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Review paper

TYPES AND AMOUNTS OF METALS PRESENT IN THE RAILWAY BODY

**Jelena Dimitrijević[1], Zoran Bonić[2], Elefterija Zlatanović[3],
Dragan M. Djordjević[4], Dragan Milićević[5], Zlatko Zafirovski[6]**

Abstract:

Heavy metals, polycyclic aromatic hydrocarbons and pesticides were frequently identified as compounds hazardous to human life and health when soil testing results in the area of railway lines were investigated. Our own investigations have revealed the existence of heavy metals that are harmful to human life and health, as well as the presence of other metals. This article has a particular emphasis on these other metals. The majority of registered metals are not included by the Republic of Serbia's Regulation on maximum allowable values of metals in soil. A relatively small number of metals, included by this Regulation, did not exceed the maximum allowable values but their presence was confirmed. In order to gain a complete understanding of the metals released into the soil as a result of railway operations and their possible sources, these data must be evaluated.

Key words: *Railway, Railway Pollution, Metals, Environment.*

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[1] PhD, Teaching Assistant, University of Niš, Faculty of Civil Engineering and Architecture of Niš, Aleksandra Medvedeva 14, 18000 Niš, Serbia, jelena.dimitrijevic@gaf.ni.ac.rs, ORCID (0009-0006-7158-0737)

[2] PhD, Full Professor, University of Niš, Faculty of Civil Engineering and Architecture of Niš, Aleksandra Medvedeva 14, 18000 Niš, Serbia, zoran.bonic@gaf.ni.ac.rs, ORCID (0000-0002-7452-6756)

[3] PhD, Associate Professor, University of Niš, Faculty of Civil Engineering and Architecture of Niš, Aleksandra Medvedeva 14, 18000 Niš, Serbia, elefterija.zlatanovic@gaf.ni.ac.rs, ORCID (0000-0001-6783-1325)

[4] PhD, Full Professor, University of Niš, Faculty of Sciences and Mathematics, Višegradska 33, 18000 Niš, Serbia, dragan.djordjevic1@pmf.edu.rs, ORCID (0000-0001-9797-663X)

[5] PhD, Full Professor, University of Niš, Faculty of Civil Engineering and Architecture of Niš, Aleksandra Medvedeva 14, 18000 Niš, Serbia, dragan.milicevic@gaf.ni.ac.rs, ORCID (0000-0003-0617-2682)

[6] PhD, Associate Professor, University "Ss. Cyril and Methodius" of Skopje, Faculty of Civil Engineering, Blvd. Partizanski odredi 24, 1000 Skopje, North Macedonia, zafirovski@gf.ukim.edu.mk, ORCID (0000-0003-2099-0710)

1. INTRODUCTION

Contrary to previous beliefs that rail is an environmentally friendly mode of transport, it is now possible to argue that this is not entirely true when considering the pollution that railway traffic causes to the surrounding environment [1–4]. Serious environmental contaminants from the influence of railway traffic include heavy metals, polycyclic aromatic hydrocarbons and herbicides, according to a number of studies that highlighted the findings of soil tests conducted both on the railway body and in the surrounding area [1]. A significant number of those studies emphasize heavy metals, since they have detrimental effects on human health.

The main reason heavy metals are harmful is that they can accumulate into the human body through the food chain through contaminated food or water.

The primary objective of this research was to determine the presence and quantity of lead in the railway track. Due to the peculiarity of the formation source and the mode of migration, lead is one of the most frequently registered metals that exceeded the allowed amounts. According to current studies, this metal is the most commonly registered metal in the soil surrounding railways, in addition to cadmium [5–10].

Interest in lead arises as a result of long-term research into the impact of lead on human health. A single exposure to lead has been proved to have a wide range of harmful consequences on human health like fatigue, dizziness, arthralgia, impaired memory, nausea, sleep disorders, dermatological disorders, coxarthrosis, balance disorders, paresthesia, abdominal pain and others [11].

Most studies concerning environmental contamination caused by railway traffic indicated the permitted amounts of heavy metals in the soil, without paying special attention to metals that did not exceed the permitted values, but were recorded in the soil. Since the method of heavy metal migration through the soil has not been completely clarified, it is hard to identify the actual released quantities, i.e., what amounts entered the soil and were transported further, perhaps into ground water.

Based on the own research [12], the most important conclusions regarding the concentration of lead within the railway body were highlighted and a comparison was made with the results of other researchers, when it comes to this metal.

