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Transformation of Urbanozems in the Areas of Gas Stations

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ABSTRACT

The areas near gas stations are places of local specific environmental pollution. The purpose of this work was to study the environmental consequences of gas station functioning on the surrounding soils (urbanozems). The content of oil products (OP), bulk and mobile forms of heavy metals, acute toxicity (*Ceriodaphnia affinis* Lillieborg, *Paramecium caudatum* Ehrenberg, *Escherichia coli* Migula), chronic toxicity (*C. affinis*), and the state of soil microphotrophs were determined. The content of OP was from 520 ± 130 to 4820 ± 100 mg/kg, which is significantly higher than the concentrations of OP in the soils of the transport zone of cities. The exceeding of the Russian standards for HM was found only for zinc (the maximum for the total form – 1.7 MPC, for the mobile form – 1.4 MPC). The urbanozems samples did not have acute toxicity; however, chronic toxicity in the bioassay for the mortality of *C. affinis* (up to 85%) and a decrease in the fertility of crustaceans (2–3 times compared to the control) were observed. In the structure of the community of soil microphototrophs, cyanobacteria dominated both in biomass and in abundance: (up to 748±10 thousand cells/1 g of soil) compared with green algae and diatoms (1.1–5.5 and 1.2–19.8 thousand cells/1 g of soil, respectively). As a result of the work, it was concluded that the quantitative algological analysis and biotest with the assessment of chronic toxicity in terms of mortality and fertility of *C affinis* for the diagnosis of local soil contamination in the areas of gas stations were of the highest informative value.

Keywords: urbanozems, gas stations, oil products, heavy metals, bioassay, Ceriodaphnia affinis, soil phototrophs.

INTRODUCTION

In order to understand the functioning of the complex "man-environment" system, it is important to study all levels of anthropogenic transformation of the environment: not only global, but also regional and local changes in the components of the nature. Currently, the urban environment demonstrates a combination of many local environmental problems: waste dumps, polluted areas of industrial enterprises, transformation of plant communities in park zones, and so on.

The environmental risks of the urban environment increase every year both for the resident population and for the biota (Flies et al. 2019; Murray et al. 2019). Among the negative anthropogenic impacts inherent in any city, the pollution associated with the automobile transport can be distinguished (Minenko and Kusmorova 2014; Myung et al. 2014; Johnson 2016). The increase in the number of cars leads to an increase in the automobile transport service and an increase in the number of gas stations. A high concentration of cars in the city, fuel spills, and the evaporation of volatile fractions of oil products lead to the formation of local pollution of the urban environment (Hsieh et al. 2021).

This environmental problem has different consequences. Volatile organic compounds such as benzene, toluene, ethylbenzene and xylene are known to pose a threat to the human health (Correa et al. 2012; Barros et al. 2012). On the other hand, a significant part of aerosol oil pollution settles on the territory of the gas station, contaminating the surrounding soils (Mayorova 2020). The environmental situation near gas stations is worsened as the tire, brake and clutch wear as well as the road surface wear contributes to road dust. In this case, the soil is saturated not only with oil products, but also with heavy metals (Adamiec et al. 2016). Such anthropogenic impacts become the reasons for the transformation of urban soils in the areas of gas stations. These consequences of specific pollution of the urban environment are more dangerous for the representatives of the soil biota.

The purpose of this work is to study the local environmental consequences of the gas stations functioning for surrounding soils.

MATERIAL AND METHODS

The studies were carried out on operating gas stations in the city of Kirov (Russia). Kirov is located in the northeast of the European part of Russia, on the Russian Plain, in the zone of taiga forests. In terms of climatic and natural features, Kirov is close to the cities of Northern Europe: the climate is temperate continental, the average temperature is 3.1 °C, the prevailing natural soils are sod-podzolic. The soil samples were taken on the territory and near four gas stations, two of which were located on the outskirts of the city (gas station-1; gas station-2), the other two were in urban areas with dense continuous traffic flows (gas station-3; gas station-4).

The soil samples were taken from the following studied plots:

- on the lawns separating gas stations from highways;
- on the gas station sites free of hard surface;
- outside the asphalt site of the gas station, on the opposite side of the road (Fig. 1).

