Polycyclic aromatic hydrocarbons in bottom sediments of an inner-city lake in the zone of discharge of surface runoff

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Abstract. The study determined the content of polycyclic aromatic hydrocarbons (PAHs) in the bottom sediments of an inner-city Sredny Kaban Lake (Kazan, Russia) in the places of the organized release of untreated surface stormwater runoff within the catchment of the city. The content of 15 PAHs included in the priority list of PAHs for environmental research in the Russian Federation and in other countries was experimentally studied. The average content of the total PAHs studied (333.4 μg/kg) in the bottom sediments of the lake indicates a low degree of pollution. The analysis of the ratio of the content of individual PAHs reveals the main sources of their entry: fuel combustion (vehicles) and oil pollution of the surface water. Benzo(g,h,i)perylene and Benz(a)pyrene represent the largest contribution to the hazard coefficient of all studied PAHs for bottom sediments of the studied water body. Bottom sediments are composed mainly of particles with a size of 1–100 μm; the contribution of particles with a size of 0.1–1 μm was estimated to be up to 1%.

1. Introduction
Surface stormwater runoff from urban areas is an intensive factor in anthropogenic pressure on inner-city water bodies. A large amount of the pollutants entering the surface water into the water body is polycyclic aromatic hydrocarbons (PAHs), which belong to the group of priority pollutants that are formed mainly during the operation of industrial enterprises, in internal combustion engines, during the operation of thermal power plants and boiler houses and are extremely dangerous for humans and animals [1], [2], [3], [4], [5], [6].

The aim of this work is the determination of PAHs in the bottom sediments of an inner-city water body in places of organized discharge of untreated stormwater runoff from the urban area. The object of the study was the bottom sediments of the Sredny Kaban Lake (Kazan, Russia; 55°45′07.0″N, 49°08′42.5″E) and the subject of the study was the level of PAHs accumulation in bottom sediments.

2. Materials and methods
The studied Lake is the most anthropogenically loaded water body in Kazan and is affected by large highways, a number of industrial enterprises located on the shores of Sredny Kaban Lake (Kazan CHPP-1; Kazan plants of synthetic rubber, artificial leather, building materials, electrical factory, concrete goods factory no. 3, Tatstroy); it is the receiver of almost half (49%) of the total surface runoff from the
urban areas from 44 organized releases to water bodies in Kazan) [7], [8]. In order to reduce the intensity of all releases of surface water from the corresponding watersheds in Lake Sredniy Kaban can be arranged in the order: Pervomayskaya > VIKO > Modelnaya > Avangardnaya > Tehnicheskaya. Therefore, in this work, the PAHs content in bottom sediments was experimentally investigated in the places of the most powerful first two releases: Pervomayskaya (No. 1/16) and VIKO (No. 1/15).

The studied compounds include 15 PAHs that are included in the priority list of PAHs for environmental research in the Russian Federation and other countries (anthracene, fluorene, naphthalene, phenanthrene, benz(a)anthracene, 3,4-benz(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoranthene, pyrene, acenaphthene, indeno(1,2,3-c,d)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(g,h,i)perylene).

Samples of bottom sediment were taken at a depth of 10 cm using a DAK-250 (250 cm²) automatic bottom grab sampler (IBIW RAS, Russia) to determine the PAHs content. In this work, we used unified methods of sample preparation of bottom sediments in determining the content of PAHs in them (HPLC, Perkin Elmer, USA) at the accredited laboratory base of UGAC RB. To determine the particle size of dried samples of bottom sediments, a Bluewave laser diffraction system (Microtrac, USA) was used; studies were carried out at the Institute of Environmental Sciences of KFU.

The possible sources of PAHs entering the Lake were determined based on the analysis of the ratio of the content of individual PAHs with equal molecular weight [9]; assessment of the level of pollution of bottom sediments of PAHs – using Russian-Dutch norms and criteria, for water bodies of Saint Petersburg [10]; the hazardous level of bottom sediment was characterized using PAH carcinogenic hazard coefficient (K_{PAH}), calculated as the product of hazardous content in bottom sediments and toxicity index [11], [12].

Statistical data processing was performed using the Statistica 8.0 (StatSoft, Tulsa, USA) software package.

3. Results and discussion
The results of determining the content of the studied PAHs are presented in figure 1 (a, b).
Figure 1. PAHs content in bottom sediment samples of Sredny Kaban Lake in the area of surface stormwater runoff: a) – VIKO (No. 1/15) and b) – Pervomayskaya (1/16).

