10.7251/AGSY1203423P
UDK 546.62:631.445.1

CONTENTS OF PB, CU AND HG IN SOIL AND IN PLANT MATERIAL ON AGRICULTURAL LAND SURROUNDING THE MOTORWAY E75 IN THE SECTION BELGRADE-PRESEVO

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Abstract

The study included examination of soil and plant material for the contents of some elements along the motorway E 75 through Serbia, the section from Belgrade to Presevo, a length of 400 km. Samples of soil and aerial parts of plant material were sampled from both sides of lanes at a distance of about 8 km and at 10, 30, 50 and 400 m perpendicular to the direction of the highway. In the study area it was registered over forty varieties of soil, where twelve separate zones different plant cover was registered.

In the soil samples was determined pH in 1MKCl and content of total forms of Pb, Cu and Hg. The plant materials were analyzed for Pb, Cu and Hg.

The content of total forms of Pb above the MAC (maximum allowable concentration), was found in 5.28%, Cu in 0.25%, Hg in 0.75% of the studied samples.

In the examined plant material there were not detected toxic concentrations of Hg. Toxic Pb content above the value recorded in 3.3% of plant samples in zones in the distance from 10 m to 50 m from the road. The element Cu in the plant material is present in toxic concentrations in 1.27% samples of which two samples were from the vineyards at a distance of 50 m from the motorway, while the three samples from the zone at distance of 400 m.

By the analysis of obtained results it can be concluded that besides of anthropogenic pollutions, which is reflected in the excessive use of plant protection products and fertilizers, also the impact of air pollution from motor vehicles in certain sections of the examination, including the available literary sources, the dominant contamination of examined elements comes from geochemical composition of bedrock.

Key words: *soil, plant, highway*

Introduction

The highway is the highest traffic class of roads. It is exclusively designed for fast motor traffic, which is operating in physically separated carriageway, usually width of 27.5 meters, with at least two running and one stopping lane.

Observations presented in this paper were performed on the section of the highway E75, which is very frequent throughout the year, so the impact of emissions from motor vehicles on soil and plant is especially emphasized. Since the soil along the highway mainly belongs to agricultural area, examinations were aimed to determine whether there is and what is the level of the pollution of the soil in the examined area.

Soil as an essential natural element represents a very complex system, sensitive to different influences. It responds to small changes and this can cause a degradation of its main characteristics. Therefore, the relations arising from the different spheres of influence on soil also define the whole question of the relationship between the highway and the environment.

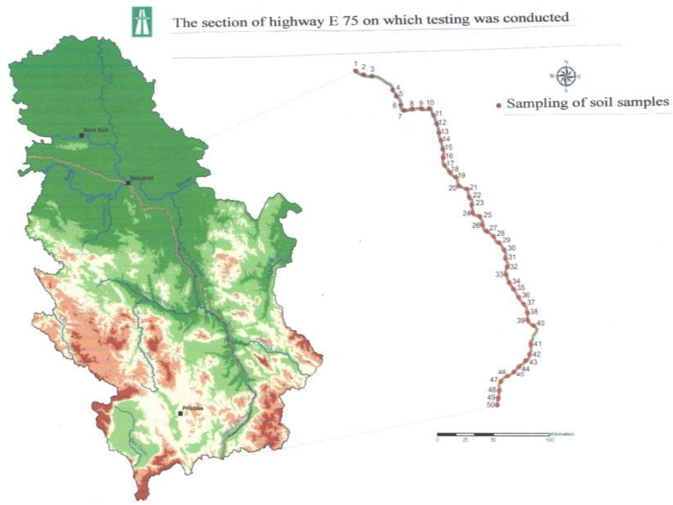

Figure 1.-The route of the highway and sampling spots

Materials and methods

The area of study included the route of the E 75 in the section from Belgrade, capital city of Serbia, to the Preševo, near the border with FYROM, (Figure 1.), a distance of about 400 km. Composite soil samples were taken from each side of the lane at a distance of 8 km and at 10, 30, 50 and 400 m perpendicular to the direction of the highway from a depth of 0 do30 cm. Sampling was conducted during August and September 2010.

Composite soils samples were carried to the laboratory, dried, and passed through a 2-mm sieve. Soil pH in water and 1M KCl was analyzed potentiometric with glass electrode (SRPS ISO 10390:2007- Determination of pH). Microelements and heavy metals were determined on ISP emission spectrometer ICAP 6300 (ICP-OES), after the soils were digested with concentrated HNO_3 for extraction of total forms (Soltanpour et al., 1996).

