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PETROCHEMICAL EMISSIONS PRODUCED BY THE OBJECTS OF THE AUTOMOBILE AND HIGHWAY COMPLEX

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Abstract. *As a result of experimental researches it was established that the flow of petrochemicals from the objects of the automobile and highway complex that spreads over the adjoining roadside areas correlates with the traffic intensity at objects of the same applicability. The highest specific flow of petrochemicals (per 1 vehicle of traffic) is emitted by gas stations.*

Key words: *objects of automobile-highway complex, environmental safety, emissions, petrochemicals, snow cover, soil, alkanes, PAH.*

ЭМИССИЯ НЕФТЕПРОДУКТОВ ОТ ОБЪЕКТОВ АВТОМОБИЛЬНО-ДОРОЖНОГО КОМПЛЕКСА

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Аннотация*. Установлено, что среди исследованных объектов автомобильно-дорожного комплекса самый большой удельный поток нефтепродуктов (рассчитанный на 1 автомобиль трафика) образуют автозаправочные станции, загрязняя прилегающие территории высоко опасными углеводородами.*

Ключевые слова *объекты автомобильно-дорожного комплекса, экологическая безопасность, эмиссия, нефтепродукты, снежный покров, почвы, алканы, ПАУ.*

ЕМІСІЯ НАФТОПРОДУКТІВ ВІД ОБ'ЄКТІВ АВТОМОБІЛЬНО-ДОРОЖНЬГО КОМПЛЕКСУ

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Анотація. *Встановлено, що серед досліджених об'єктів автомобільно-дорожнього комплексу найбільший питомий потік нафтопродуктів (розрахований на 1 автомобіль трафіку) утворюють автозаправні станції, забруднюючи прилеглі території високонебезпечними вуглеводнями.*

Ключові слова: *об'єкти автомобільно-дорожнього комплексу, екологічна безпека, емісія, нафтопродукти, сніжний покрив, ґрунти, алканы, ПАВ.*

Introduction

The automobile and highway complex (AHC) includes the roadway with the moving on it vehicles, road-shoulders and the objects of road infrastructure (gas stations, parking lots, car washes, recreation areas, etc.). Environmental studies of the effect of these objects on the

environmental safety of adjacent roadside territories are primarily focused on the analysis of exhaust emissions into the atmosphere and the negative impact of noise. However, soil and water ecosystems are also subjected to intensive ingredient pollution on these areas [1, 2].

In the soil (environment with the lowest mass transfer characteristics) of the areas adjacent to AHC objects, the highest environmental risk in terms of excess of the maximum permissible concentration (MPC) is created by petrochemicals (PC) [3]. Petrochemicals have a heterogeneous composition, which is a mixture of different compounds, mainly hydrocarbons. There are fractions with the moderate environmental hazard (naphthenes and paraffins) and extremely dangerous ones (aromatics and polycyclic aromatic hydrocarbons – PAH) among them. PC cause a specific hazard to soil ecosystems, the soil fauna, flora and microflora [4].

Analysis of publications

The widespread use of oil as fuel causes the prevalence of PC among organic pollution of the atmosphere and is a major source of hydrocarbon pollution of anthropogenic origin found in the atmosphere [2, 5]. Automobile emissions of PC on the roadside area essentially consist of unburned gases, aerosols, and dust particles [1, 6, 7]. As reported, the emission rate of PC varies from one milligram to a few milligrams per second from vehicles [8]. PCs entering the roadside area are actively adsorbed by soils. Thus, according to [9], the concentration of PC at the edge of the road at Liski of Voronezh Region (traffic density up to 600 veh./h) is 5100 ± 1530 mg/kg, and at a distance of 10 m from the roadway - 3078 ± 923 mg/kg. The average background concentration of PC in the soils of the Voronezh Region is 15 mg/kg. In Ukraine, the MPC of PC for soils of urban areas is not specified; the standard of allowable concentration is tentatively known to be 200 mg/kg (for oil-producing areas), which corresponds to the MPC for soils in Moscow (300 mg/kg) and of St. Petersburg - 180 mg/kg.

At present, the quantitative characteristics of PC transfer from the objects of the AHC on soils of adjacent areas and the composition of hydrocarbons in PC accumulated by soils are practically unknown.

The aim of this study was to determine the kinetic characteristics of the PC flow and accumulation in soils of areas adjacent to the AHC, and the composition of these PC.

Objects and research methods

Deposition of PC transferred through the air from the objects of the AHC on the roadside area was estimated on the basis of the study of snow cover formed over a period of time in a certain area. The chemical composition of the filtrates obtained from melted snow is formed by adsorption of snow gases, aerosols and particulates [10].

