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EFFECT OF TRAFFIC ON THE SOIL CONTAMINATION WITH POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

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ABSTRACT

The level of the environment pollution with polycyclic aromatic hydrocarbons is mainly in correlation with degree of the region industrialization and the traffic density. The aim of this study was to determine the effect of exhaust gases of gasoline and diesel motors on the polycyclic aromatic hydrocarbons (PAHs) accumulation in the soil, along the main road M-21. Soil samples were collected from seven localities, at two depths (0-20 and 20-40 cm). The method used for PAHs determination was gas chromatography – mass spectrometry (GC-MS). The obtained results showed that PAH concentrations, mainly originating from diesel motors, were lower than 1 mg/kg soil. Concentrations of phenanthrene, benzo(a)anthracene and benzo(b)fluoranthene were elevated at all chosen localities and at depths of 0-40 cm.

Keywords: Exhaust gasses, PAHs, soil contamination, National Park "Fruška Gora"

Introduction

The occurrence and frequency of higher concentrations of pollutants in the atmosphere primarily depend on the magnitude and distribution of the sources of emissions, local topography, climate conditions and type of pollutant. The level of the pollution is mainly in correlation with the degree of the industrialization of the region and the traffic density (13, 15).

In addition to the primary pollutants, carbon monoxide and nitrogen oxides, the third fraction in automobile exhaust is formed by incomplete combustion of hydrocarbons in oil and its derivations, which are probably directly less hazardous than the former two (they are weaker irritants), but they form very toxic and carcinogenic PAH compounds. Automobile exhausts consist of benzopyrene, an already identified carcinogen (14).

Polycyclic aromatic hydrocarbons are neutral, nonpolar, organic molecules which consist of two or more condensed benzene rings interconnected in different combinations, with hydrophobicity which increases with the molecular weight (1). PAHs have low solubility in water, but they stick to solid particles of clay, and in organisms they readily make bonds in fat tissues. Almost all PAHs are known as carcinogens (12).

Natural sources of PAHs are forest fires and volcanic eruptions. Also, traffic exhaust (15) and hazardous waste sites (12) are recognized as important producers of these compounds.

In the soil, PAHs make the strongest bonds along the particles. Some PAHs in the soil also contaminate the subterranean water. The contact of surface water and subterranean water with tar (which also contain PAHs) results in the dissolving of tar constituents, particularly benzene, which is carcinogenic, and naphthalene, both soluble in water. PAHs can be decomposed into the products by the reaction with sunlight and other chemical substances in the air, which lasts for days and weeks. The decomposition in the soil and water requires months and years and it is mainly caused by the impact of micro-organisms (3, 11).

One of the main effects on PAH formation from gasoline and diesel fuels is the relation of air and fuel, and the use of catalysts considerably decreases the concentration of PAHs in exhaust gases. All the motors with internal combustion have different characteristics of PAH emissions, depending on the motor temperature, charge, fuel quality and the velocity. Urban zones with heavy traffic and with vehicles traveling short distances have high PAHs emission. Emission is also increased by engine troubles and worn out motors. Previous studies (13) show that release of these compounds could be reduced by 80-90%. The catalysts for diesel motors also decrease the total emissions of PAHs, but not so much as in gasoline motors. The reduction of PAH emission by exhaust gases can be achieved by lowering the PAH content in the fuel. Vehicles using diesel fuel have higher emissions of PAHs than vehicles powered by gasoline.

Bioremediation, by using fungi (3) and bacteria (11) and phytoremediation (8, 21) can lead to PAH decomposition or absorption. The goal of this study is determination of the effect of exhaust gases of gasoline and diesel motors on the accumulation of polycyclic aromatic hydrocarbons (PAHs) in the soil, along the main road M-21, through the National Park "Fruška Gora".

Materials and Methods

Studied area

Fruška Gora mountain is located in the Pannonian lowlands (45°10' North Geographical Width and 19°40' East Geographical Length). Most of it is in the Vojvodina province, Serbia, and a

smaller part, in the west, is in Croatia, bounded by the Danube River at the north side. It is about 80 km lengthwise east to west, about 15 km north to south. The highest peak is Crveni Čot at 539 m. A large part of the area (25525 km²) has been a National Park of Serbia since 1960.

The studied area was National Park "Fruška Gora", i.e. the part of the main road M-21: Irig - Iriški Venac – Paragovo, with a length of 12 km.

Soil sampling

Seven localities along the road Irig - Iriški Venac – Paragovo were chosen (**Fig. 1**). Three soil samples were collected at each locality, at two depths: 0-20 and 20-40cm. For the purpose of comparison of obtained results it was necessary to find and select a control locality (locality 7) as much as possible outside the influence of pollution. The old downward road, closed for traffic 40 years ago, was chosen for this purpose.

