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Persistent Pollutants in Urban Soil

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Abstract. The paper presents an analysis of the content of PAHs and total petroleum hydrocarbons in the urban soil of the Kazan city (Russia). The soil was sampled in the areas of vehicles and industrial impact. There was no exceeding of standards neither by the sum of PAHs nor by the individual compounds. Compounds with high-molecular-weight, which indicates a pyrolytic origin of their intake from air aerosols during fuel combustion, made the main contribution to the sum of PAHs content. The relative uniformity of the PAHs content in the soil was determined with the exception of the area with a high traffic activity, where the excess of the standards were 3.2 and 96 times for the sum of PAHs and benzo(a)pyrene respectively. The average content of total petroleum hydrocarbons did not exceed the regional standards in urban soil.

1. Introduction

The content of polycyclic aromatic hydrocarbons (PAHs) and petroleum products (NP) in soils has been studied by many authors [1-9]. The authors indicate as sources of receipt of these compounds thermal installations, vehicle emissions, waste incineration, coke ovens, coke and aluminium production, catalytic cracking towers and related works at oil refineries, extraction, transportation and storage of petroleum products, emergency spills, etc. There are also natural sources of receipt of Steam the environment - it is volcanic activity and natural fires.

After entering the atmosphere, PAHs are redistributed between the gas and solid phases and then settle by means of dry or wet deposition. Until the moment of precipitation, they can be transported over long distances. Thus, the urban soil is polluted by the PAH due to sedimentation from the atmosphere or through vegetation, and the NP directly from the atmospheric air. PAHs and NPAs are markers of soil contamination because of human activities [8,9].

The purpose of this paper was to assess the content of persistent pollutants - polycyclic aromatic hydrocarbons in soils in the cities of Kazan in the areas affected by vehicles and industrial enterprises.

2. Materials and Methods

In the course of the study, fourteen soil samples were selected in six locations in Kazan, which were analyzed for PAH and petroleum products. The samples were analyzed and averaged over the sampling points: No. 1-4 places with intensive traffic load; No. 5 - area of impact of emissions of industrial



enterprises of CHPP-1, JSC "Nefis Cosmetics"; No. 6 (background section) - residential area far from the industrial zone and traffic interchanges; No. 7 is an area close to a complex intersection.

Soil samples were taken in accordance with GOST 17.4.4.02-84 Nature Conservation Soils Methods of sampling and preparation of soil samples for chemical, bacteriological and helminthological analysis [10]. In the selected soil samples, the particle size distribution was determined using a Microtrac S-3500 laser-particle sized analyzer [11], pH [12].

PAH content in soil samples was determined in accordance with [13], and NP by the method [14].

3. Results and Discussion

The acidity of the soil has a strong influence on the development of plants, soil microorganisms, and physicochemical processes in the soil, and the assimilation of nutrients by plants, the effectiveness of fertilizers applied. In terms of pH, ten of the fourteen soil samples had a neutral reaction, and four - weakly acid.

An important factor affecting the migration of PAHs and NPs in the surface layer of the soil is the mechanical (granulometric) composition, namely the size of the sorbing soil particles. If the particles adsorbing the PAH cannot move through the soil, then the PAH motion will be limited, since they, as a rule, remain associated with particles [9].

Of the selected soil samples, eight were characterized as light loam, four (4) – sandy loam, one (1) – medium loam and one (1) – loose sand.

The results of PAHs and NP analysis of selected soil samples are given in table 1.

Table 1. Content ($\mu\text{g/kg}$) of polycyclic aromatic hydrocarbons and petroleum products (mg/kg) in soil (mean \pm SE).

Compound	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7
Naphthalene	n/o	n/o	n/o	n/o	n/o	n/o	n/o
Ascenaphthylene	n/o	3.09 \pm 1.18	n/o	5.81 \pm 2.32	8.88 \pm 5.88	7.66 \pm 3.06	13.13 \pm 5.25
Acenaphthene	n/o	69.28 \pm 27.71	n/o	13.13 \pm 5.25	n/o	n/o	n/o
Fluorene	11.55 \pm 1.66	11.49 \pm 1.92	n/o	6.33 \pm 2.81	7.73 \pm 3.35	15.43 \pm 6.17	1.68 \pm 0.67
Phenanthrene	n/o	n/o	n/o	n/o	26.55 \pm 13.28	n/o	n/o
Anthracene	0.63 \pm 0.32	n/o	n/o	n/o	n/o	n/o	n/o
Fluoranthene	n/o	64.64 \pm 42.18	n/o	n/o	8.84 \pm 4.15	1.91 \pm 0.88	145.12 \pm 55.15
Pyrene	n/o	n/o	n/o	n/o	n/o	n/o	n/o
Chrysene	n/o	33.48 \pm 18.90	n/o	n/o	8.94 \pm 2.73	6.93 \pm 3.60	n/o
Benz(b)fluoranthene	12.76 \pm 10.42	17.91 \pm 9.08	3.46 \pm 1.07	0.78 \pm 0.56	11.36 \pm 5.29	1.49 \pm 0.59	966.50 \pm 259.09
Benz(a)pyrene	3.76 \pm 2.46	5.05 \pm 3.25	1.25 \pm 0.27	0.27 \pm 0.20	3.82 \pm 1.70	0.17 \pm 0.10	1915.50 \pm 344.79
Benzo(k)fluoranthene	1.41 \pm 0.32	13.38 \pm 6.36	0.94 \pm 0.18	0.06 \pm 0.06	39.39 \pm 35.09	4.70 \pm 2.26	185.50 \pm 44.52
Dibenz(a,h)anthracene	n/o	n/o	n/o	n/o	n/o	n/o	n/o
Benz(g,h,i)perylene	n/o	35.51 \pm	n/o	n/o	23.12 \pm	n/o	n/o

