 2. Extraction of PAHs from bottom sediment samples using subcritical water at different temperature and extraction time parameters

Not contaminated						Contaminated					
Temperature	Time					Temperature	Time				
	10	20	30	40	50		10	20	30	40	50
1	2	3	4	5	6	7	8	9	10	11	12
Naphthalene						Naphthalene					
230	0.84	0.92	0.86	0.79	0.74	230	12.10	13.19	12.37	11.29	10.61
240	0.90	0.95	0.93	0.81	0.71	240	12.66	13.33	13.06	11.33	9.99
250	0.87	0.91	0.88	0.72	0.66	250	12.64	13.18	12.77	10.44	9.61
260	0.81	0.73	0.70	0.68	0.62	260	11.79	10.68	10.26	9.99	9.02
270	0.76	0.69	0.67	0.65	0.61	270	10.66	9.73	9.46	9.06	8.53
Phenanthrene						Phenanthrene					
230	42.09	64.58	70.39	66.04	65.31	230	133.91	205.48	223.95	210.10	207.79
240	56.60	68.94	72.57	71.12	61.68	240	181.90	221.55	233.21	228.55	198.23
250	38.46	66.76	69.66	67.49	55.15	250	126.07	218.85	228.36	221.22	180.79
260	35.56	41.36	43.54	46.44	47.89	260	116.56	135.59	142.73	152.24	157.00
270	34.83	40.64	42.09	45.72	46.44	270	114.18	133.21	137.97	149.86	152.24
Fluoranthene						Fluoranthene					
230	12.42	15.05	18.25	17.12	15.81	230	20.05	24.31	29.47	27.65	25.52
240	13.17	15.99	18.82	18.44	15.99	240	21.05	25.57	30.08	29.48	25.57
250	13.36	15.81	18.06	17.50	17.50	250	22.23	26.30	30.05	29.11	29.11
260	13.17	13.92	14.11	14.68	14.30	260	21.91	23.17	23.48	24.42	23.79
270	12.42	12.98	13.55	13.36	13.17	270	20.26	21.18	22.10	21.79	21.48
Benzo(a)pyrene						Benzo(a)pyrene					
230	2.39	3.71	3.89	4.48	4.06	230	5.97	9.25	9.70	11.19	10.14
240	3.47	5.32	5.80	5.44	4.18	240	8.82	13.54	14.76	13.85	10.65
250	4.60	5.68	5.98	5.86	5.08	250	11.37	14.03	14.77	14.47	12.55
260	2.99	5.50	5.74	5.56	4.54	260	7.53	13.86	14.46	14.01	11.45
270	2.69	3.41	3.59	3.83	3.95	270	6.71	8.50	8.95	9.55	9.84
Benz(g,h,i)perylene						Benz(g,h,i)perylene					
230	1.87	3.12	4.37	4.56	4.62	230	5.58	9.29	13.01	13.57	13.76
240	2.50	4.24	4.49	4.68	4.68	240	7.44	12.64	13.38	13.94	13.94
250	2.81	4.31	5.55	6.05	5.68	250	8.62	13.22	17.05	18.58	17.43
260	3.74	4.80	5.93	6.24	6.11	260	11.49	14.75	18.20	19.16	18.77
270	4.06	4.74	5.74	5.99	5.80	270	12.21	14.27	17.28	18.03	17.46

During the experiment with pollutant additions to bottom sediment samples, the effect of PAH extraction methods on pollutant concentrations in extracts was compared. It was found that the extraction methods form a series in terms of efficiency: saponification method < subcritical extraction < ultrasonic extraction (Figure 3, 4). The differences between the methods are more pronounced when adding 132 ng g^{-1} PAH to the original bottom sediment samples, especially for naphthalene, which is easily desorbed compared to other PAHs, from a contaminated bottom sediment sample (Rhodes et al. 2012). On average, the proportion of naphthalene extracted from unpolluted and polluted bottom sediment samples during extraction in subcritical water is 77-78%, phenanthrene 78-81%, fluoranthene 78-82%, benzo(a)pyrene 79-81%, benzo(g,h,i)perylene 76-85%, during extraction by saponification method - 73-74%, 73-75%, 75-76% and 74-75%, during ultrasound extraction 94-95% 93-95%, 92-93%, 91-92% and 86-89%, respectively. The yield of PAHs in the extract can be described as desorption of pollutants from the biobone matrix, which occurs in several stages. Desorption of PAHs from soils and sediments often follows a biphasic profile, with an initial rapid desorption phase followed by slow and very slow-release phases. Slow or very slow desorption rates are due to the association of PAHs with the aromatic component of soils and can be bound or adsorbed in micropores, making them difficult to access for various extractants (Rhodes et al., 2012; Xu et al., 2014; Diagboya et al., 2018; Ren et al., 2018). Since the affinity of PAHs for organic matter in biosolids increases with increasing molecular weight of the pollutant, a consistent decrease in the efficiency of organic solvent-based extraction methods was observed in the recovery of target substances (Sushkova et al., 2015, 2024) (Figures 3, 4).