Mixed samples of urbanozems were taken from the plots with the area of 1 m² with the envelope method (5 points) from the depth of 0-15cm. The OP content was determined by infrared spectrophotometry using the KN-2M instrument (Russia) ((Environmental Regulatory Document PND F 16.1:2.2.22-98 2005). The determination of the mass fractions of total and mobile forms of metals (copper, cadmium, lead, and zinc) was carried out by means of the atomic absorption method (Federal Register FR 1.31.2012.135739 2012). The toxicity of the samples was determined by the indicators of mortality and fertility of Ceriodaphnia affinis (Federal Register FR 1.39.2007.03221 2007), changes in the chemotactic response of ciliates Paramecium caudatum

(Federal Register FR 1.39.2015.19242 2015) and changes in the bioluminescence of *Escherichia coli* Migula bacteria (Environmental Regulatory Document... 2010). The state of the soil biota was determined by the indicators of algal groups of urbanozems (number of cells, biomass of algae) (Gollerbakh and Shtina 1969). The quantitative indicators were re-counted to absolutely dry soil weight (Nekrasova and Busygina 1977).

RESULTS AND DISCUSSION

Accumulation of heavy metals and oil products

In order to assess the level of the soil pollution with oil products, the conventional background content of OP for the areas not producing oil (40 mg/kg) was used (Musikhina 2009). The content of oil products in the samples of urbanozems were also compared with the levels of pollution indicated in the methodology for "determining the extent of damage from soil pollution by chemical substances" (Letter from the Ministry of Natural Resources of the Russian Federation 1993).

The mass concentrations of HM (zinc, lead, copper, cadmium) were compared with the environmental standards adopted in Russia (Maximum permissible concentration... 2006). Table 1 illustrates the total and mobile content of HM compared to these standards in the case the value exceeded 0.5.

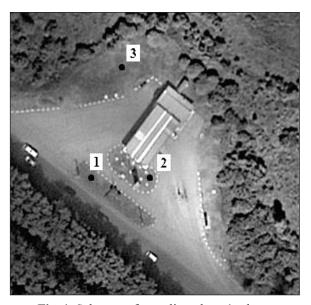


Fig. 1. Schemes of sampling plots: 1 – lawn separating the gas station from the highway, 2 – the gas station site, free of hard surface; 3 – the section outside the gas station

Variant			HI	N	OP		Pollution
			Multiplicity MPC (total form)	Multiplicity MPC (mobile form)	Content of OP, mg/kg	Multiplicity CBC*, times	level OP**
On the outskirts of the city	Gas station-1	Lawn by the road	Zn 0.5	Zn 0.6	1010±250	25,2	Low
		Lawn at the gas station	-	-	1800±450	45,0	Low
		Lawn outside the gas station	-	-	1070±270	26,7	Low
	Gas station-2	Lawn by the road	Zn 0.8 Pb 0.7 Cu 0.7	Zn 0.8 Pb 0.9 Cu 0.6	3970±990	99,2	High
		Lawn at the gas station	Zn 0.9 Cu 1.0	Zn 0.8 Pb 0.6 Cu 0.7	1840±460	46,0	Low
		Lawn outside the gas station	_	_	520±130	13,0	Acceptable
	Gas station-3	Lawn by the road	Zn 0.9	Zn 1.1	3550±890	88,7	High
In the city centre		Lawn at the gas station	Zn 0.5 Cu 0.5	Zn 0.9	4820±100	120,5	High
		Lawn outside the gas station	Zn 1.5 Pb 0.8	Zn 1.4	3920±980	98,0	High
	Gas station-4	Lawn by the road	Zn 1.7	-	1100±270	27,5	Low
		Lawn at the gas station	Zn 1.0	Zn 0.7	1570±390	39,2	Low
		Lawn outside the gas station	Zn 1.0	Zn 0.6	810±200	20,2	Acceptable
	ventionally b areas not pro	ackground OP content ducing oil	_	_	40	1	_

Table 1. Content of heavy metals and oil products in urbanozems in the areas of gas stations in Kirov

The content of cadmium in all analyzed samples was below 0.5 MPC, which is quite natural: the accumulation of this metal is not associated with general industrial and transport emissions, most often it is associated with specialized metallurgical industries (Davydov and Tagasov 2008).

