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Original Research

Assessment of Soil and Plant Contamination by Select Heavy Metals Along a Major European Highway

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Abstract

Our study examined soil and plant material for the contents of some elements along route E 75 through Serbia (the section from Belgrade to Preševo), a length of 400 km. European route E 75 is part of the International E-road network, which is a series of main roads in Europe.

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 route. In the soil samples we determined pH in 1MKCl and content of total concentrations of Pb, Cu, Ni, and Hg. Plant materials were analyzed for Pb, Cu, Ni, and Hg.

It can be concluded that, besides anthropogenic pollution that is reflected in the excessive use of plant protection products and fertilizers and also the impact of air pollution from motor vehicles in certain sections of the examined area, the dominant influence on concentration of some examined elements comes from geochemical composition of parent material from which the soils were developed.

Keywords: soil, plant, route

Introduction

The part of route E 75 that we examined is the highest traffic class of highway roads. It is exclusively designed for fast motor traffic, operating in physically separated carriageways (usual width of 27.5 m), with at least two running lanes and one stopping lane. Observations presented in this paper were performed on the section of the route with steady traffic throughout the year, so the impact of emissions from motor vehicles on soil and plants is especially emphasized. Since the soil along the route mainly belongs to agricultural areas, examinations were aimed to determine whether there is and what is the level of the pollution of the soil in the examined area.

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Soil as an essential natural element represents a very complex system, sensitive to different influences. During the last few decades we have witnessed an increasing influence of anthropogenic factors on content of metals in soils and plants. Human activities have dramatically changed the balance and biochemical and geological cycles of many heavy metals. An assessment of environmental risk caused by soil contamination is especially important for agricultural as well as non-cultivated areas due the fact that metals potentially harmful to human health persist in soils for a relatively long time and may transfer into the food chain in considerable amounts [1]. The content of heavy metals in soil and their impact on ecosystems can be influenced by many natural factors, such as parent material, climate, and soil processes, and anthropogenic activities such as industry, agriculture, and transportation [2]. 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 [3, 4]. Automobile traffic pollutes roadside environments with a range of contaminants. Heavy metals are found in fuels, in the walls of fuel tanks, in engines and other vehicle components, and in catalytic converters, tires, and brake pads, as well as in road surface materials [5, 6]. Contamination of the soil over the natural level by Pb, Zn, Cr, and Co could be one of the indicators of anthropogenic environmental pollution. Fast development of industry, continuously increasing population, and intensification of road traffic are regarded as the foremost causes of ecosystem pollution in urban areas [7]. Averages of Cu and Pb compared with other cities around the world are significantly lower [8-13], meaning the anthropic activities have a low impact on the soil heavy metal concentrations in the study area.

Soil 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 route and the environment.

Numerous studies on roadside soil pollution have focused on total emission loads of heavy metals into open grassland and agricultural areas [14-19]. Generally, total heavy metal contents in roadside soils were found to be strongly dependent on traffic density and showed an exponential decrease with distance from the road, reaching background levels of 10-100 m. The natural soil concentration of heavy metals depends primarily on the parent material composition [20]. 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 [21-25].

The most frequently reported heavy metals of concern have been Pb, Zn, and Cu. These heavy metals in roadside soils are principally derived from vehicle emissions, and wear and tear on automobile parts [26].

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 plants toxically. An assessment of the environmental risk caused by soil contamination is especially important for agricultural as well as non-cultivated areas due to the fact that metals potentially harmful to human health persist in soils for a relatively long time and may transfer into the food chain in considerable amounts [1].

Concentrations of metals in plants vary with plant species [27]. Plant uptake of heavy metals from soil occurs either passively with the mass flow of water into the roots, or through active transport across the plasma membrane of root epidermal cells [28]. A common source of soil and plant contamination with heavy metals is traffic [29]. Although heavy metals are naturally present in the environment, the dynamic development of industry and motorization, as well as the continuing over-intensive use of various chemical compounds in agriculture, causes constant increases of toxic heavy metals in the environment [30].

