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CHEMICAL POLLUTANTS IN SOIL IN VRNJAČKA BANJA

Svetlana K. Belošević[1], Emin Memović[1], Saša Jovanović[1], Julijana Lekić[1], Jovana S. Belošević[2]
[1]University of Priština in Kosovska Mitrovica, Faculty of Technical Sciences, Kosovska Mitrovica, Serbia
e-mail: svetlana.belosevic@pr.ac.rs; emin.memovic@pr.ac.rs; sasa.m.jovanovic@pr.ac.rs; julijana.lekic@pr.ac.rs
[2]University of Belgrade, Faculty of Pharmacy, Belgrade, Serbia
e-mail: jovanabelosevic2@gmail.com

Abstract: This report presents a comprehensive analysis of soil chemical pollutants in the municipality of Vrnjačka Banja, Serbia, based on a recent soil quality report. The primary objective was to characterize the geochemical composition of soil from various land-use types, including agricultural, recreational, roadside, and a site adjacent to a landfill. The study method involved the analysis of five soil samples for a suite of parameters, including heavy metals, organic matter content, and physical properties. The measured concentrations were systematically compared against national Serbian regulations and recommendations for future actions were given.
Key words: soil, chemical pollutants, environment

INTRODUCTION

Global context of soil pollution

Soil is a finite and indispensable resource that forms the foundation of terrestrial ecosystems, providing a multitude of vital functions and ecosystem services. It is the primary medium for food and biomass production, a critical component of the water cycle responsible for filtration and purification, and a significant reservoir for carbon and nitrogen. [1] Globally, however, this essential resource is under increasing threat from a wide range of degradation processes, including erosion, loss of organic matter, compaction, and, most critically, pollution. Soil contamination, stemming from both point source and diffuse pollution, represents a major challenge to human health, food security, and environmental stability. Anthropogenic activities such as industrial production, intensive agriculture, transportation, and waste disposal introduce a diverse array of chemical pollutants into the soil matrix. These contaminants, which include heavy metals and persistent organic pollutants, can compromise soil fertility, enter the food chain, and leach into groundwater, posing long-term risks to both human and ecological systems. Addressing this complex issue requires a holistic and multi-faceted approach, encompassing comprehensive monitoring, robust regulatory frameworks, and targeted remediation strategies.

The study area: Vrnjačka Banja

Vrnjačka Banja is a health resort located in the central part of the Republic of Serbia, situated at 43° 37' North latitude and 20° 54' East longitude. The town's unique geographical setting lies partly on the gentle slopes of Mount Goč and partly within the valleys of the Lipovačka and Vrnjačka rivers, which flow towards the Zapadna Morava River. The region's temperate continental climate and abundant thermal-mineral springs have established it as one of Serbia's most renowned and popular spa towns. However, Vrnjačka Banja is also a modern municipality with diverse land-use patterns, including agricultural areas, recreational zones, major roadways, and waste disposal sites.

Research rationale and objectives

The aim of this study is to provide a comprehensive analysis of soil quality in the Vrnjačka Banja municipality by evaluating the concentration of various chemical pollutants.

Pollutants of concern and their environmental fate

The analysis of soil quality in this study focuses on two primary categories of chemical pollutants: heavy metals and organic compounds. Heavy metals, such as copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni), cobalt (Co), and cadmium (Cd), are naturally occurring elements that become environmental contaminants when their concentrations are elevated by human activities. Common anthropogenic sources include industrial emissions, vehicle exhaust (historically from leaded gasoline), and agricultural inputs such as fertilizers and animal manure, which can contain high concentrations of Cu and Zn. Once deposited, the environmental fate and bioavailability of these metals are strongly influenced by soil characteristics, particularly pH, organic matter content, and clay percentage. Generally, a higher pH and increased organic and clay content promote the sorption of heavy metals, reducing their mobility and potential for leaching or plant uptake.

Organic pollutants, specifically Polycyclic Aromatic Hydrocarbons (PAHs) and mineral oil hydrocarbons, are also of significant concern. PAHs are a group of chemical compounds formed during the incomplete combustion of organic materials such as coal, oil, gas, wood, and garbage. Sources include industrial emissions, vehicle exhaust, and waste incineration. [2] Similarly, mineral oil hydrocarbons are found in crude oil and refined petroleum products, and their presence in soil is typically the result of accidental spills from industries, transportation, or unmanaged waste. These compounds are highly hydrophobic, meaning they have a strong affinity for soil organic matter. This characteristic causes them to bind tightly to soil particles, limiting their mobility but also contributing to their long-term persistence in the environment. The degradation of these compounds is primarily mediated by microbial metabolism, a process that can be supported by phytoremediation techniques.