The table 1 shows the total mass of PAHs in the composition of bottom sediments in the area of releases of surface stormwater, toxicity coefficients ($K_{PAH}$) of all studied PAHs for bottom sediments, characteristics of the watershed area and bottom sediment particles.

**Table 1.** The total mass of PAHs in the composition of bottom sediments in the area of surface stormwater discharges, toxicity coefficients ($K_{PAH}$) of all studied PAHs for bottom sediments, characteristics of the watershed area and bottom sediment particles.

| No. | Place of discharge | $S^a$ Watershed, ha | Total PAH, $\mu$g/kg | PAH toxicity coefficient ($K_{PAH}$) | Characteristics of bottom sediment particles |
|-----|-------------------|---------------------|----------------------|-----------------------------------|---------------------------------------------|
|     |                   |                     |                      |                                   | Size, $\mu$m                              | Content, % |
| 1/15| Lake Kaban, VIKO  | 200                 | 442.9                | 70.9                              | 0.01-0.1                                  | 0.00 |
|     |                   |                     |                      |                                   | 0.1-1                                      | 0.88 |
|     |                   |                     |                      |                                   | 1-10                                       | 28.86 |
|     |                   |                     |                      |                                   | 10-100                                     | 70.26 |
|     |                   |                     |                      |                                   | 100-1000                                  | 0.00 |
|     |                   |                     |                      |                                   | >1000                                      | 0.00 |
| 1/16| Lake Kaban, Pervomayskaya | 2000  | 222.1                | 52.3                              | 0.01-0.1                                  | 0.00 |
|     |                   |                     |                      |                                   | 0.1-1                                      | 0.94 |
|     |                   |                     |                      |                                   | 1-10                                       | 40.20 |
|     |                   |                     |                      |                                   | 10-100                                     | 58.84 |
|     |                   |                     |                      |                                   | 100-1000                                  | 0.00 |
|     |                   |                     |                      |                                   | >1000                                      | 0.00 |

$^a$ Area which corresponds to the catchment area of the water body in hectares.

Despite the significantly smaller catchment area for release No. 1/15, the total PAH content in bottom sediments of this release is twice as high, which can probably be attributed to a greater load of technogenic sources of pollution. Analysis of the ratio of the content of prioritize PAHs (possible within
a single molecular weight) according to [9] the composition of bottom sediments indicates pyrogenic sources of PAHs from atmospheric aerosols when burning fuel, including automotive (fluoranthene and pyrene; benz(a)anthracene and chrysene containing 4 rings), and anthracene and phenanthrene molecules containing 3 rings were detected for petroleum sources of PAHs.

The total content of all studied PAHs in the bottom sediments of the inner-city water body in the area of surface runoff discharge indicates a low degree of contamination [10]. This conclusion is also consistent with the coefficient values (KP\text{PAH} = 66.6) carcinogenic hazard of PAH (table 1), which is the benzpyrene equivalent of the studied PAHs and calculated by the formula [11]: KP\text{PAH} = \Sigma (I_t \times C_i), where CI – content of PAH, μg/kg, It – PAH toxicity index, expressed in fractions of a unit relative to the carcinogenic hazard of benz(a)pyrene (It = 1.000) [11]. In general, despite the low content of benzo(g,h,i)perylene and benz(a)pyrene in the studied samples of bottom sediments (figure 1, 2), they make the greatest contribution to the value of the hazardous coefficient (KP\text{PAH}) of all studied PAHs for the bottom sediments of the Sredny Kaban Lake due to its high carcinogenic hazard.

Special experiences to determine the granulometric composition of the studied samples of bottom sediments (table 1) as one of the factors of PAHs sorption during the formation and migration of surface runoff entering the lake, it was not possible to identify any relationships between the PAHs content in bottom sediments and dispersion of particles, which requires additional research. It was shown that each of the studied samples of bottom sediments is composed mainly of particles with a size of 1–100 μm; a slightly larger contribution of particles in the range of 10–100 μm is typical for sample No. 1/15 with a maximum amount of PAHs; the contribution of particles with a size of 0.1–1 μm is estimated to be up to 1%.

4. Conclusion
Thus, the data obtained indicate that the suspended substance of surface stormwater runoff contributes not only to the siltation of the water body [8], but it also supplies into aquatic ecosystems and contributes to the accumulation of PAHs in bottom sediments, which are extremely dangerous for hydrobionts and humans.

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