Material and Method

Study Area

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

Soil Analysis

In the laboratory, composite soil samples were dried and passed through a 2-mm sieve. Soil pH in 1M KCl was analyzed potentiometrically using a glass electrode [31]. Microelements and heavy metals were determined using ICP (inductively coupled plasma optical emission spectrometer ICAP 630 (ICP-OES)), after the soils were digested with concentrated HNO_3 for extraction of total concentrations [32].

Hg concentration was determined using flame atomic adsorption spectrophotometry (AAS, GBC, SensAA Dual HG), by the method of hydration, after digestion of the samples with nitric acid and hydrogen peroxide [33].

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

Plant Analysis

Analyzed aboveground parts of the study plant species were dried for 2 hours at 105ºC, using the gravimetric method for determination of dry matter content of plant tissue [34]. The content of heavy metals (Pb, Cu, Ni) in collected plant samples 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. The concentration of the Hg in plant samples was determined using AAS method by hydration after the “wet” combustion of the plant samples, meaning boiling in a mixture of concentrated acids (HNO_3 and $HClO_4$) with filtration and the necessary dilution.

Statistics and Cartographic Data Processing

Statistical analyses were performed with SPSS version 16 software [35]. Results are presented in Tables 1 and 2. Cartographic data processing was performed using ESRI’ ArcView GIS 8.3.

Table 1. Statistical summary of select soil properties and trace element concentrations.

	Statistical parameters	Soil pH (1M KCl)	Total Pb	Total Cu	Total Ni	Total Hg
			(mg·kg^{-1})			
Surface layer (0-30 cm)	Total No. of soil samples	398	398	398	398	398
	Min	3.60	8.70	4.64	4.83	0.00
	Max	7.50	215.45	223.82	438.08	4.84
	Mean	6.02	40.94	25.25	47.83	0.13
	SD	0.93	27.19	19.53	43.30	0.39
	VC	0.86	665.67	283.95	1501.6	0.10
	Median	6.00	32.24	22.12	37.73	0.08
	Modus	7.30	27.53	17.73	37.68	0.05
Limits	Usual		<50	<50	1-25	>0.1
	Higher		50-100	50-100	25-50	1-2
	MAC*		100	100	100	2
	Extreme		>150	>200	>200	

SD – standard deviation, VC – variation coefficient
*Official Gazette of Republic of Serbia, 23/94 [36]

Results and Discussion

Soil Properties

Based on the examination (a total of 398 soil samples), the following results were obtained: The examined area includes 40 types of soils, with 12 separate zones with different plant cover. Fields dominate with 43% of the examined area, abandoned production areas (neglected land- parlog) are 23% of areas, and meadows 20%. The rest of the area is occupied by orchards, vineyards, gardens, vegetable gardens, forests, industrial crops, and swamps. Based on