Geogenic sources of heavy metals in Serbia

A critical factor in the interpretation of soil heavy metal concentrations in Serbia is the country's unique geological background. Numerous studies have established that certain regions, particularly in central and western Serbia, are underlain by ultramafic rocks, commonly referred to as serpentinites. These parent rocks are naturally enriched with specific trace elements, including nickel (Ni), chromium (Cr), and cobalt (Co). [3]
The presence of these geogenic sources means that background concentrations of Ni and Cr can be significantly higher in these soils compared to typical values found in other parts of Europe.

Serbian regulatory frameworks

The Republic of Serbia has established a legal framework for environmental protection, with a specific focus on soil quality. This regulation defines Maximum Allowed Quantities (MDK) for a list of hazardous and harmful substances. [4,5]
The Serbian legal framework also includes a provision for systematic soil quality monitoring and emphasizes the "polluter pays" principle, placing the responsibility for remediation on the party that caused the pollution.

MATERIAL AND METHODS

Sample locations

Five soil samples were collected from different land-use types within the Vrnjačka Banja municipality. Each sample was taken from a depth of 0-30 cm, representing the topsoil layer most susceptible to contamination. The sampling sites were chosen to represent a cross-section of land uses in the region. The locations, along with their geographical coordinates and land-use classifications, are as follows:

- Sample ID A: Agricultural land located at 43° 39' 53.6" N, 20° 54' 53" E.
- Sample ID B: Recreational zones 1 located at 43° 37' 03.7" N, 20° 53' 39.2" E.
- Sample ID C: Main traffic road located at 43° 38' 17.2" N, 20° 55' 01.3" E.
- Sample ID D: Recreational zone 2 located at 43° 36' 36.7" N, 20° 53' 38.3" E.
- Sample ID E: Near a landfill located at 43° 40' 39.5" N, 20° 51' 29.1" E.

Techniques of UV/VIS spectrophotometry, AAS-F, AAS-ES, direct analysis technique Hg (DMA), ICP-MS, ICP-OES were applied for the analysis of sediment samples.

Analytical parameters

The soil samples were analyzed for a comprehensive suite of physical, chemical, and pollutant parameters. These parameters can be grouped into the following categories:

- **Physical/Chemical Properties:** Organic matter content, Coarse sand, Silt, Moisture content, pH in KCl and pH in H_2O.
- **Heavy Metals and Other Elements:** Copper (Cu), Zink (Zn), Cobalt (Co), Lead (Pb), Cadmium (Cd), Nickel (Ni), Chromium (Cr), Arsenic (As), Mercury (Hg), Antimony (Sb), Barium (Ba), and Beryllium (Be).
- **Organic Pollutants:** Toluene, Xylene, Ethylbenzene, Styrene, Anthracene, Benzene, total Polychlorinated Biphenyls (PCBs), and total Polycyclic Aromatic Hydrocarbons (PAHs), along with the sum of C10-C40 mineral oil hydrocarbons.

RESULTS AND DISCUSSION

The analysis of the five soil samples from Vrnjačka Banja provides a detailed profile of their physical, chemical, and pollutant characteristics. The results are presented in a series of tables to facilitate a direct comparison and assessment.

Table 1. *Physical and Chemical Properties of Vrnjačka Banja Soils*

Sample ID	Location type	Organic matter (%)	Coarse sand (%)	Silt (%)	Water content (%)	pH (KCl)	pH (H_2O)
A	Agricultural land	18.04	6.8	84.9	2.99	6.01	6.9
B	Recreational zones 1	7.92	22.4	69.4	2.42	6.97	7.55
C	Main traffic road	5.03	24.3	74.4	1.37	7.11	7.66
D	Recreational zones 2	6.59	40.7	48.2	1.97	7.19	7.86
E	Near a landfill	5.99	34.0	62.8	3.15	7.55	8.07

As shown in Table 1, the sampled soils exhibit a range of physical and chemical properties. The agricultural land sample is distinguished by a significantly higher organic matter content (18.04%) and a more acidic pH (pH(KCl)=6.01, pH(H_2O)=6.9) compared to the other sites. In contrast, the other four locations have lower organic matter content (5.03% to 7.92%) and are more neutral to alkaline (pH(KCl)=6.97−7.55, pH(H_2O)=7.55−8.07). The texture of the soil varies, with the agricultural and recreational sites having a high silt content, while the second recreational site has a higher coarse sand percentage. [6]