The object of study was the areas adjacent to the objects of the AHC in Kharkiv and Kharkiv Region: urban highways (Akademika Pavlova str., Traktorostroiteley ave., Pushkinskaya str.), country roads (highways of national and regional significance) - M03 Kyiv-Dolzhanskaya, R46 Kharkiv-Akhtyrka, and the road infrastructure – GFS №1, GFS №2 on the highway R46 Kharkiv-Akhtyrka and a parking-lot.

Snow samples (to the full depth of the snow cover) covering the areas adjacent to the objects of the AHC were taken at 3 points of 400 cm^3 in area at a distance of 1 m from the roadway. Soil samples were collected in the autumn before the snow falls by the "envelope" method at a distance of 1, 8 and 10 m from the roadway.

The concentration of PC in the soil and snow samples was determined gravimetrically [11] according to the method recommended by the regulations and by the method of infrared photometry, using the oil analyzer AN-2 [7]. The flow of PC deposited on the snow of the survey area was calculated by the formula

$$Q = \frac{\tilde{N}_{\text{mw}} \cdot V_s}{S \cdot t} \qquad (1)$$

where C_{mw} – concentration of PC in the snow melt, mg/dm^3; V_s – the volume of the tested sample, dm^3; S – area of the surface where the sample was taken, m^2, t – time of snow accumulation, days.

PC extracts were prepared, using chloroform and then it was evaporated and the residue was dissolved in hexane [7]. PC were simultaneously extracted, using only hexane [7]. This made it

possible to separate the conditionally light PC from conditionally heavy PC. The flow of relatively heavy PC was determined as the difference between the flow of PC extracted with the help of chloroform, and the flow of PC extracted with hexane. The qualitative and quantitative composition of PC in the soils of roadside territories was determined by gas-liquid chromatography (chromatograph Fisons 8065, HT8 column) with the use of the mass spectrometry detector (Fisons MD800). For quantification and identification of the total hydrocarbon content and n-alkanes there was respectively used the commercial diesel fuel and Hewlett Packard alkane standard Part. No. 18710-60170. During the research they determined the intensity of the traffic flow.

Results obtained and discussion

PC flows on the soil of areas adjacent to the objects of the AHC are shown in table 1. As can be seen, the total flow of PC on adjacent territories (1 m from the roadway) increases with the density of traffic in each group of objects (urban roads, country roads, gas stations). PC flux distribution on various sides of the roads is significantly different (t-test, $p < 0,05$) due to the prevailing wind direction in relation to the road and other conditions of dispersion, such as urban wind canyons. The ratio of conditionally heavy PC in the vicinity of the highway is the same on different sides of the same road, and even at different roads.

Table 1The deposited flow of PC from AHC objects on the surface of adjacent soils (1 m from the roadway)

Object of AHC	Traffic density, veh./hour	PC flow		
		Total, $mg(m^2 \cdot day)^{-1}$	Relatively light, $mg(m^2 \cdot day)^{-1}$	Relatively heavy, $mg(m^2 \cdot day)^{-1}$
Ac. Pavlov Str.	2050	94*	51*	43*
		44**	24**	20**
Pushkin Str.	1090	20**	not determined	not determined
M03 Kyiv-Dolzhanskaya	1052	not determined	45	not determined
R46 Kharkiv -Akhtyrka	800	114,8	91,5	23,3
GFS №1	46	49,6***	24,1	25,5
		49,3****	23,3	26,0
GFS №2	19	17,4		
Parking		281,3	123,6	157,7

* - The windward side of the road, ** - the leeward side of the road, *** - entrance to the gas station, **** - leaving a gas station.

On urban roads (with curbs) at respectively the same traffic density the flow of PC on the adjacent soils is almost 5 times lower than on country roads (without curbs) - Pushkinskaya str. and Highway R46. This phenomenon is probably due to the lack of curbs, which shield the low content of exhaust vehicle emissions as well as entrainment from roads. The reported flow of PC produced by one vehicle at various auto-road complexes will constitute $(mg(m^2 \cdot day \cdot auth)^{-1})$ for objects with curbs - $2,1 \cdot 10^{-3}$ (Pushkinskaya str.), $38,2 \cdot 10^{-3}$ (GFS №2), 44,6·10-3 (GFS №1). Thus, gas stations produce a specific flow of PC by an order superior than the flux of PC generated by the highway.