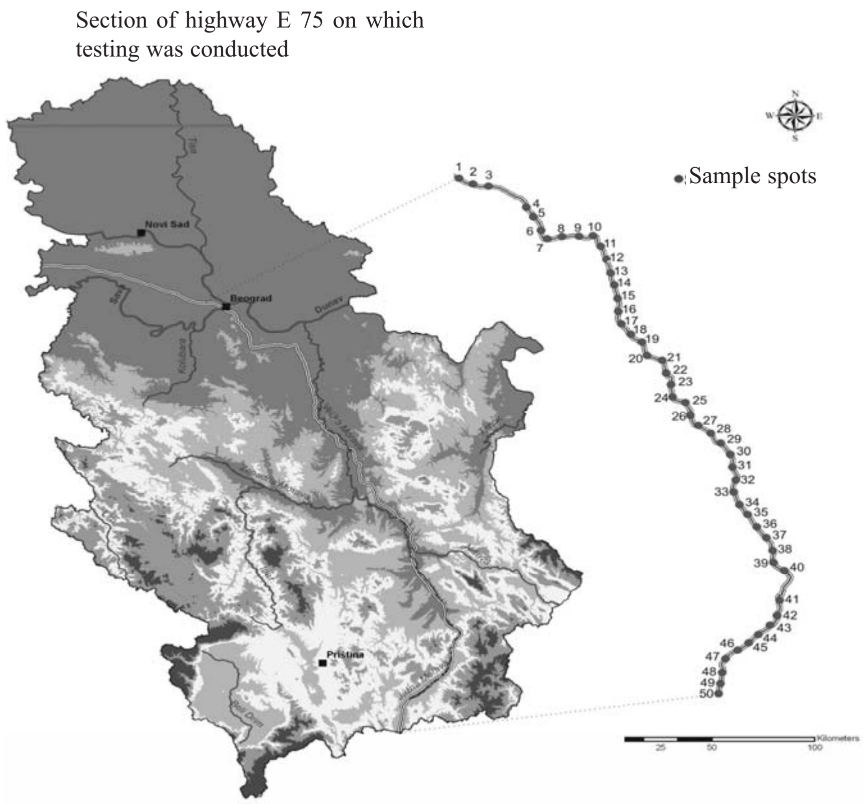

Fig. 1. The highway route and sampling spots.

Table 2. Average and toxic concentrations of heavy metals in plants.

Element	Normal content in plants [41]	Critical contents for plant food [41]	Critical concentration [42]	Toxic concentration [42]
	(mg·kg^{-1})			
Cu	3-15	15-20	15	20
Ni	0.1-5	20-30	20	30
Pb	1-5	10-20	10	20
Hg	<0.1-0.5	0.5-1	2	5

recorded results, 40% of soil samples have 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.

Total concentrations of Ni above the MAC (maximum allowable concentration) were recorded in 8.3% of all samples and are equally spread out along the area of research [36]. Extreme concentration of this element (over 200 mg·kg^{-1}) was registered in 0.8% of the samples in the zone at 10 m distance from the route.

The concentration of Cu above the MAC was recorded in 0.25% of the studied samples. Half were located in the vineyards, which are a consequence of the century-old practice of using copper-sulphate (Bordeaux mixture) and other copper-containing fungicides to control vine downy mildew [37].

Concentrations of Pb above the MAC were recorded in 28.5% of the samples, except one sample that registered an extremely high concentration of this element of 215.45 mg·kg^{-1}, and the position of the sample was from an area 10 m from the road.

Concentrations of Hg above the MAC were recorded in 0.75% of samples in a zone of 10-50 m from traffic lanes.

It can be concluded that in addition of anthropogenic pollution (excessive use of plant protection products and fertilizers), as well as the impact of air pollution from motor vehicles, in the Morava Valley geochemical pollution dominates. 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, 26 mg·kg^{-1} for Ni, and 18 to 23 mg·kg^{-1} for Pb [38]. Namely, Ni was found in increased concentrations in the ultrabasic rocks that have formed the soil.

The origin of increased concentrations of Pb also are linked with ultrabasic rocks, but the causes of pollution should also be linked to anthropogenic influence.

Plant Chemical Composition

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

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 [39, 40].

It is important in which part of the plant the elements are collected. It is well known that Cu is more present in the root than in the stem, and Pb also has a predominant presence in the root, while in the stem are low concentrations.

Table 2 presents average critical and toxic concentrations of heavy metals in plats according to Kloke et al. [41] and Kastori et al. [42].

Table 3 presents the percentage share of total number of samples, where Cu, Ni, Pb, and Hg were determined 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.

Fig. 2 presents the toxic concentrations of Cu. The increased concentrations of this element were present in locations of vineyards and cultivated soil, where it was noted that the values of this element in the soil are above the MAC, probably as a result of excessive use of pesticides.

Fig. 3 shows the toxic concentrations of Ni.

Fig. 4 presents the distribution of collected samples of plant material in which toxic levels of Pb were determined.