The content of total and mobile forms of copper and lead does not exceed the established standards at any of the gas stations. However, in several samples, mass concentrations are close to the critical level. For example, in the samples taken near the gas station-2, there is a relatively high content of copper and lead, not only in total, but also mobile forms, which have a direct toxic effect on the inhabitants of the soil.

Zinc accumulation is observed near all gas stations. We found that in the city center the excess of MPC for zinc was 1.7 and 1.4 times (for gross and mobile forms, respectively). At the same time, in the samples from the gas stations located on the outskirts of the city, its mass concentrations are lower: the maximum for the total form is 0.9 MPC, for the mobile form -0.8 MPC. The found data indicate not only the accumulation of zinc compounds, but also their presence in urbanozems in mobile forms. This feature is explained by the properties of the pollutant. It

is proven that zinc binds to soil organic matter nonspecifically, which leads to its greater mobility compared to lead and copper (Ufimtseva and Terekhina 2005).

The analysis of the content of heavy metals in urbanozems near the gas station showed that the copper and lead compounds are found locally within ecologically significant limits, but their accumulation does not exceed the established standards. Total and mobile forms of zinc are found in all areas of the study, the standards are exceeded near the gas stations in the city center. The obtained data are consistent with the data of other authors. It was shown that near gas stations in Poland, significant soil accumulation in Pb and moderate accumulation in Cd, Cu, and Zn are observed (Rolka, Zolnowski and Kozlowska 2020). It is also known that the accumulation of copper, lead and zinc compounds in urban soils may be associated with automobile transport (Manta et al. 2002).

The analysis of the content of oil products in urbanozems of the gas stations showed a tendency of their significant accumulation in comparison with the soils of the areas not producing oil (Musikhina 2009). The excess of the conventionally background oil content at the gas stations remote from the city center varied from 13.0 to 99.2 times, at the gas station near busy highways this range was 20-120 times. The ranking of pollution levels in accordance with the recommendations of the Ministry of Natural Resources of the Russian Federation showed that the high level of OP pollution is observed both in the center and on the outskirts of the city. Consequently, the reason for the resulting level of OP pollution is the activity of the gas stations. This conclusion is confirmed by the data we obtained earlier. When studying the pollution of various functional zones of the city of Kirov, in the soils confined to large road junctions, the maximum level of OP was 270±21 mg/kg, which is 2 times lower than in the "cleanest" sample from the gas station (Olkova, Berezin and Ashikhmina 2016).

Thus, local pollution of the urbanozems near gas stations is mainly formed by oil products. HM accumulation near gas stations is associated with automobile transport.

Responses of laboratory test-organisms

The toxicological characteristics of the samples of urbanozems were studied using *Ceriodaphnia affinis* Lillieborg, *Paramecium caudatum* Ehrenberg, and *Escherichia coli* Migula bacteria.

No acute toxicity of the samples was found. Low sensitivity of express-biotests was stated earlier [Fokina et al. 2016]. Most often, such a phenomenon for the test-organisms recognized in biotesting practice is observed when testing soil extracts or natural waters containing dissolved organic matter. The physical and chemical processes occurring in this case "mask" the pollution by reducing the bioavailability of toxicants (Benedetti et al. 1995).

The most interesting results were obtained in the bioassay of *C. affinis* responses, which makes it possible to assess not only acute, but also chronic toxicity in terms of fertility (Table 2).

The samples of urbanozems from 3 out of 4 investigated gas stations in Kirov inhibited the ability of C. affinis to reproduce, and also caused the death of adult specimen during the experiment. With the minimum values of fertility (0.2 specimen per female, etc.), not all adult specimen were able to produce offspring. During the experiment, the effect of water extracts from the samples on the morphology of crustaceans was also noted: the specimen acquired a transparent appearance, there were no eggs in the brood chambers, and the crustaceans became inactive. The Pearson correlation coefficient (r) between the fertility indicators and the content of OP in the samples turned out to be -(-0.45), which indicates the weak inverse relationship. The low correlation coefficient indicates the presence of complex contamination that affects the state of test-organisms.