If we compare the contamination of soils by PC in the areas adjacent to various objects of the AHC (Table 2), it is shown that gas stations have a greater impact on the surrounding areas than highways because at a much lower traffic density the concentration of PC in soils at a distance of 1 m from these objects is comparable with this index on urban and country roads. Similarly, high concentrations of PC in soils at a relatively low traffic density were also registered on the territory adjacent to the car park.

With increasing the distance from the objects of the AHC the concentration of PC in soils compared with the original one (PC content in the soil of the closest to the roadway area - 1 m) is reduced. And at a distance of 8-10 m this reduction is on average 63.8 on city roads, 36,8 - on country roads, 57,8% - at gas stations and parking areas.

Increased emissions of PC produced by petrol stations is probably due to the differences between the modes of vehicle movement on the

highway and on the territory of gas stations (start and stop of vehicles is the mode of highest exhaust gas emission level) [9].

Table 2 Contamination of soils adjacent to the objects of AHC byPC

Объект АДК	Concentration of PC (mg/kg) on the distance, m	
	1	8-10
Ac. Pavlov Str.	3149	740
Pushkin Str.	1900	930
M03 Kyiv-Dolzhanskaya	3280	n.d.
P-46 Kharkov - Ahtyrka	1095	692
GFS №1	2960	1610
GFS №2	695	205
Parking	820	350
Control	50,0	

Also, increased emissions of PC from gas stations is caused by such phenomena as breathing of gas stations (evaporation from reservoirs of GFS), evaporation from open tanks of vehicles during refueling, leakage of idle vehicles, leaks and spills of fuel at certain violations of vehicle fueling technology, etc.

Therefore, the composition of PC emitted by the gas station and the highway must be different. This assumption is confirmed by experimental studies on the identification of alkanes in PC polluting the soil in the areas adjacent to the objects of the AHC (Fig. 1-5).

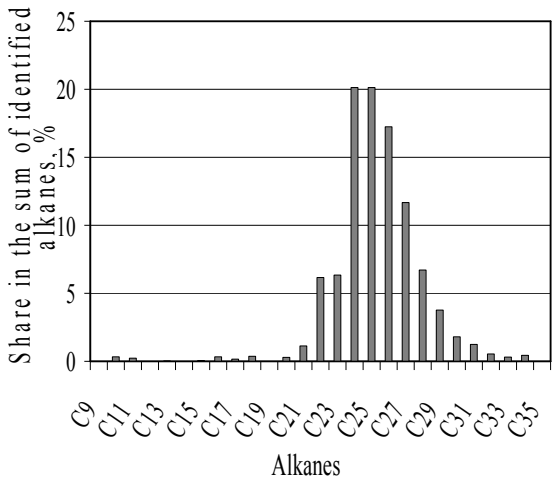

Fig. 1. Identification of saturated hydrocarbons polluting the soil in the areas adjacent to the Urban highway

As can be seen, in the studied soil samples alkanes prevailing among the saturated hydrocarbons with a few exceptions are in the range of C24-C28, which distinguishes them from the diesel fuel, in which the dominating alkanes are in the range of C19-C23, and C19 has the maximum concentration. Although, in the soil of the roadside area of filling stations among alkanes C19 also has the maximum concentration, besides it is practically equal to concentrations of C19 among alkanes in the diesel fuel. It should be noted that the most environmentally hazardous alkanes with carbon number less than 16 are present in significant amounts (> 1%) only in the diesel fuel and in the soil in the areas adjacent to gas stations, etc. on the area where there is fuel emission, as well as its possible leak.

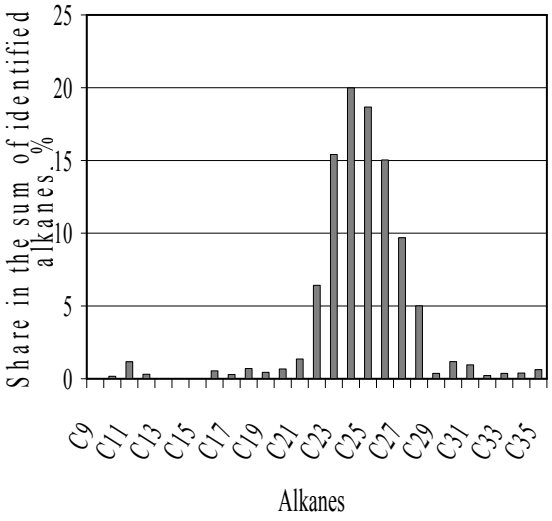

Fig. 2. Identification of saturated hydrocarbons polluting the soil in the areas adjacent to the Rural road