Locations on which the plant material with determined toxic level of Cu was collected

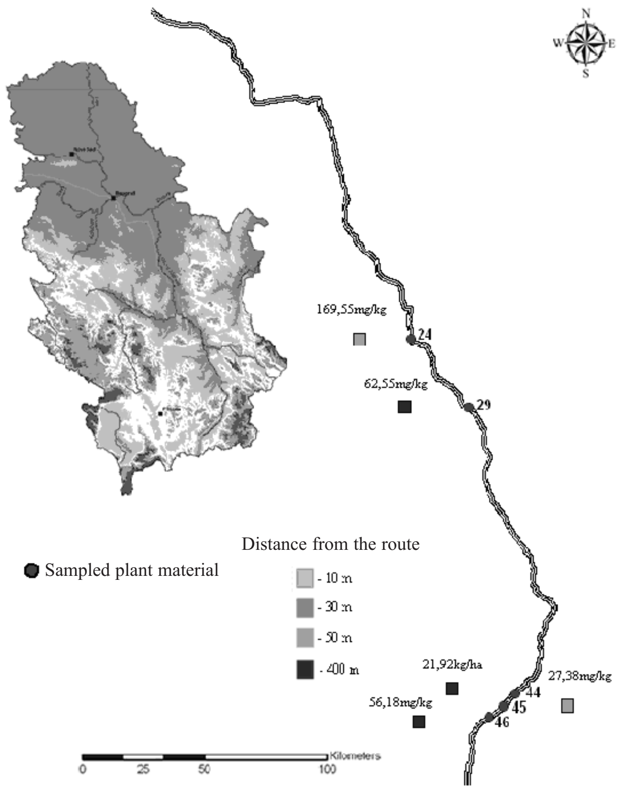

Fig. 2. Locations of plant material in which the toxic concentration of Cu was determined.

Table 3. Percentage share of total number of samples in which Cu, Ni, Pb, and Hg were determined in the aboveground plant material tested depending on distance from the road lane.

Limit values		Distance 10 m	Distance 30 m	Distance 50 m	Distance 400 m	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%
Ni (mg·kg^{-1})						
<10	Desirable	96.97%	94.00%	94.00%	93.68%	94.67%
10-20	Critical	0.00%	3.00%	4.00%	4.21%	2.79%
>20	Toxic	3.03%	3.00%	2.00%	2.11%	2.54%
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%

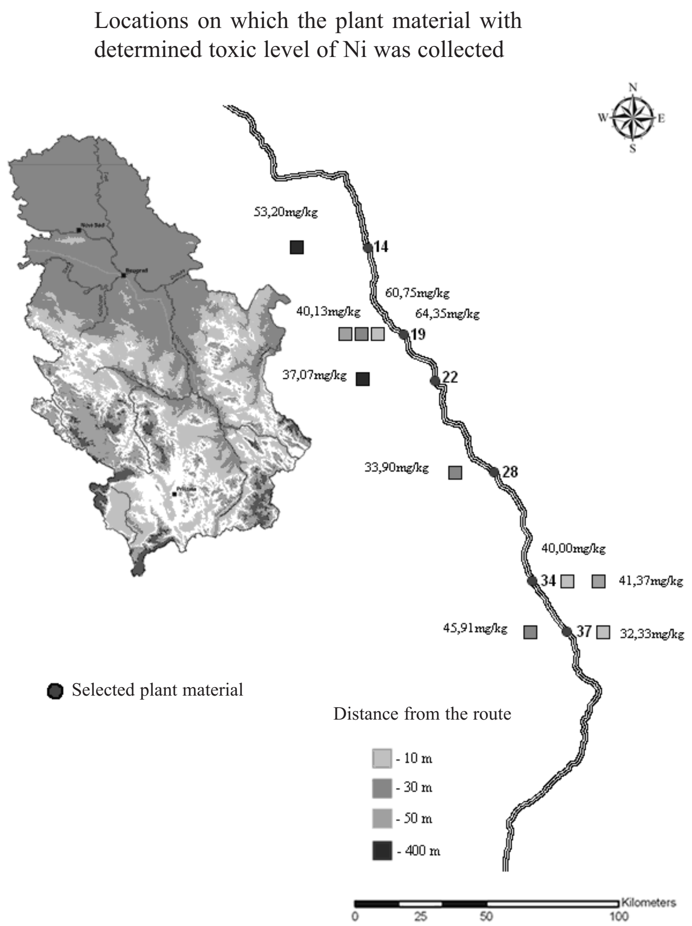

Fig. 3. Locations of plant material in which the toxic concentration of Ni was determined.