Analytical procedure

Samples of soil were dried to a constant mass, crushed in a mortar, and sieved. From such samples portions of 20 g were used for PAHs analysis. The determination of these compounds was performed by the extraction from the soil, at room temperature, followed by mixing on magnetic mixer for one hour in the mixture of dissolvents: water, methanol, n-hexane, acetone, and methylene-chloride. Samples were centrifuged on ultracentrifuge, the organic layer was pipetted and concentrated in the current of nitrogen. Purification was performed on gel (10), and both quantitative and qualitative analyses were performed by gas chromatography – mass spectrometry (GC-MS).

Results and Discussion

Traffic frequency on the main road M-21

The data on traffic density (2007) on the study road M-21 (**Table 1**) indicate that the total number of vehicles per day is 7989, which is total of 6475 passenger cars using gasoline and 1514 vehicles using diesel fuel. As the measuring point is located in Irig, the total number of vehicles passes the road Irig-Iriški Venac, half of them along the downward road Iriški Venac-Paragovo, and the other half along the upward road Paragovo-Iriški Venac. It can be assumed that the degree of pollution is different because the number of vehicles, the pull-up time and the traveling time are different.

There is a permanent measuring station on the road Irig - Iriški Venac - Paragovo for continuous registering the number of vehicles. The data presented in **Table 1** highlight the tendency of increase of total number of vehicles in the following years, primarily passenger cars using gasoline with lead additives, but also diesel fuel.

Concentration of polycyclic aromatic hydrocarbons in soil

PAH content mainly decreases with soil depth, but they can also be found at the depths up to 2 m, such as for example, phenanthrene (21), and their quantity is narrowly related to biodegradation, which is in turn conditioned by external factors.

Plants can absorb and decompose some of PAHs (16), which are mostly deposited in the soil, some of them in the roots. The highest concentrations in leaves occur in the plants of the family *Asteraceae*.

PAH concentration was analyzed at two depths (0-20 cm and 20-40cm) and concentration of 16 PAH components ranges mainly below the threshold - detection limit (MDL = 2 ppm) or below the practical quantization limit, i.e. the threshold above which it is possible to determine the quantity (PQL = 5 ppm). Depending on the localities and depth, the following PAHs between 16 analyzed in all were quantified: phenanthrene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, dibenzo(a,h)anthracene and indeno(1,2,3,c,d)pyrene.

The greatest number of detected PAHs was found at the localities 3 and 4 (9 PAHs), at the localities 5 and 6 (4 PAHs), locality 1 (3 PAHs), whereas 2 PAHs were detected at the locality 7 in the surface layer (0-20 cm), and 8 PAHs at the

TABLE 1

Average and expected number of vehicles per day in the period 2004-2008 on the M-21 (Irig – Iriški Venac-Paragovo)

Year	Vehicles per day										
	Total	PC	B	V_{3T}	V_{7T}	HV		TC			
						HV_1	HV_2	Total TC	TC_1	TC_2	TC_3
2004	7001	5647	180	258	189	153	17	557	155	89	313
2005	7337	5929	186	266	197	159	18	582	162	81	339
2006	7656	6196	192	274	203	166	18	607	169	73	365
2007	7989	6475	197	282	211	172	19	633	176	65	392
2008	8337	6766	203	290	218	178	20	660	184	57	420

Abbreviations:

PC - passenger car; B - bus; V_{3T} - vehicle for carrying freight (up to 3t); V_{7T} - vehicle for carrying freight (7t); HV - heavy vehicle for carrying freight; HV_1 - heavy vehicle for carrying freight (one driving ahle); HV_2 - heavy commercial vehicles (two driving ahles); TC - freight train; TC_1 - freight train carrying cars; TC_2 - freight train carrying cars (two driving ahles); TC_3 - freight train carrying cars (three driving ahles).