In addition, another goal of the present study was to list all registered metals for which the relevant legislation have established a regulated permissible values.

2. SOIL SAMPLING AND EXAMINATION TECHNIQUES

Soil sampling, for the purpose of examining the presence of heavy metals in the railway body, was carried out on two cross-sections (cross-section 1 and cross-section 2) in the embankment on the Belotinac–Medjurovo section of the Serbian railway line Niš–Preševo–border with the Republic of North Macedonia, from km 253+072.00 to km 253+283.00, which was in the reconstruction stage and which enabled the implementation of these tests.

Initially, sampling was carried out in top subgrade layer on characteristic positions: in the track axis (samples: 1’ for cross-section 1; 1’’ for cross-section 2) and at the positions on the feet of the ballast (samples: 3’ and 4’ for cross-section 1; 3’’ and 4’’ for cross-section 2). In addition, soil was sampled in the drainage channels on the both sides of the embankment (samples: 7’ and 8’ for cross-section 1; 7’’ and 8’’ for cross-section 2).

In order to determine the degree of infiltration of heavy metals into the soil, at a depth of 1.3 m, the soil was sampled at the projection of the sampling point on the substructure itself (axis (samples: 2' for cross-section 1; 2'' for cross-section 2) and feet of the ballast (samples: 5' and 6' for cross-section 1; 5'' and 6'' for cross-section 2)),

Soil samples were examined using X-ray fluorescence (XRF) spectrometry and optical emission spectrometry with induced coupled plasma (ICP-OES). The concentration of heavy metals in the samples in its original form was recorded using the XRF method. Using the ICP-OES technique, the samples were treated with water and hydrochloric acid for testing, and there were certain protocols involved in sample preparation.

The results of both methods were analyzed according to the maximum limited values of polluting, harmful and hazardous substances in soil prescribed by the Regulation of the Republic of Serbia (RS Regulation) [13] and according to the maximum values recommended by the EU Directive in the countries of the European Union [14]. The values prescribed by the EU Directive represent a recommendation for the range of permissible values of cadmium, chromium, copper, nickel, lead, zinc and mercury. EU Directive is not literally obligatory, since each of the EU member states can make corrections, most often in accordance with the pH value of the observed soil of a country or a specific area. Concentrations of metals not covered by the EU Directive were considered according to the RS Regulation. Maximum allowable concentrations (MAC) of polluting, harmful and dangerous metals in soil according to the RS Regulation and the recommended maximum values of individual heavy metals according to the EU Directive are presented in Table 1.

Table 1. Maximum allowable concentration of heavy metals in soil

Metal (symbol)	MAC* (ppm)	EU Directive** (ppm)
Cadmium (Cd)	0.8	1.0–3.0
Chromium (Cr)	100	100
Copper (Cu)	36	50–140
Nickel (Ni)	35	30–75
Lead (Pb)	85	50–300
Zinc (Zn)	140	150–300
Mercury (Hg)	0.3	1.0–1.5
Arsenic (As)	29	-
Barium (Ba)	160	-
Cobalt (Co)	9.0	-
Molybdenum (Mo)	3.0	-
Antimony (Sb)	3.0	-
Beryllium (Be)	1.1	-
Selenium (Se)	0.7	-
Thorium (Th)	1.0	-
Vanadium (V)	42	-

* Concentrations allowed by the Regulation on the maximum concentrations of polluting, harmful and hazardous substances in soil in the Republic of Serbia [13]

**European Union Directive 86/278/EEC [14]

3. CONCENTRATIONS OF LEAD OBTAINED BY XRF AND ICP-OES TECHNIQUES

The registered amounts of lead (Pb), obtained by the XRF technique, exceeded the permitted value prescribed by the EU Directive in several samples. The highest exceeded values were recorded at the foot of the ballast (samples 3' and 4") and at the point of drainage channel within the cross-section 1 (sample 7’). According to the RS Regulation (MAC), the measured amounts of Pb in ppm units (ppm ±5%) were within the permitted value (Figure 1).