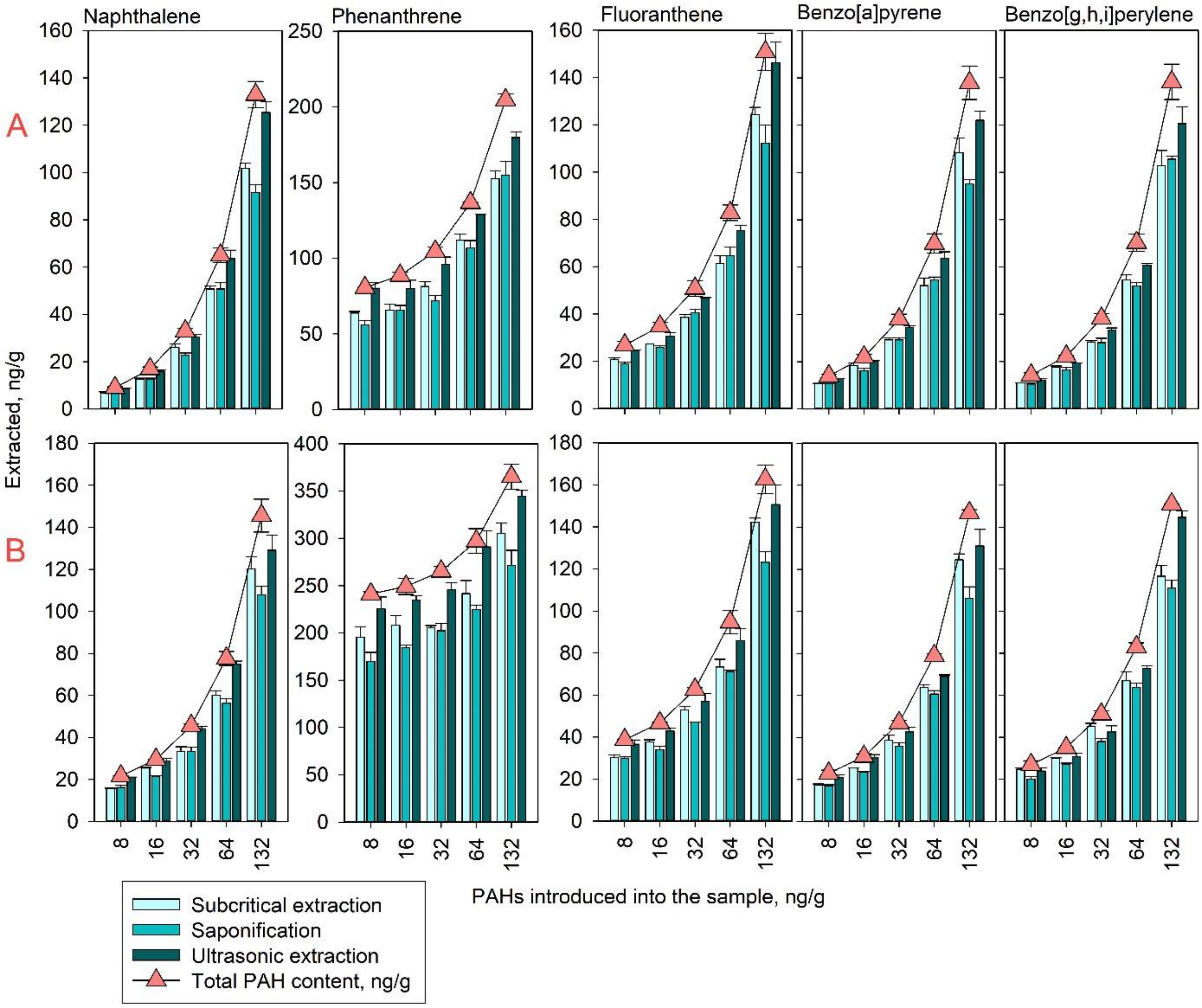

Figure 3. Extraction of PAHs from uncontaminated bottom sediment samples using subcritical water at different extraction temperature and time parameters