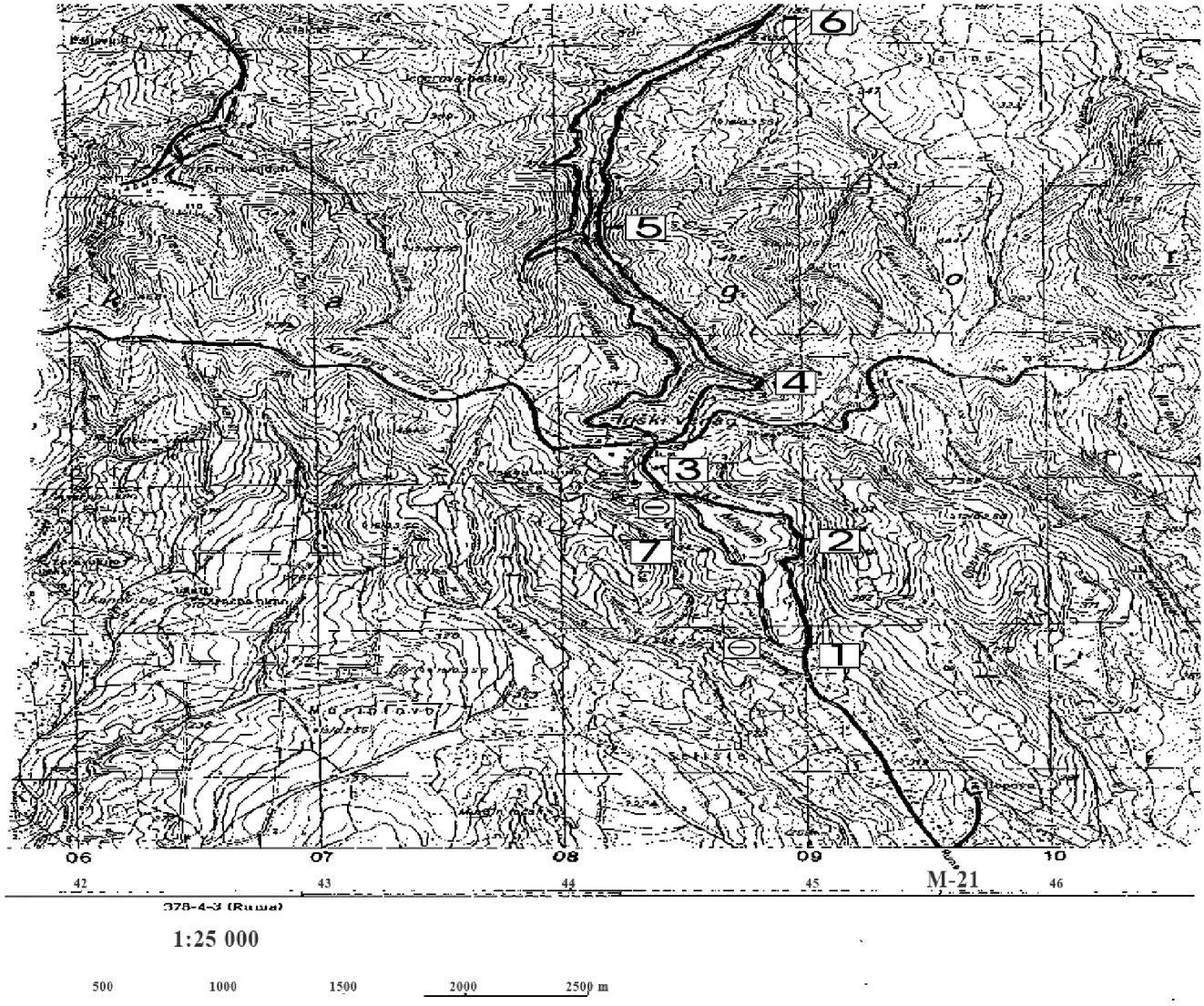

Fig. 1. Part of the main road M-21 Irig-Iriški Venac-Paragovo

The localities are as follows:

Locality 1 – at the entrance of Hopovo - Irig

Locality 2 – half-way to Iriški Venac (1.5 km)

Locality 3 – Iriški Venac

Locality 4 – 500 m from Iriški Venac towards Paragovo

Locality 5 – 2.5 km from Iriški Venac towards Paragovo

Locality 6 –crossroads at Paragovo of the road entering the town and the downward M-21

Locality 7 – control (the road closed for traffic)

depth 20-40 cm. Of these components, benzo(a)anthracene and benzo(b)fluoranthene have the highest concentrations and were detected at the majority of localities.

According to results from contaminated and uncontaminated sites in Poland (19), there are 6 - 16 different PAHs. Their concentrations in uncontaminated soils ranged from 1.5 to 30.1 μg/kg, while in very contaminated soils around petrochemical complex their content amounted 33100 μg/kg. Also, results of this author for vicinity of road, with traffic density of 8000 cars per day, indicate that concentration of benzo(a)pyrene varied between 7.1 and 10.6 μg/kg. The present study's results indicate that certain localities, characterized by the same traffic density, had 5.8 - 6 μg/kg benzo(a)pyrene. Interesting results were obtained for locality 7, i.e. road closed for traffic at least for forty years. A great number of PAHs was detected at deeper depths. This is related to intensive traffic of heavy transport vehicles using diesel fuel, and low frequency of automobiles, in the past.

