Polycyclic aromatic hydrocarbons in sediments of water reservoirs (middle Volga region, Russia)

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Abstract. Bottom sediments from the Kuibyshev and Cheboksary reservoirs were sampled and the content of anthracene, acenaphthylene, acenaphthene, benz (a) pyrene, benz (b) fluoranthene, benzo (k) fluoranthene, benz (g, h, i) perylene, dibenz (a, h) anthracene, pyrene, fluorene, fluoranthene, phenanthrene, chrysene was analyzed. The level of the total polycyclic aromatic hydrocarbons (PAH) content in the bottom sediments of the Cheboksary and Kuibyshev reservoirs was lower in comparison with the standards adopted in foreign countries. A tendency of increasing the PAHs content from the upper to the lower parts of the reservoirs, in the area of the Kama river mouth and the upper reach of the Samara hydroelectric power plant, was noted. PAHs with three benzene rings prevailed in the bottom sediments of the Cheboksary reservoir, and two and five benzene rings - in the Kuibyshev reservoir.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds with two or more aromatic rings. These widespread pollutants are mainly by-products from the combustion of fossil fuels, chemical, metallurgy industry, pulp-and-paper industries [1].

At the present time, PAHs are a pollutant of all components of the biosphere, such as the atmosphere, hydrosphere, and soil. PAHs entering the atmosphere occurs with industrial emissions, exhaust gases from internal combustion engines, from energy industries, during forest fires. PAHs enter the hydrosphere with precipitation, surface runoff, and wastewater from oil refineries. PAHs pollute soils as a result of atmospheric transport [2].

The difficulty of protecting the environment from the negative effects of PAHs is associated with their wide distribution; they can be found in the form of aerosols in the atmospheric air, in the aqueous phase, or adsorbed on solid particles. The wide distribution of PAHs in trace amounts and their ability to accumulate in the environment makes it necessary to analyze and strictly control the PAHs content in environment [1].

Bottom sediments are a special bioinert structure, an organomineral substance formed due to the inflow from the catchment area of suspended particles with surface runoff (allochthonous component) and formed as a result of the life activity of the aquatic ecosystem (autochthonous component). Sediments are able to accumulate PAHs, increasing their concentration, and retain information on the PAHs input in retrospective years.
The object of the study was to assess and compare the PAHs content in bottom sediments of the Kuibyshev and Cheboksary reservoirs.

2. Materials and methods

The Cheboksary reservoir is one of the reservoirs of the Volga-Kama cascade, located on the Volga river, in the territory of Chuvash Republic, the Republic of Mari El and the Nizhny Novgorod region (Russia). The catchment area is 604,000 km², the length is 341 km, the width of the reservoir is 16 km, the surface area is 2190 km², the length of the coastline is 2431 km, the water volume is 13.85 km³, the average depth of the reservoir is 6 m, the maximum depth is located at 21 m [3].

The Kuibyshev Reservoir is located on the Volga River, in the Samara Region, the Chuvash Republic, the Republic of Mari El, the Republic of Tatarstan and the Ulyanovsk Region. The length of the reservoir along the Volga is 510 km, the greatest width is 40-44 km at the mouth of the Kama, the area of the water surface is 6450 km², and the volume of water is 58 km³. The main purpose of the reservoir is to generate electricity, improve navigation, water supply, irrigation [4].

The sampling of bottom sediments from the Kuibyshev and Cheboksary reservoirs (figure 1) was carried out in 2015 with a Petersen scoop grab (table 1). Chemical analysis of samples for the determination of PAHs (anthracene, acetonaphthylene, acenaphthene, benz (a) pyrene, benz (b) fluoranthene, benzo (k) fluoranthene, benz (g, h, i) perylene, dibenz (a, h) anthracene, pyrene, fluorene, fluoranthene, phenanthrene, chrysene) was carried out on a Flexar chromatograph (Perkin Elmer, USA) with a Brownlee Analytical C18 reverse phase column, where an acetonitrile-water mixture was used as a mobile phase; detection was carried out using fluorescent and ultraviolet detectors [5].