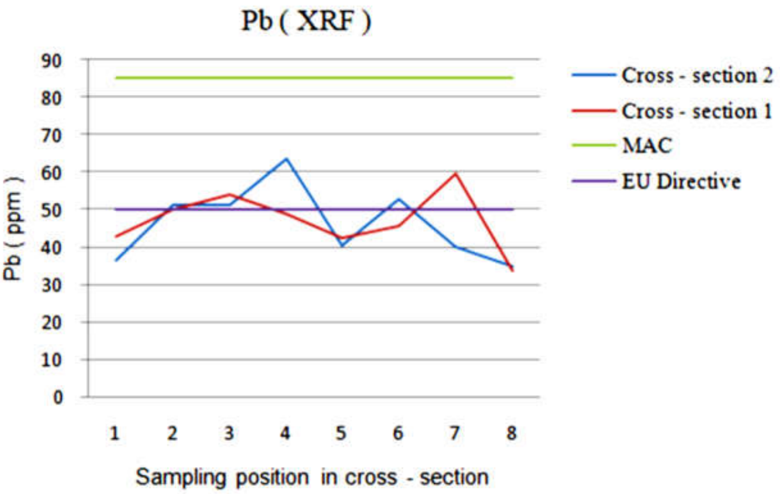

Figure 1. XRF-registered concentration of lead (Pb) on the cross-section 1 and cross-section 2 in comparison with the maximum allowable concentration (MAC) according to the RS Regulation and the maximum value recommended by the EU Directive

Using the ICP-OES technique for determining Pb concentration in ppm units (ppm ± 5%), on the other hand, no exceedance of the allowable value was found according to both the EU Directive and the MAC (Table 2). It was observed that the highest concentration of Pb in this case was in the samples from feet of the ballast (samples 4’ and 4”).

Table 2. ICP-OES-registered concentration of lead (Pb) on the cross-section 1 and cross-section 2 in comparison with the maximum allowable concentration (MAC) according to the RS Regulation and the maximum value recommended by the EU Directive

Pb			Pb		
MAC (ppm)		85	MAC (ppm)		85
EU Directive (ppm)		50	EU Directive (ppm)		50
Cross-section 1	1’	10.1	Cross-section 2	1”	15.0
	2’	20.2		2”	21.1
	3’	21.9		3”	12.1
	4’	28.9		4”	33.0
	5’	13.1		5”	19.6
	6’	23.9		6”	20.7
	7’	19.8		7”	20.5
	8’	11.7		8”	13.5

A review of the available literature including soil testing on the railway track and surrounding environment, as well as other track elements, has established that, in addition to cadmium, lead stood out as one of the most examined metals.

A number of studies have confirmed that Pb concentrations increase with distance from the track, indicating lead origin from exhaust gases [5–10].

Significant number of researchers also confirmed that the concentration of Pb did not decrease at a distance of 50 m from the track. This characteristic distinguishes lead from other heavy metals, due to the manner in which it is emitted into the environment. The region of lead dispersion into the environment is slightly narrower near the cut, suggesting that lead emission through the air is the most likely mode of migration [9].

According to the results of the present research, while screening with the XRF technique, the allowable levels for lead were exceeded, but when analyzing with the ICP-OES technique, the lead values were below the recommended ranges. Lower values of Pb obtained with the ICP-OES spectrometer can be explained by the fact that the soil sample was diluted with a moderate solution (deionized water - HCl) rather than concentrated hydrochloric acid. The solution prepared only with hydrochloric acid would result in a larger concentration of Pb.

Studies that included a wider area next to the railway track led to conclusion that the registered amounts of lead could be exceeded multiple times with the distance from the railway body. In this regard, it is very important that even when the measured quantities do not reach the permissible values, it is necessary to consider the known facts related to the behavior of the metal itself and the ways of emission of the observed metal into the environment.

4. CONCETRATIONS OF OTHER METALS OBTAINED BY XRF AND ICP-OES TECHNIQUES

Another part of this work was a special analysis of metals that are covered by the relevant legislation regarding the permitted concentration in the soil, but according to these criteria they did not exceed the permitted values.

As part of the own research [15], concerning the examination of the presence of heavy metals in the railway body, the results regarding heavy metals that exceeded the permissible values according to the MAC and the EU Directive were already highlighted. There was no discussion concerning metals, for which limited content in soil is defined, but they did not exceed these limits.

According to Table 3 and examination carried out by the XRF technique, such metals were arsenic (As), selenium (Se), molybdenum (Mo) and mercury (Hg). In the case of determining the presence of heavy metals in the soil using the ICP-OES technique, these metals were again arsenic (As), as well as chromium (Cr), vanadium (V) and barium (Ba) (Table 4).The reason that the values obtained by the XRF technique are higher than those obtained by the ICP-OES method is identical to the determination of Pb levels and is related to the solution.