The highest concentrations of fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene,

benzo(k)fluoranthene, dibenzo(a,h)anthracene and indeno(1,2,3-c,d) pyrene (12, 65, 8.9, 65, 18, 23 and 83 μg/kg, respectively) were recorded at locality 4, in soils sampled at the depth 20-40 cm, while the highest amount of indeno(1,2,3-c,d)pyrene in the upper soil layers (0-20 cm) was measured at locality 3 (92 μg/kg). Differences among PAH concentrations in three designated areas (industrial areas, city centres, suburbs) were found in agricultural soils as well at 0-20 cm (9). The authors reported the highest concentrations of all congeners in the industrial areas. Mean amounts of benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-c,d)pyrene in these samples were 17.2, 64.9, 26.3 and 14.2 ng g^{-1}, respectively. Considering a lack of other PAH sources in the area of soil sampling, it seems that these congeners originate from the motor vehicle traffic. The level of emission is dependent on the type of vehicle, the conditions of the engine and the environment in which it is being used (20). Furthermore, the PAHs emitted depend on the type of fuel used: petrol-fuelled vehicles emit predominantly fluoranthene and pyrene whereas diesel-fuelled vehicles emit naphthalene and acenaphthene (5). Our results showing amounts of naphthalene, acenaphthylene, acenaphtene, fluorine and anthracene below the MDL or PQL at all localities elucidate the prevalence of vehicles using the petrol fuel.

Previous investigations have showed that the total levels of PAHs in soils could be increased in industrial and agricultural areas, as well as along main roads. After Edwards (6), typical endogenous concentrations of PAH's in soil and vegetation range from 1 to 10 μg/kg and from 10 to 20 μg/kg, respectively. Endogenous PAH's are due to plant synthesis, forest and prairie fires, volcanoes, etc. In our study, the total amounts of PAHs ranged from 10 μg/kg (locality 1, 20-40 cm) to 306.9 μg/kg (locality 4, 20-40 cm). The highest total PAHs concentrations in the surface soil (0–5 cm) samples from different functional areas at Ji'nan city in Shandong Province of China were in the range from 1.31 mg kg^{-1} to 254.08 mg kg^{-1} (dry weight), and the average level of total PAHs was 23.25 mg kg^{-1} (4). The highest amounts were found in industrial areas, while along the main roads up to 53.97 mg kg^{-1}.

The most abundant PAHs in our study were four- and five- ring compounds (**Table 2**), and these findings are in accordance with other published results. For example, Hao and coworkers (9) also reported the prevalence of these compounds in agricultural soils in China. Such results could be explained by the PAH compounds change from the vapor phase to particulates with increasing molecular weight. Also, lower molecular weight PAHs are more volatile and photooxidative to the atmosphere, in contrast to PAHs with higher molecular weight mainly associated with the soil particles (6).

In order to prevent environment contamination and human health risks, processes related to removal of the PAHs from soils are very important. The rate and extent of the biodegradation of PAHs by soil microorganisms depends on their molecular weight and the soil aeration (18). Slow biodegradation of all

TABLE 2

Contents of polycyclic aromatic hydrocarbons in the soil at different localities (μg/kg)