Characteristics of natural biota - soil algae

Further, the quantitative algological analysis of the samples under study from the territories of the gas stations with the highest level of

Table 2. Assessment of the degree of toxicity in terms of the mortality and fertility of *Ceriodaphnia affinis*

			Results of biotesting of soil extracts in the experiment				
	Variant	No. points of sampling (p.s.)	Mortality of specimen, %		Fertility, pcs./1 female	Presence of toxicity	
		(p.o.)	in 48 hours	in 12 days		ATE	CTE
Control			0	0	20.4±0,04	—	—
(0	Gas station-1	Lawn by the road	0	15	8.7±0.58*	Samples have do not have ATE do not do not	Samples have CTE
outskirts e city		Lawn at the gas station	0	15	8.2±0.36*		
outsk e city		Gas station periphery	0	40	7.3±1.65*		
the ou of the	Gas station-2	Lawn by the road	0	65	0.2±0.01*		
On the of the		Lawn at the gas station	0	50	2.3±0.22*		
		Gas station periphery	0	40	1.2±0.01*		nave of E
ω	Gas station-3	Lawn by the road	5	85	1.8±0.18 [*]		
entr		Lawn at the gas station	0	35	4.0±1.16*		
In the city centre		Gas station periphery	0	5	9.4±0.36*		
		Lawn by the road	0	0	20.4±2.59		
the	Gas station-4	Lawn at the gas station	0	0	20.0±0.36		do not have CTE
-		Gas station periphery	0	0	27.9±2.59		0.2

Note: ATE – acute toxic effect; CTE – chronic toxic effect; * – experimental values significantly differ from control values.

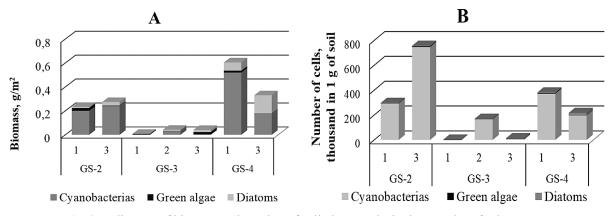


Fig. 2. Indicators of biomass and number of soil phototrophs in the samples of urbanozems from the territories of the gas stations: A – biomass (g/m²), B – number (thousand cells in 1 g of soil): 1 – lawns by the road; 2 – lawns at the gas station; 3 – lawns outside the gas station

contamination (gas station-2, gas station-3, gas station-4) was carried out.

The results of the studies of the abundance and biomass of soil algae and cyanobacteria (CB) showed a wide range of variation of these bioindicators (Fig. 2). The number of algal cells in the soil ranged from 3 to 758 thousand cells per 1 g of soil, the biomass – from 0.01 to 0.61 g/m².

Non-heterocyst cyanobacteria dominated in all studied areas, accounting for up to 98% of the total number of cells of soil phototrophs. This significantly distinguishes urbanozems from natural biogeocenoses of the middle and southern taiga, where green algae prevail in dry meadows and ecotopes with closed vegetation cover, cyanobacteria usually occupy the second place (Kondakova and Pirogova 2014).

The dominance of CB, established for the zones of local contamination of the gas stations, is consistent with the general regularities described in the literature. A significant species diversity of cyanobacteria in the transport zone of cities is shown (Khaibullina, Sukhanova and Kabirov 2011; Guilland et al. 2018).

When analyzing the diversity of phototrophs, it was found that the species of the Phormidium genus reach the greatest development in urbanozems near the gas station. These CB belong to the P-life form, whose representatives usually gravitate towards bare areas of mineral soil and are resistant to extreme environmental conditions due to the properties of the protoplast (Shtina and Gollerbakh 1976).

The highest values of algal biomass were noted at the sites of the gas station-4, characterized by a low and acceptable level of the content of oil products in soils. The minimum biomass values were established for the least greened and the most polluted by OP and HM territory of the gas station-3. Thus, near this station on the lawn near the highway, the biomass of algae was only 0.01 g/m^2 .