Locations of plant material with determined toxic levels of Pb

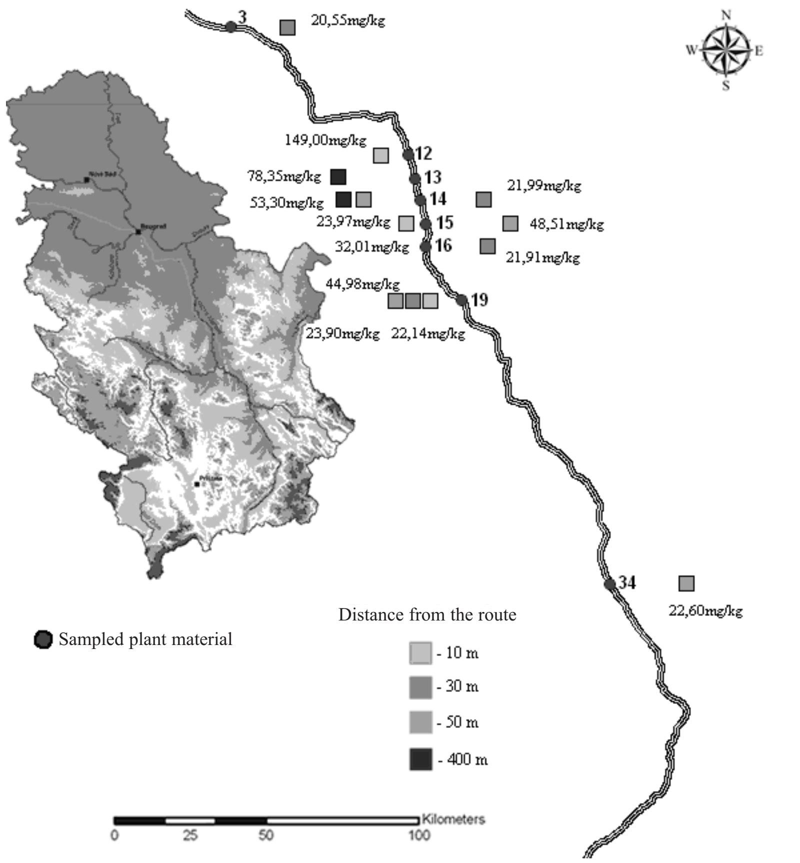

Fig. 4. Locations of plant material in which toxic concentrations of Pb were determined.

It is evident that the points where the samples of plant material with increased concentrations of this element are matched with the locations where the total concentration of Pb was above level of MAC. In the zone of examination up to 50 m from the road lane, the number of samples where the concentrations of Pb in plants were toxic is constant.

Based on the performed examinations, it was determined that in all samples concentration of Hg were in values that correspond to desirable limits. There were no samples with critical or toxic values.

Conclusion

Analysis of obtained results drive us to the conclusion that besides anthropogenic pollution, which is reflected due to excessive use of plant protection products and fertilizers, the impact of air pollution from motor vehicles in certain sections of the examined area, including the available literary sources and the dominant enrichment of examined elements, comes from geochemical composition of parent material. The total concentrations of Pb above the MAC was found in 5.28%, Cu in 0.25%, Ni in 8.3%, and Hg in 0.75% of the studied samples. In the examined plant material we did not detect toxic concentrations of Hg. Toxic Pb concentration above the MAC value was recorded in 3.3% of plant samples in zones at a distance of 10 m to 50 m from the road. Toxic Ni concentrations above the MAC value were recorded in 2.54% of plant samples. Concentrations of Ni in plant material corresponds with geochemical compositions of parent material. Cu in the plant material is present in toxic concentrations in 1.27% samples, of which two were from the vineyards at a distance of 50m from the route, and three samples from the zone at a distance of 400 m.

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