![Figure 1](image-url)

**Figure 1.** Schematic map of the sampling sites of bottom sediments in the Cheboksary and Kuibyshev reservoirs.

| №  | Sampling site          | Location                |
|----|------------------------|-------------------------|
| 1  | Below Kstovo           | 56° 9.800'С; 44° 13.628'В |
| 2  | Lyskovo - Makariev     | 56° 4.832'С; 45° 4.650'В |
3. Results and its discussion

When we analyzed individual PAH components, we revealed that the content of naphthalene, acenaphthene, fluorine, phenanthrene, chrysene, benzo(k)fluoranthene is higher in bottom sediments of the Cheboksary reservoir in comparison with the Kuibyshev reservoir. However, we found a wider range of components in the bottom sediments of the Kuibyshev reservoir (table 2).

| Table 2. Content of PAHs (ng/g) in bottom sediments of Cheboksary and Kuibyshev reservoirs. |
|---------------------------------------------------------------|
| **Content, ng/g** | Cheboksary reservoir |  | Kuibyshev reservoir |  |
|  | Average | SD | Average | SD |
| Naphthalene | 6.32 | 4.24 | 4.09 | 3.73 |
| Acenaphthylene | 0.00 | 0.00 | 0.31 | 0.73 |
| Acenaphthene | 13.55 | 30.30 | 2.26 | 7.82 |
| Fluorene | 0.83 | 0.47 | 0.00 | 0.00 |
| Phenanthrene | 14.58 | 18.91 | 1.45 | 2.54 |
| Anthracene | 0.00 | 0.00 | 0.81 | 1.32 |
| Fluoranthene | 0.00 | 0.00 | 0.26 | 0.90 |
| Pyrene | 0.00 | 0.00 | 0.57 | 0.91 |
| Chrysene | 6.08 | 7.93 | 2.86 | 2.56 |
| Benzo[b]fluoranthene | 2.30 | 1.99 | 4.13 | 5.83 |
| Benzo[a]pyrene | 1.50 | 1.48 | 3.90 | 2.06 |
| Benzo[k]fluoranthene | 3.81 | 3.81 | 0.00 | 0.00 |
| Dibenz[a,h]anthracene | 0.00 | 0.00 | 0.00 | 0.00 |
| Benzo[ghi]perylene | 0.00 | 0.00 | 0.00 | 0.00 |
Ingredient analysis of PAHs components showed that hydrocarbons with 3 benzene rings (acenaphthene and phenanthrene) predominated in the Cheboksary reservoir; PAHs with two and five benzene rings (naphthalene and benz (b) fluoranthene) prevailed in the Kuibyshev reservoir (figure 2).

![Figure 2](image2.png)

**Figure 2.** Content (%) of PAH components in bottom sediments of the Cheboksary and Kuibyshev reservoirs.

The total content of PAHs in sediments of the Cheboksary Reservoir ranged from 5.58 to 153.43 ng/g (figure 3). The highest content of PAHs was noted in the area of town Kozmodemyansk (No. 6), which may be a consequence of the influence of the city's industry [6]. There is a tendency to an increase in the content of the total PAHs in sediments downstream, from the upper points to the lower ones.

![Figure 3](image3.png)

**Figure 3.** Content of sum of PAHs in sediments of the Cheboksary reservoir.
In sediments from the Kuibyshev Reservoir, the highest PAHs content was recorded at the mouth of the Kama (No. 12). PAHs can enter the river Kama and its tributaries with wastewater discharges from chemical, petrochemical and oil production enterprises. The increased content of PAHs in sediments of the upstream of the Samara HPP, at the dam site (No. 19) relative to other sampling points, may be a consequence of their accumulation in sediments and their input from the upstream territories (figure 4).

![Figure 4](image)

**Figure 4.** The content of the sum of PAHs in the bottom sediments of the Kuibyshev reservoir.

In comparison the average concentrations of PAHs in the Kuibyshev and Cheboksary reservoirs, we noted more high content in sediments of Cheboksary reservoirs, which may be associated with the influence of chemical industry enterprises of the Chuvash Republic (figure 5).

![Figure 5](image)

**Figure 5.** Average content of the sum of PAHs in bottom sediments of the Cheboksary and Kuibyshev reservoirs.
There are no approved standards for the content of PAHs in bottom sediments in the Russian Federation, therefore, the assessment was made according to the criteria adopted in other countries: 1000 ng / g - the Netherlands [7], 1610 ng / g - the United States [8], 4022 ng / g - China [9]. The analysis showed that the content of PAHs in bottom sediments of the Cheboksary and Kuibyshev reservoirs is significantly lower than the above mentioned standards.

4. Conclusion

The level of the total PAHs content in the bottom sediments of the Cheboksary and Kuibyshev reservoirs is lower in comparison with the standards adopted in foreign countries. A tendency towards an increase in the PAH content from the upper to the lower parts of the reservoirs, as well as in the area of the Kama river mouth and the upper reach of the Samara HPP, was noted. In the bottom sediments of the Cheboksary reservoir, PAHs with three benzene rings prevailed, in the Kuibyshev reservoir - with two and five benzene rings, which indicates both pyrogenic and petrogenic sources of their input.

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