On the contrary, when the samples were exposed to water in a subcritical state, an increase in the extraction efficiency was observed for heavier molecular weight substances, such as 5-ring benzo(a)pyrene and 6-ring benzo(g,h,i)perylene, which is most likely due to some destruction of 2-4-ring compounds during the extraction process. The coefficients of PAH extraction from bottom sediments with different levels of contamination were determined. It was shown that the average coefficient of PAH extraction during subcritical extraction from uncontaminated bottom sediments was 1.29, from contaminated ones – 1.23, during extraction by the saponification method – 1.35 and 1.34, during ultrasonic extraction – 1.10 and 1.08, respectively (Figure 4).

Conclusion

It has been established that the extraction of PAHs from bottom sediments depends on the level of the initial content of pollutants in them, the type of pollutant, temperature and extraction, and the time of exposure to the sample. The optimal parameters for naphthalene extraction are 240°C for 20 minutes, phenanthrene and fluoranthene - 240°C for 30 minutes, benzo(a)pyrene - 250°C for 30 minutes, and benzo(g,h,i)perylene -

260°C for 40 minutes. The efficiency of PAH extraction methods decreases in the following order: ultrasonic extraction (86-95%) > subcritical extraction (76-85%) > extraction by saponification (73-76%). The extraction of pollutants from bottom sediments increases with an increase in the initial content of pollutants in them and a decrease in the molecular weight of the substance. The average recovery factor for subcritical extraction of naphthalene in uncontaminated and contaminated bottom sediment samples is 1.29 and 1.23, respectively.

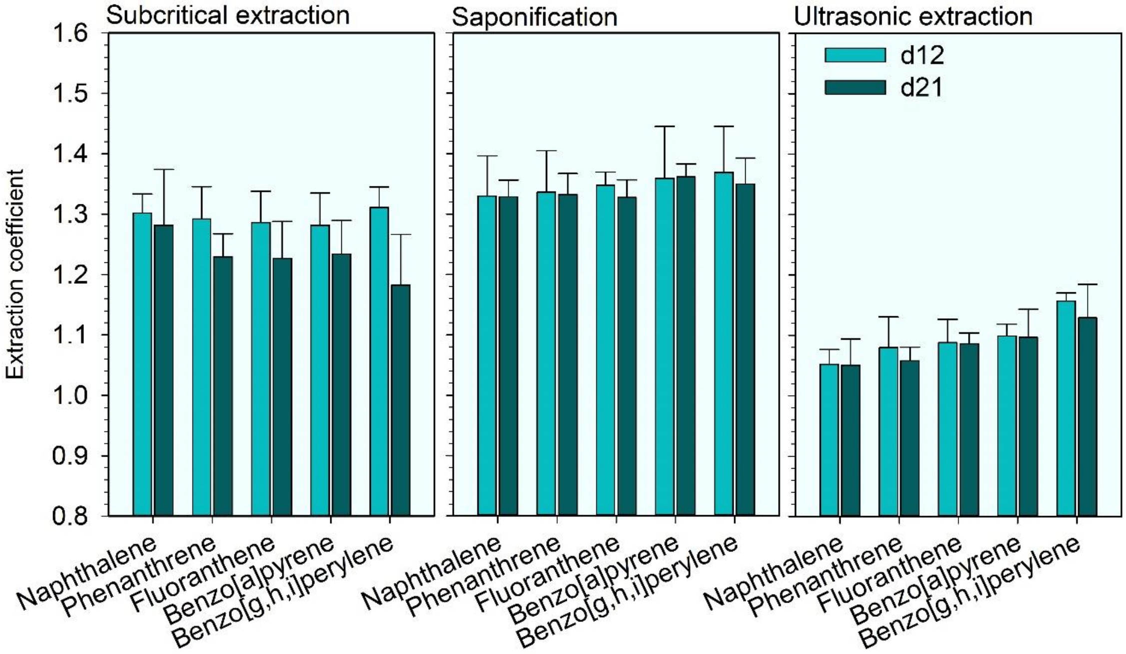

Figure 4. PAH extraction coefficient from unpolluted and polluted bottom sediments of the Lena River using different extraction methods

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