Compound	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7
Amount of PA	30.12 ± 15.18	9.28 175.31 ± 64.08	5.66 ± 1.51	16.92 ± 13.11	1.97 138.63 ± 71.91	38.30 ± 18.22	3227.43 ± 764.57
Petroleum products	336.38 ± 88.34	465.14 ± 218.64	369.96 ± 32.92	196.27 ± 74.91	160.26 ± 16.60	88.63 ± 22.16	424.45 ± 106.11

n/o -below the sensitivity limit of the technique

One can note the relative uniformity of the PAH content in the soil samples studied, with the exception of the anomalous sample (No. 7) selected near the complex traffic intersection.

The total PAH content in urban soils does not exceed the standards established in a number of countries at 1000 µg / kg [15,16], and varied within 5.66-175.31 µg/kg. In the soil in the area of intensive motor traffic - 3227.43 mg/kg, which exceeds the standard by 3.2 times.

If we compare the total PAH content with respect to the background sample (Figure 1). A significant excess was noted in sample No. 3 (4.6 times) and No. 5 (3.6-fold). In an anomalous sample from a complex traffic intersection, the background content exceeded 84 times.

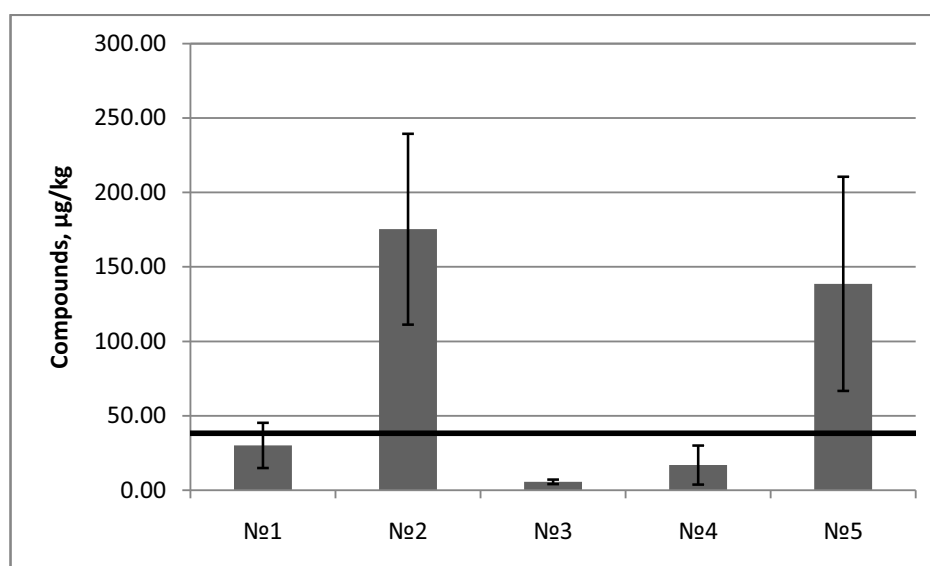


Figure 1. Total PAH content relative to the background.

The obtained values of PAH content are significantly lower than the values given in the literature. Thus, in [8], the total content of ten (10) PAHs in Czech urban soils ranged from 860-10840 µg / kg (at an anomalous value of 35140 µg / kg). In the urban soils of Beijing [17], the total content of sixteen PAHs was noted at a level of 467 to 5.470 µg / kg. In the soils of Moscow [2], the content of the sum of ten PAH compounds fluctuated between 156 and 6118 µg / kg.

The greatest contribution to the total content of PAHs is made by fluoranthene (1.91-145.12 µg / kg), fluorene (1.68-15.43 µg / kg), chrysene (6.02-56.63 µg / kg), benzene(b)fluoranthene (0.22-966.50 µg / kg), benzo(a)pyrene (0.07-1915.50 µg / kg) and benz(g,h,i)perylene (20.71-46.88 µg / kg). The content of high molecular weight polycyclic aromatic compounds, to which the majority of the above-listed compounds refer, is evidence of a pyrogenic source of their supply from atmospheric aerosols during fuel combustion, incl. [18, 19, 9].