Locality	Sampling depth	Naphthalene	Acenaphthylene	Acenaphtene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a) anthracene	Chrysene	Benzo(b) fluoranthene	Benzo(k) fluoranthene	Benzo(a) pyrene	Dibenzo(a,h) anthracene ntracen	Benzo(g,h,i) perylene	Indeno(1,2,3-c,d) pyrene
1	0-20 cm	<MDL	<PQL	<MDL	<PQL	**5.0**	<PQL	<PQL	<PQL	**7.6**	<PQL	**7.6**	<PQL	<PQL	<PQL	<MDL	<PQL
	20-40 cm	<MDL	<MDL	<MDL	<PQL	<PQL	<PQL	<PQL	<PQL	**5.0**	<PQL	**5.0**	<PQL	<PQL	<PQL	<MDL	<PQL
2	0-20 cm	<MDL	<MDL	<MDL	<MDL	<PQL	<MDL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<MDL	<PQL
	20-40 cm	<MDL	<MDL	<MDL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<MDL	<PQL
3	0-20 cm	<PQL	<PQL	<PQL	<PQL	**25**	<PQL	**11**	**11**	**54**	<PQL	**54**	**15**	**6.0**	**15**	<PQL	**92**
	20-40 cm	<MDL	<MDL	<MDL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<MDL	<MDL	<MDL	<MDL
4	0-20 cm	<PQL	<PQL	<PQL	<PQL	**5.0**	<PQL	<PQL	<PQL	**9.9**	<PQL	**9.9**	<PQL	**5.8**	**5.0**	<PQL	**25**
	20-40 cm	<PQL	<PQL	<PQL	<PQL	**21**	<PQL	**12**	**11**	**65**	**8.9**	**65**	**18**	<PQL	**23**	<PQL	**83**
5	0-20 cm	<MDL	<PQL	<MDL	<PQL	**6.2**	<PQL	<PQL	<PQL	**11**	<PQL	**11**	<PQL	<PQL	<PQL	<MDL	**8.6**
	20-40 cm	<MDL	<PQL	<PQL	<PQL	**7.2**	<PQL	<PQL	<PQL	**10**	<PQL	**10**	<PQL	<PQL	<PQL	<MDL	**7.7**
6	0-20 cm	<PQL	<PQL	<PQL	<PQL	**7.4**	<PQL	<PQL	<PQL	**12**	<PQL	**12**	<PQL	<PQL	<PQL	<PQL	**17**
	20-40 cm	<MDL	<MDL	<MDL	<MDL	<PQL	<MDL	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL	<MDL	<MDL	<MDL	<PQL
7	0-20 cm	<MDL	<MDL	<MDL	<PQL	<PQL	<PQL	<PQL	<PQL	**5.1**	<PQL	**5.1**	<PQL	<PQL	<PQL	<MDL	<PQL
	20-40 cm	<MDL	<MDL	<MDL	<PQL	**11**	<PQL	**7.4**	**6.5**	**23**	**5.9**	**23**	**9.8**	**7.1**	<PQL	<MDL	<PQL

MDL = 2.0 μg/kg (Method Detection Limit), PQL = 5.0 μg/kg (Practical Quantisation Limit)

PAHs has been found under anaerobic conditions (5). Hence, low concentrations of the lighter PAHs obtained in this work could be the result of their short half-life i.e. higher rates of biodegradation.

Along with the uptake of PAHs into plant roots, the indirect uptake into the foliar part of the plant through volatilization is also involved in their removal from the soil (5). Volatilization is a significant removal process for naphthalene and for compounds with similar characteristics (i.e. with two or three rings) (20), while for those with four or more rings it was not found to be an important loss mechanism. However, both direct and indirect uptake pathway is most likely to be realized for the lower molecular weight PAH compounds due to their better volatilization and low sorbtion capacity to soil organic matter, relative to heavier ones (5). These facts could also contribute to low levels of the low molecular weight PAHs obtained in our study. Considering that possible human or animal carcinogens include benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene and indeno(l,2,3-cd)pyrene (17), it seems unlikely for them to enter the food chain through plants. Actively growing green plant parts may naturally contain benzo(a)pyrene in the range 10 to 20 μg/kg, but storage tissues generally contain 1-10% of that in green plant portions (6). Washing leaves of vegetation contaminated with PAH's removes no more than 25% of the contamination, whose concentrations in plant skin and peel are higher than those in internal tissues (6). There is some evidence that plants can catabolize PAH's, but metabolic pathways have not been defined well.

The comparison of the study values of PAH quantity with the maximum permitted concentrations according to American regulations (2), because there are no regulations in our country, shows that the examined soil has the concentration below 1 mg/kg (target value), which means that soil is not in the category of contaminated soils. Intervening values are 40 mg/kg for standard soil i.e. the soil with 10-30% organic matter and 25% of clay. However, if we take into account the standards for human health and hazardous concentrations, the MPC (Background) for drinking water is 4 to 24 ng/L, for food 2μg/kg, and for air 0.02-1.2 ng/m^3 for rural area, and 0.15-19.3 ng/m^3 for urban area (10).

Conclusions

The main road M-21 has heavy traffic of passenger cars using gasoline with lead additives, and heavy transport vehicles, which use diesel fuel, with the tendency of increasing traffic intensity in the following years. The upward - downward part of the road Irig - Iriški Venac, where there is two-way traffic with one lane each, is loaded with pollutants from the road Paragovo-Iriški Venac, where there is two-way traffic with two lanes. PAH concentrations, mainly originating from diesel motors, in the soil are below the permitted values, and according to foreign regulations, because this is not regulated by our regulations, the concentrations are lower than 1mg/kg soil. Although the PAH concentrations are lower than permitted concentrations, there are elevated concentrations of benzo(a)anthracene, benzo(b)fluoranthene and phenanthrene at all examined localities and at the depths of 0-40cm.

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