Table 2. *Concentration of Heavy Metals in Vrnjačka Banja Soils*

Pollutant (mg/kg dry matter)	Agricultural land	Recreational zones 1	Main traffic road	Recreational zones 2	Near a landfill	Serbian MDK
Cu	31.86	23.4	23.25	19.66	31.39	100
Zn	87.73	86.0	89.25	75.0	130.05	300
Co	24.32	26.7	19.25	20.72	23.08	N/A
Pb	26.82	37.71	49.0	40.86	84.61	100
Cd	<0.8	<0.8	<0.8	<0.8	<0.8	3
Ni	239.32	304.21	182.5	267.55	296.39	50
Cr	174.09	368.28	224.5	266.83	194.23	100
As	11.1	14.23	14.07	12.25	22.97	25
Hg	<0.25	<0.25	<0.25	<0.25	0.41	2
Sb	<0.5	<0.5	<0.5	<0.5	<0.5	N/A
Ba	43.73	58.2	58.95	13.22	49.71	N/A
Be	<0.5	<0.5	<0.5	<0.5	<0.5	N/A

The results in Table 2 highlight a key finding: a significant discrepancy between the measured concentrations of nickel (Ni) and chromium (Cr) and the Serbian regulatory limits. All five samples show Ni concentrations ranging from 182.5 mg/kg to 304.21 mg/kg, and Cr concentrations from 174.09 mg/kg to 368.28 mg/kg. These values are consistently 3 to 6 times higher than the Serbian MDKs of 50 mg/kg for Ni and 100 mg/kg for Cr. Conversely, other heavy metals show concentrations well below their respective MDKs. For instance, lead (Pb) concentrations range from 26.82 mg/kg to 84.61 mg/kg, remaining below the 100 mg/kg limit. Zinc (Zn), Copper (Cu), and Arsenic (As) are also well within their permissible limits, with the highest concentration for all three found at the agricultural and landfill-adjacent sites. Cadmium (Cd) and mercury (Hg) are below detection limits for most samples, except for a trace amount of Hg at the landfill-adjacent site. [6]

Table 3. *Concentration of Organic Pollutants in Vrnjačka Banja Soils*

Pollutant	Agricultural land	Recreational zones 1	Main traffic road	Recreational zones 2	Near a landfill
Toluene (mg/kg)	<0.002	<0.002	<0.002	<0.002	<0.002

Xylene (mg/kg)	<0.002	<0.002	<0.002	<0.002	<0.002
Styrene (mg/kg)	<0.002	<0.002	<0.002	<0.002	<0.002
Total PCB (mg/kg^2)	<0.01	<0.01	<0.01	<0.01	<0.01
Ethylbenzene (mg/kg)	<0.002	<0.002	<0.002	<0.002	<0.002
Anthracene (µg/kg)	<0.03	<0.03	<0.03	<0.03	<0.03
Benzene (µg/kg)	<0.03	<0.03	<0.03	<0.03	<0.03
Total PAH (µg/kg)	<0.03	<0.03	<0.03	<0.03	0.164
Total mineral oils (C10-C40) (mg/kg)	<1	<1	<1	<1	254

Table 3 reveals a distinct pattern for organic pollutants. For the majority of the samples (agricultural, recreational, and traffic-exposed), most organic compounds, including various PAHs, PCBs, and mineral oils, were found to be below the detection limits. This indicates that diffuse, widespread organic contamination is not a significant issue in the sampled areas. However, the sample taken near the landfill presents a clear exception. This site shows a total PAH concentration of 0.164 µg/kg and, more notably, a significant level of C10-C40 mineral oils at 254 mg/kg. This finding is consistent with the land-use classification and suggests a direct, localized source of contamination. [6]

Assessment of Soil Quality: A Dual Narrative

The analytical results from the Vrnjačka Banja soil samples paint a complex picture of soil quality, revealing a composition influenced by both the region's unique geological makeup and specific human activities. On a general level, the soil appears to be in good condition, with the most common contaminants, such as lead, cadmium, and various organic compounds, present at concentrations well below national regulatory limits or even below detection. The samples from the traffic road and recreational zones, for example, show no evidence of significant contamination from vehicle exhaust or other urban sources, such as Pb, PAHs, and mineral oils are all at very low or non-detectable levels. This is particularly noteworthy for the Main traffic road site, as traffic has historically been a major source of lead pollution from the use of leaded gasoline. The current low concentrations may reflect the effectiveness of past environmental policies and a low volume of heavy vehicle traffic on that specific roadway, contrasting with findings in more densely urbanized areas like Belgrade where Pb levels near traffic arteries were found to be significantly higher. [7,8]

However, the most striking finding is the consistently high concentration of nickel (Ni) and chromium (Cr) across all five samples. As presented in Table 2, these values universally exceed the Serbian regulatory MDKs. A superficial analysis would classify these soils as polluted and in need of remediation. A deeper investigation, however, requires a critical evaluation of the underlying geology. Research on Serbian and Balkan geology confirms that the region contains significant areas of ultramafic (serpentine) parent rocks that are naturally rich in Ni, Cr, and Co. The observed levels of Ni (182.5-304.21 mg/kg) and Cr (174.09-368.28 mg/kg) in Vrnjačka Banja soils, while high in a regulatory sense, are well within the range expected for an area influenced by this geogenic background. This suggests that the measured concentrations are not the result of human-caused pollution but are, in fact, a natural characteristic of the local soil. [9,10]

This situation underscores the need for a more nuanced regulatory approach that distinguishes between natural geochemical anomalies and genuine anthropogenic contamination.