MPC of benzo(a) pyrene, established in Russia at the level of $20 \mu\text{g} / \text{kg}$ [20], not exceeded in any sample. except sample No. 7, where the content of benzo(a)pyrene was $1915.5 \mu\text{g} / \text{kg}$, which exceeds the established standard by 96 times.

If we compare the content of benzo(a)pyrene with the background content, then the excess was noted in the soils of all the investigated regions (Figure 2).

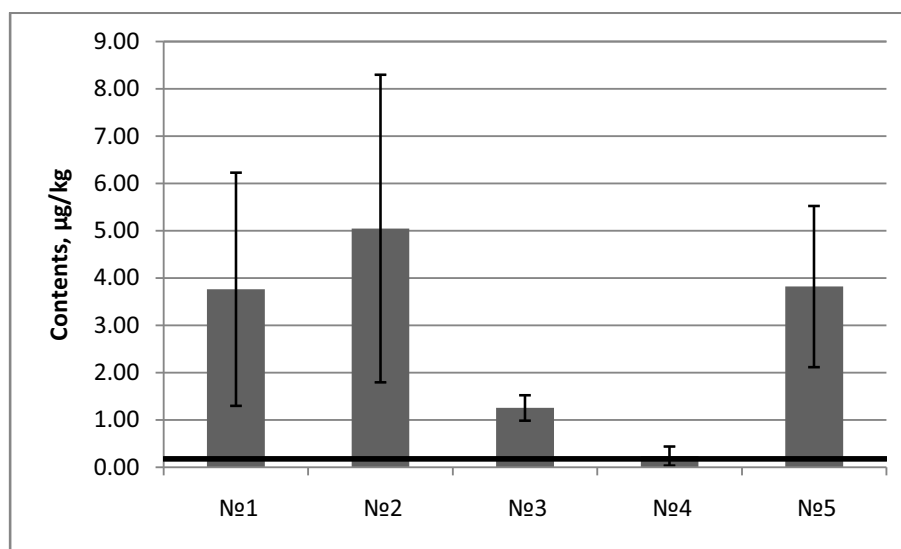


Figure 2. The content of benzo(a)pyrene in urban soil relative to the background.

The average content of NP in the sampled samples ranged from $160.26 - 369.97 \text{ mg}/\text{kg}$, which does not exceed the regional standard of $1500 \text{ mg}/\text{kg}$ [21]. Exceeding the background was respectively from 1.81 to 4.2 times (Figure 3).

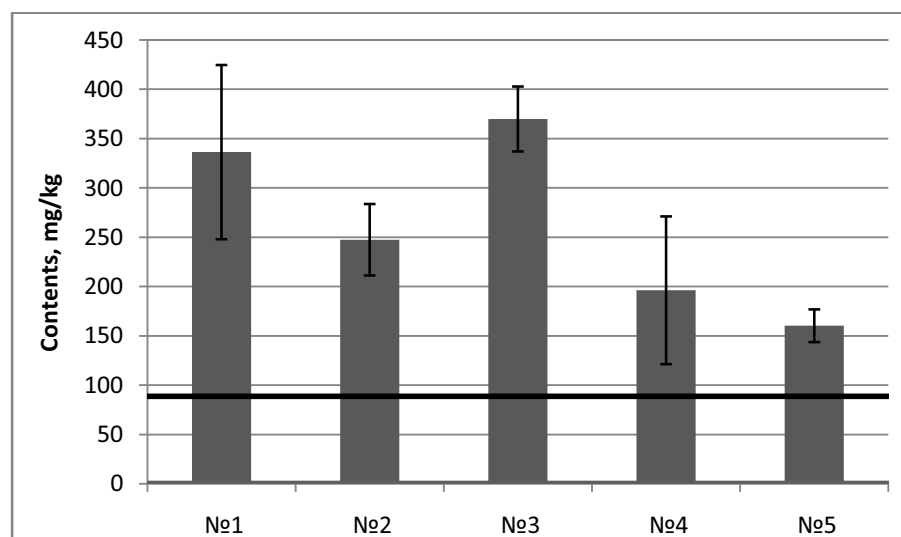


Figure 3. The content of petroleum products in urban soils relative to the background.

4. Conclusion

The study of the content of PAHs and petroleum products in urban soils showed that most of the samples are characterized by a low content of both individual indicators and amounts of PAH and petroleum products. The only exception is the soil of the square located next to the busy road intersection where the benzo(a)pyrene content exceeded the MPC by 96 times, and the PAH amount 3.2 times. The predominance of high molecular compounds in all studied soils indicates a pyrolytic source of their intake from atmospheric aerosols in the combustion of fuel, incl. Comparison with background soil revealed an increased content of petroleum products in all samples and PAHs in soils near a traffic junction and in an area experiencing the impact of industrial facilities.

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