The concentration of trace elements Hg was determined by a flame atomic adsorption spectrophoto-meter (AAS, GBC, SENSA DUAL HG), method by hydration after the so-called "wet" combustion of samples, i.e. boiled in the mixture of concentrated acids: HNO_3 and H_2O_2, with filtration and the necessary dilution.

Reference soils NCS ZC 73005, Soil Certificate of Certified Reference Materials approved by China National Analysis Center Beijing China, and reagent blanks were used as the quality assurance and quality control (QA/QC) samples during the analysis.

Analyzed aboveground parts of the study plant species were dried at $105^{o}C$ for a period of 2 hours, using gravimetric method for determination of dry matter content of plant tissue. The dry matter determination is used to correct the sample element concentration to an absolute dry matter basis (Miller R.O.1988).

The content of heavy metals (Pb, Cu) in selected plants was determined with an inductively coupled plasma optical emission spectrometer ICAP 630 (ICP-OES), after the samples were digested with concentrated HNO_3/H_2O_2 for total form extraction (Soltanpour et al., 1996).

The concentration of trace element Hg in plant materials was determined by AAS method by hydration after the "wet "combustion of plant samples, that is boiling in the mixture of concentrated acids: HNO_3 and $HClO_4$, with filtration and the necessary dilution.

Statistical analyses were performed with SPSS version 16 software. The effects of treatments are presented in Tables 1 and 2 for all the variables using Analysis of Variance (ANOVA) method.

Cartographic data processing was performed by using ArcView GIS 8.3.

Results and discussion

Based on the exanimations, (398 soil samples), the following results were obtained:

In the examined area it is represented forty types of soil, with twelve separate zones with different plant cover. Fields are dominating with 43% of examined area, abandoned production areas (neglected land) with of about 23% of areas and meadows with about 20%. The rest of the area is occupied by orchards, vineyards, gardens, vegetable gardens, forests, industrial crops and swamp surface.

Based on the results of some basic parameters of fertility, it was noted that about 40% of soil samples has limitations, such as strong acid reaction. In Table 1, statistical description of pH in 1MKCl and heavy metals in soils samples in the study area is shown.

The content of heavy metals in soil and their impact upon ecosystems can be influenced by many natural factors, such as parent material, climate, soil processes, and anthropogenic activities such as industry, agriculture, and transportation (Wei et al. 2007).

Urban roadside soils are the ‘‘recipients’’ of large amounts of heavy metals from a variety of sources including vehicle emissions, coal burning waste and other activities (Jose A. Acosta et al.2009; Mohsen S. et al. 2009). Averages of Cu and Pb are compared with other cities around the world are significantly lower (Ruiz-Cortes et al. 2005;Ljung et al. 2006; Bretzel and Calderisi 2006),meaning the anthropic activities have a low impact on the soil heavy metal concentrations in the study area.

The content of total forms of copper above the MAC(maximum allowable concentration)- Official Gazette of Republic of Serbia, 23/94, was found in 0.25% of the studied samples. Of these, half were located in the vineyards, so the reason for the appearance of increased concentrations of this element may be excessive use of plant protection products based on copper, which are used on these surfaces.

The content of total forms of Pb above the MAC was registered in 28.5% of the samples, except that in one sample at a distance of 10m from the highway route registered an extremely high concentration of this element of 215.45 mg kg^{-1}.

The content of total Hg above the MAC was determined in 0.75% of samples in the zone of 10-50 m, from the traffic lanes.

Table 1.- Statistical description of pH in 1MKCl and heavy metals in soils samples in the study area

	Statistical parameters	**Soil pH** (1MKCl)	**Total Pb**	**Total Cu**	**Total Hg**
			($mg \cdot kg^{-1}$)		
Surface layer (0-30 cm)	Total N° of soils samples	398	398	398	398
	Min	3.60	0.00	4.64	0.00
	Max	7.50	1108.16	223.82	4.84
	Mean	6.02	74.56	25.25	0.13
	SD	0.93	81.34	19.53	0.39
	VC	0.86	1501.86	1108.16	2398.00
	Mediana	6.00	37.72	67.71	66.05
	Modus	7.30	37.67	43.85	71.05
Limits	Lower				/
	Usual		<50	<50	>0.1
	Higher		50-100	50-100	1-2
	MAC*		100	100	2
	Extreme		>150	>200	