Analysis of Anthropogenic Pollutants

While the heavy metal profile is dominated by a geogenic signature, the analysis of organic pollutants reveals a clear and direct link to a specific anthropogenic activity. The four samples representing agricultural, recreational, and traffic-exposed land uses show virtually no detectable levels of PAHs or mineral oils. This indicates a general absence of widespread organic contamination in the Vrnjačka Banja area.

The sole exception is the sample from the location "Near landfill". This site exhibits a total PAH concentration of 0.164 µg/kg and a substantial concentration of C10-C40 mineral oils at 254 mg/kg. This finding is a strong example of point-source pollution. While the measured PAH concentration is relatively low compared to industrial "hot spots" in Europe, where levels can reach thousands of µg/kg, it is a definitive signature of localized human impact. [11]

The presence of other heavy metals at the landfill-adjacent site also merits consideration. The concentrations of Cu (31.39 mg/kg) and Zn (130.05 mg/kg) are the highest among all samples, although still well below the Serbian MDKs. This is consistent with the literature, which identifies industrial waste and municipal garbage as sources of these metals. Furthermore, the sample from the agricultural site shows the highest levels of Cu (31.86 mg/kg) and Zn (87.73 mg/kg), which is likely due to the application of fertilizers and animal manure in farming practices. [12,13]

This observation demonstrates how different land uses create distinct pollution signatures, with agriculture contributing to elevated levels of essential micronutrients like Cu and Zn, while waste disposal creates localized organic contamination. The findings confirm that even in a region celebrated for its natural qualities, localized human activity can create distinct and measurable environmental impacts.

CONCLUSION

Summary of Findings

The geochemical assessment of soil in Vrnjačka Banja reveals a complex environmental profile shaped by both natural and human influences. The study's central finding is the pervasive presence of nickel (Ni) and chromium (Cr) at concentrations that significantly exceed Serbian regulatory thresholds. This phenomenon is not attributed to pollution but is a natural, geogenic characteristic of the region's soils, likely stemming from underlying ultramafic rocks. All other major heavy metals, including lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn), are well below their respective regulatory limits, suggesting a low level of widespread contamination. However, a distinct anthropogenic signature was identified at the site adjacent to a landfill, where measurable levels of polycyclic aromatic hydrocarbons (PAHs) and a substantial concentration of mineral oil hydrocarbons were detected. This localized organic pollution provides a clear example of point-source contamination linked to human activity. In summary, the soil of Vrnjačka Banja presents a dual narrative: one of a natural, geochemically rich environment with naturally high levels of certain elements, and another of a contemporary landscape with localized, human-induced environmental impacts.

Recommendations for Future Action

Based on the findings of this report, the following recommendations are proposed to guide future policy, monitoring, and research in Vrnjačka Banja and similar regions of Serbia:

- **Review and Modernize Regulatory Frameworks:** A critical review of the Serbian soil quality standards, particularly the Maximum Allowed Quantities for nickel and chromium, is necessary. The current single-value thresholds do not account for natural geogenic background levels, leading to the misclassification of natural soils as contaminated.

- **Implement Systematic Soil Monitoring:** A comprehensive, long-term soil quality monitoring program should be established for the municipality of Vrnjačka Banja, focusing on high-risk land-use categories such as agricultural zones, main traffic routes, and, most importantly, waste disposal sites. This monitoring should track both heavy metals and organic pollutants to identify changes over time and confirm that pollution prevention measures are effective.
- **Prioritize Risk-Based Management and Remediation:** Given the confirmed point-source contamination at the landfill-adjacent site, immediate action should be taken to assess the risk posed by the detected PAHs and mineral oils.
- **Conduct Further Geochemical Research:** To fully understand the potential risks associated with naturally elevated heavy metal levels, further research is required. This should include speciation analysis of the Ni and Cr to determine their bioavailability and mobility in the soil. Furthermore, an expanded sampling program across the entire municipality would provide a more complete picture of the spatial distribution of contaminants and allow for the creation of a detailed geochemical map of the region. This research is crucial for a health resort like Vrnjačka Banja, where environmental quality is inextricably linked to its reputation and function as a therapeutic destination.

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