The analysis of the samples taken in the center of the gas station and on the lawns near the roads showed that the contribution of blue-green algae to the structure of the biomass of phototrophs was also significant here (Table 3). The situation changes at the periphery of the gas station sites: CB are giving way to diatoms (at the gas station-4 -44%) and green (at the gas station-3 - 52%) algae, which may be associated with an increase in the projective area of coverage by higher plants in these areas and a change in their species composition. With a thin vegetation cover, for example, at the gas station-2, CB continued to play a leading role in the periphery of the station. The obtained data correspond to the minimum values of the number of algal cells for the transport zone of the city of Kirov (Domracheva et al. 2013). Along with the changes in quantitative indicators, a change in the dominants of algal groups was observed in the studied areas (Table 3).

On the lawns in the center of the gas station, *Microcoleus vaginatus* (Vauch) Gom. and *Chlamydomonas* sp. are dominant. These are algae belonging to the M- and C-life forms, capable of producing a significant amount of mucus, which protects them from the toxic effects of HM (Kabirov and Sukhanov 1997). Moreover, the CB *Plectonema boryanum* Gom (Proshkina 1997) can be classified as dominants with a known resistance to HM. It has been shown that this species is able to

	Sampling area	Dominant species		
	Lawn by the road	Phormidium autumnale (Ag.) Gom.		
Gas station - 2	Lawn outside the gas station	Phormidium autumnale (Ag.) Gom.; Hantzschia amphioxys (Ehr.) Grun. var. amphioxys		
	Lawn by the road	Chlorococcum sp.		
Gas station - 3	Lawn at the gas station	<i>Microcoleus vaginatus</i> (Vauch) Gom.; <i>Chlamydomonas</i> sp.		
	Lawn outside the gas station	Plectonema boryanum Gom.; Chlorococcum sp.		
	Lawn by the road	Microcoleus vaginatus (Vauch) Gom.		
Gas station - 4	Lawn outside the gas station	Hantzschia amphioxys (Ehr.) Grun. var. amphioxys; Phormidium formosum (Bory ex Gom.) Anagn. et Kom.		

Table 3. Composition of dominants of algal groups in the territories of the gas stations in Kirov

dominate in the algae community of coal dumps with an increased content of zinc (40–50 mg/kg) and nickel (50 mg/kg) compounds (The natural environment of the tundra... 2005).

At the periphery of the gas station sites, under the canopy of higher plants, under conditions of low OP doses, a diatom alga – *Hantzschia amphioxys*, which is an ubiquist, appears in the composition of dominants. The *H. amphioxys* diatom is found among the few species (5 species) that are able to actively develop in the areas of streets with a high traffic load (Kondakova and Domracheva 2011).

In general, near the gas stations and on their territories, algae that are resistant to extreme ecotopic conditions, belonging to C–, P– and M–life forms dominate.

CONCLUSIONS

As a result of the carried out studies it was shown that gas stations are places of increased local pollution of urbanozems with oil products: the found indicators in the areas where gas stations are located turned out to be several times higher than in the soils of the transport zone. At the same time, the content of total and mobile forms of heavy metals turned out to be comparable with the similar pollution of surrounding soils to highways. Exceeding of the current standards was observed for zinc compounds, both for gas stations in the city center and those located on its outskirts.

Biotesting of the urbanozems samples did not reveal acute toxicity. However, the prolongation of the experiment showed the presence of chronic toxicity of the studied samples in terms of a decrease in fertility of *Ceriodaphnia affinis*, as well as in terms of mortality of adult specimen within 12 days. The ecological problems of the studied urbanozems were also confirmed by bioindication. A change in the dominants of soil phototrophs was shown: from green algae, which dominate in natural biogeocenoses of the studied latitude, to resistant species of cyanobacteria. Moreover, low levels of biomass and the number of phototroph cells were shown in ubanozems near the gas station.

Thus, in residential places, gas stations are locations of local complex environmental nonobservances that manifest themselves along the logical chain: pollution (PP + HM) – an increase in toxicity – suppression of the natural biota. Determination of chronic toxicity of soil samples and bioindication of the areas near gas stations could become valuable indicators of their "cleanliness" and environmental friendliness, which the entire world community is striving.

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