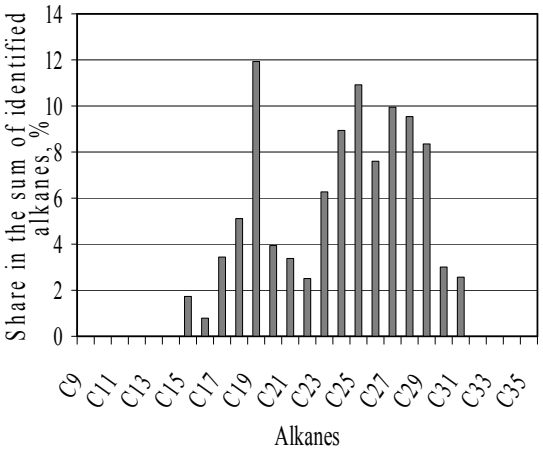

Fig. 3. Identification of saturated hydrocarbons polluting the soil in the areas adjacent to the GFS

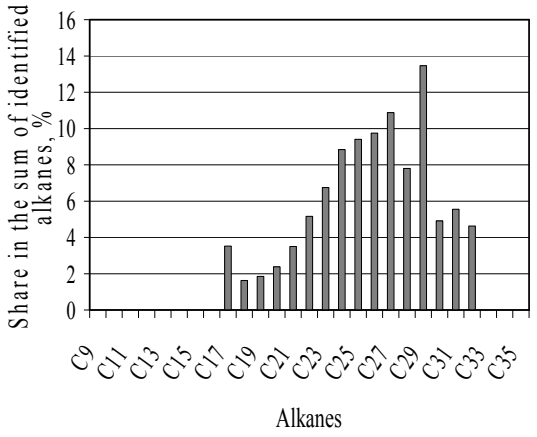

Fig. 4. Identification of saturated hydrocarbons polluting the soil in the areas adjacent to the Parking-lot

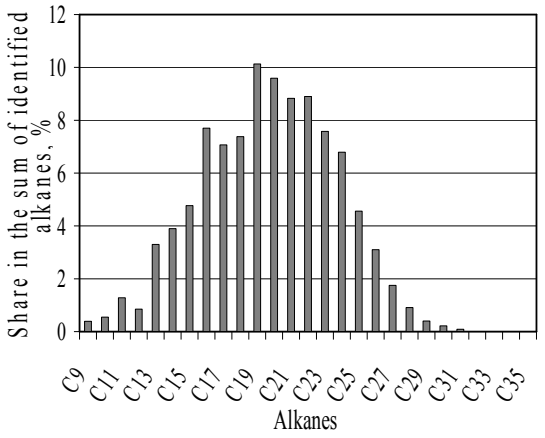

Fig. 5. Identification of saturated hydrocarbons polluting the soil in the areas adjacent to the Diesel fuel

The highest environmental hazard in gaseous emissions of the road transport is caused by PAH - substances of hazard class 1. Their accumulation in soils is also a serious threat to the soil flora and fauna. The identification data of aromatics and PAHs in soils of the roadside area in Kharkiv is shown in table 3.

Table 3 The concentration of the most environmentally hazardous aromatic hydrocarbons in the surface layer of soils (0.5 cm) adjacent to the road of Pushkin str.

The distance from the road, m	Content of aromatic hydrocarbons		Content of PAH	
	mg / kg	in PC, %	mg / kg	in PC, %
1**	30,0	11,2	1,7	0,6
60**	5,0	2,5	0,9	0,5
1*	128,0	10,8	7,8	0,7
15*	22,0	4,9	3,8	0,8
40*	3,0	1,0	2,0	0,6
100			1,4	0,1

In Ukraine, the concentration of PAHs in the soil is not standardized, but if you focus on the MPC amount of PAH (1 mg/kg), established for soils in Belarus, their content in almost all the samples of studied soils of the roadside area is 3-128 MAC.

Conclusion

The flow of OPs from the objects of the ARC of different groups (urban roads, country roads, gas stations and car parks) on the surrounding areas is correlated with the intensity of traffic on the sites of each group.

Filling stations produce a higher level of specific emissions of OPs (produced by one car of the traffic) as well as specific contamination of soils of the surrounding area by this pollutant in comparison with the roads.

The most environmentally hazardous alkanes with carbon number less than 16 are present in significant amounts among the saturated hydrocarbons (> 1%) only in diesel fuel and in the soil on the areas adjacent to filling stations.

The concentration of PAH - compounds of the 1st hazard class in the soils of the roadside area in Kharkov was 3-128 times higher than the maximum permissible concentrations of these contaminants established in Belarus (in Ukraine, the content of these compounds in the soil is not standardized).

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