SD-standard deviation; VC-variation coefficient

*Official Gazette of Republic of Serbia, 23/94

Numerous studies on roadside soil pollution have focused on total emission loads of heavy metals into open grassland and agricultural areas (Donaldson and Bennett 2004; Hjortenkrans et al. 2006; Nabulo et al.2006). Generally, total heavy metal contents in roadside soils were found strongly dependent on traffic density and showed an exponential-like decrease with distance from the road, reaching background levels within tens to hundreds of meters. Recently, roadside soils have been an increasingly important sampling medium for assessing anthropogenic metal concentrations. A variety of heavy metals have been measured in roadside soils and reported by many researchers (Wang et al. 2005; Manta et al. 2002; Zhang et al. 2006; Xue-Song Wang 2008). The most frequently reported heavy metals of concern have been lead, zinc and copper. These heavy metals in roadside soils are principally derived from vehicle emissions, wear and tear on automobile parts (Xue-Song Wang and Yong Qin , 2007).It can be concluded that the addition of anthropogenic pollution (excessive use of plant protection products and fertilizers, as well as the impact of air pollution from motor vehicles originating in the valley of the Morava dominant geochemical pollution (based on the available literary sources). The geological parent materials are river sediments and loess, and the geochemical background concentrations (in topsoil) range from, 8.7 to 17.5 mg kg^{-1} for Cu, 18 to 23mg kg^{-1} for Pb (Geochemical Atlas of Europe, www.gtk.fi/publ/foregsatlas).The origin of increased contents of Pb is so closely associated only with these rocks, but the causes of pollution and should be linked to anthropogenic influence.

Along with the sampling of soil material it was sampled also and plant material (vegetative mass) on corresponding locations (394), in order to determine contents of Pb,Cu,Hg.

Plants are the intermediaries through which elements from the soil and partly from the air and water are transferred to the human body by consumption. Some of the elements are necessary for growth and development of crops and without them they cannot survive, some of them have stimulating effect on plant growth, while a group of elements at high concentrations affects very toxically on the plants.

Plant metal uptake is influenced by soil factors including pH, organic matter, and cat ion exchange capacity as well as plant species, cultivars and age. The mobility and availability of heavy metals in the soil are generally low, especially when the soil is high in pH, clay and organic matter (Jung and Thornton, 1996; Rosselli et al., 2003).

Table 2 presents average critical and toxic concentration of heavy metals in plats according to Kloke et al. 1984*, Kastori et al., 1997**.

Table 2.- Average and toxic concentration of heavy metals in plants

Element	**Normal content in plants** Kloke et al. *	**Critical contents for plant food** Kloke et al. *	**Critical concentration** Kastori**	**Toxical concentration** Kastori**
	($mg\cdot kg^{-1}$)		($\mu g\cdot g^{-1}$)	
Cu	3-15	15-20	15	20
Pb	1-5	10-20	10	20
Hg	<0.1-0.5	0.5-1	2	5

Table 3., presents the percentages of Cu, Hg and Pb in the aboveground plant material tested depending on the distance from the road and values of desirable, critical and toxic value of the tested elements.

Table 3.-Percentages of Cu,Pb i Hg in the aboveground plant material tested depending on the distance from the road

Element	Limit values	Distance 10m	Distance 30m	Distance 50m	Distance 400m	Total for 394 samples
			Cu (mg·kg^{-1})			
<15	Desirable	96,97%	99,00%	93,00%	91,58%	95,18%
15-20	Critical	3,03%	1,00%	5,00%	5,26%	3,55%
>20	Toxic	0,00%	0,00%	2,00%	3,16%	1,27%
			Pb (mg·kg^{-1})			
<10	Desirable	89,90%	90,00%	90,00%	93,68%	90,86%
10-20	Critical	7,07%	6,00%	6,00%	4,21%	5,84%
>20	Toxic	3,03%	4,00%	4,00%	2,11%	3,30%
			Hg (mg·kg^{-1})			
<2	Desirable	100,00%	100,00%	100,00%	100,00%	100,00%
2-5	Critical	0,00%	0,00%	0,00%	0,00%	0,00%
>5	Toxic	0,00%	0,00%	0,00%	0,00%	0,00%

Conclusions

By the analysis of obtained results it can be concluded that besides of anthropogenic pollutions, which is reflected in the excessive use of plant protection products and fertilizers, also the impact of air pollution from motor vehicles in certain sections of the examination, including the available literary sources, the dominant contamination of examined elements comes from geochemical composition of bedrock. The content of total forms of Pb above the MAC (maximum allowable concentration), was found in 5.28%, Cu in 0.25%, Hg in 0.75% of the studied samples.

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The element Cu in the plant material is present in toxic concentrations in 1.27% samples of which two samples were from the vineyards at a distance of 50 m from the motorway, while the three samples from the zone at distance of 400 m.

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