Comparing the measured values at the surface and at depths of 1.3 m, significant metal infiltration was demonstrated into the railway body regardless of the measurement technique used. The concentration of several metals was found to be higher at a depth of 1.3 meters (samples: 2’, 5’ and 6’ for cross-section 1; 2’’, 5’’ and 6’’ for cross-section 2) in comparison with the values recorded in the surface layers (samples: 1’, 3’, 4’, 7’ and 8’ for cross-section 1; 1’’, 3’’, 4’’, 7’’ and 8’’ for cross-section 2). In the case of the XRF technique, this behavior was observed for As (the samples 2’, 6’ and 2’’ compared to the samples 1’, 4’ and 1’’, respectively) and Se (the sample 2'' compared to the sample 1''). According to the ICP-OES technique results, this phenomenon was identified in the cases of As (the samples 2', 6' and 2'' compared to the samples 1', 4' and 1'', respectively), Cr (the sample 5'' compared to the sample 3''), V (the samples 2', 6', 2'' and 5'' compared to the samples 1', 4', 1'' and 3'', respectively) and Ba (the sample 6' compared to the sample 4').

Table 3. Metal quantities determined by XRF in ppm units (ppm ± 5%)

Metal		As	Se	Mo	Hg
MAC (ppm)		29	0,7	3	0,3
EU Directive (ppm)		-	-	-	1
Cross-section 1	1'	16.0	0.3	0.8	0.1
	2'	17.3	0.3	0.8	0.1
	3'	18.2	0.3	0.9	0.1
	4'	16.9	0.2	0.7	0.1
	5'	15.6	0.3	0.9	0.1
	6'	18.5	0.1	0.4	0.1
	7'	20.2	0.3	0.9	0.1
	8'	13.1	0.1	0.9	0.1
Cross-section 2	1''	14.2	0.2	0.8	0.1
	2''	17.6	0.3	0.8	0.1
	3''	19.0	0.3	0.9	0.1
	4''	21.9	0.2	0.8	0.1
	5''	14.2	0.3	0.8	0.1
	6''	17.8	0.2	0.8	0.1
	7''	13.6	0.2	0.7	0.1
	8''	13.5	0.1	0.7	0.1

Table 4. Metal quantities determined by ICP-OES in ppm units (ppm ± 5%)

Metal		As	Cr	V	Ba
MAC (ppm)		29	100	42	160
EU Directive (ppm)		-	100	-	-
Cross-section 1	1'	5.2	30.2	32.3	94.1
	2'	5.5	28.5	33.1	82.4
	3'	6.6	29.2	29.8	88.8
	4'	6.7	25.5	27.2	66.1
	5'	4.8	24.7	28.3	78.9
	6'	7.2	24.0	30.2	82.5
	7'	7.1	29.1	32.0	91.5
	8'	4.5	25.6	25.7	75.2
Cross-section 2	1''	5.3	33.0	36.7	106.6
	2''	5.6	32.9	37.8	65.3
	3''	6.7	29.8	31.0	85.4
	4''	6.9	30.4	34.3	96.7
	5''	4.7	30.7	34.7	101.3
	6''	5.7	29.1	33.7	95.9
	7''	6.7	30.1	33.3	89.2
	8''	5.5	32.4	33.7	96.8

5. CONCLUSION

According to the results of the previous own research on the concentration of heavy metals in the railway body, an analysis of the presence and concentration of lead was performed in the present study, as well as an analysis of the amount of metals that did not exceed the permitted values prescribed by the corresponding current regulations.

The concentration of lead obtained by the XRF technique exceeded the permitted value prescribed by the EU Directive at the sample points within the feet of the ballast and the drainage channels. According to the RS Regulation, the measured amount of lead was within the permitted value. In the case of results obtained by the ICP-OES technique, there were no exceedances of the permitted values for lead with regard to both regulations. It is feasible to anticipate much higher levels of the tested metals, which would beyond the allowed limits, if the solution was prepared only with HCl. In this case, the maximum concentration of lead was registered in the samples from the feet of the ballast.

The values determined in this study as acceptable and not exceeding the permitted values should be interpreted with care, as numerous authors who have examined the concentration of lead in the area around the railway have demonstrated that the concentration of lead increases with distance from the railway track.

Additionally, while developing environmental protection measures against the adverse effects of railway traffic, significant consideration must be given to metals for which there is a legally controlled permissible limit, although it has not been exceeded. The extent of infiltration of these metals into the soil clearly demonstrated their intense migration into the subsurface, and further, into the surrounding area.

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