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SCIENTIFIC PAPER

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## CONCENTRATIONS OF Cu, Zn, Cd AND Pb IN URBAN SOILS IN PARKS AND GREEN AREAS OF BELGRADE, SERBIA

*Several metals in urban soils of Belgrade were extracted by two methods, which respectively give estimates of the available and 'quasi total' contents. Soil samples were collected from six parks and three green areas within the urban zone in November, 2003 and June, 2005 on the same sites. The concentrations of Cu, Pb and Zn at several sites exceeded the limits acceptable in residential areas established by national legislation. Comparison between the 2005 and 2003 data revealed an increase of the Cu and Zn contents and a decrease of the Pb content of the urban soils. The labile phase concentration, determined as the amount of metal extracted with HCl, was in the order Zn>Pb>Cu>Cd. Traffic seems to be one of the main sources of these metals, but the influence of other factors cannot be excluded.*

*Key words: Metals, Pollution, Urban soils, Belgrade.*

Metals, radionuclides, chloro-organic compounds and PAHs are the most common soil contaminants, mainly due to emissions of industrial plants, thermal power stations, and vehicular traffic and road infrastructures [1]. Metals remain present in the soil for many years after the removal of the pollution sources. Increased amounts of metals compared to the natural background level of soils in the examined areas [2-4] and increasing metal contents in soil with time [5] have been reported.

Soils in urban environments, particularly in parks or green areas near roads, have a direct influence on public health not related with the production of food. This is due to their frequent contact with humans and they are transferred, either as suspended dust or by direct contact [6, 7].

Most of the urban parks in Belgrade are built close to major roads or industrial areas, where they are subjected to many potential pollution sources, including vehicle exhaust and industrial emissions. The present study is the result of a preliminary sampling campaign, aimed at obtaining some knowledge on the distribution and contents of metals, and ascertaining whether some signs of pollution are likely to exist in selected green areas of public use in Belgrade. Cu, Zn, Cd and Pb were chosen for this study because they are good indicators of contamination in soils since they appear in gasoline, car components, oil lubricants and industrial and incinerator emissions.

The single 0.5 M HCl leach of urban media has been shown to be an effective and rapid approach for inorganic contaminant assessment [8]. With the goal of examining an overall labile (mobile) phase for the

examined elements, this method was also applied for the extraction of soil samples from Belgrade.

### MATERIALS AND METHODS

Soils from nine urban parks and green areas in Belgrade were sampled to reflect the different land use and traffic conditions. The location of the sampling points is given in Figure 1. The names of the public parks and green areas are also mentioned on the figure. The samples were taken in November, 2003 and June, 2005 at the same sites.

Composite samples were obtained by mixing sub-samples from three random points within about 1m<sup>2</sup> in each sampling site. At each sampling point, the top 10 cm layer of the soil profile was taken using a stainless steel trowel. Stones and foreign objects were removed by hand, and the samples were air-dried and gently crushed and sieved to 2 mm. Metals were extracted in triplicates by 0.5 M HCl [9] and by digestion with *aqua regia* [10]. The extracts were filtered and made to 50 ml with deionized water. The concentrations of Cu, Zn Cd and Pb were determined by AAS (Atomic Absorption Spectroscopy). The detection limit for metal analysis was 0.1 mg L<sup>-1</sup> for Pb, 0.05 mg L<sup>-1</sup> for Zn and Cu, and 0.01 mg L<sup>-1</sup> for Cd.

HCl has been used to assess anthropogenic metal signals in sediments [11], soils and road-deposited sediments [8]. During extraction the crystal lattice is minimally affected, which is an important aspect for environmental pollution studies, thus it is widely acknowledged that only the labile phases are key components in bioconcentration and biotoxicity. The *aqua regia* digestion procedure is considered to be adequate for analysing the total recoverable metals in soils [12]. The residual elements not released by *aqua regia* are mostly bound to silicate minerals, and are considered unimportant when estimating the mobility and behaviour of the elements [13,14]. The amount extracted by *aqua regia* is sometimes called the 'pseudo total content', and has been used to assess the risks of

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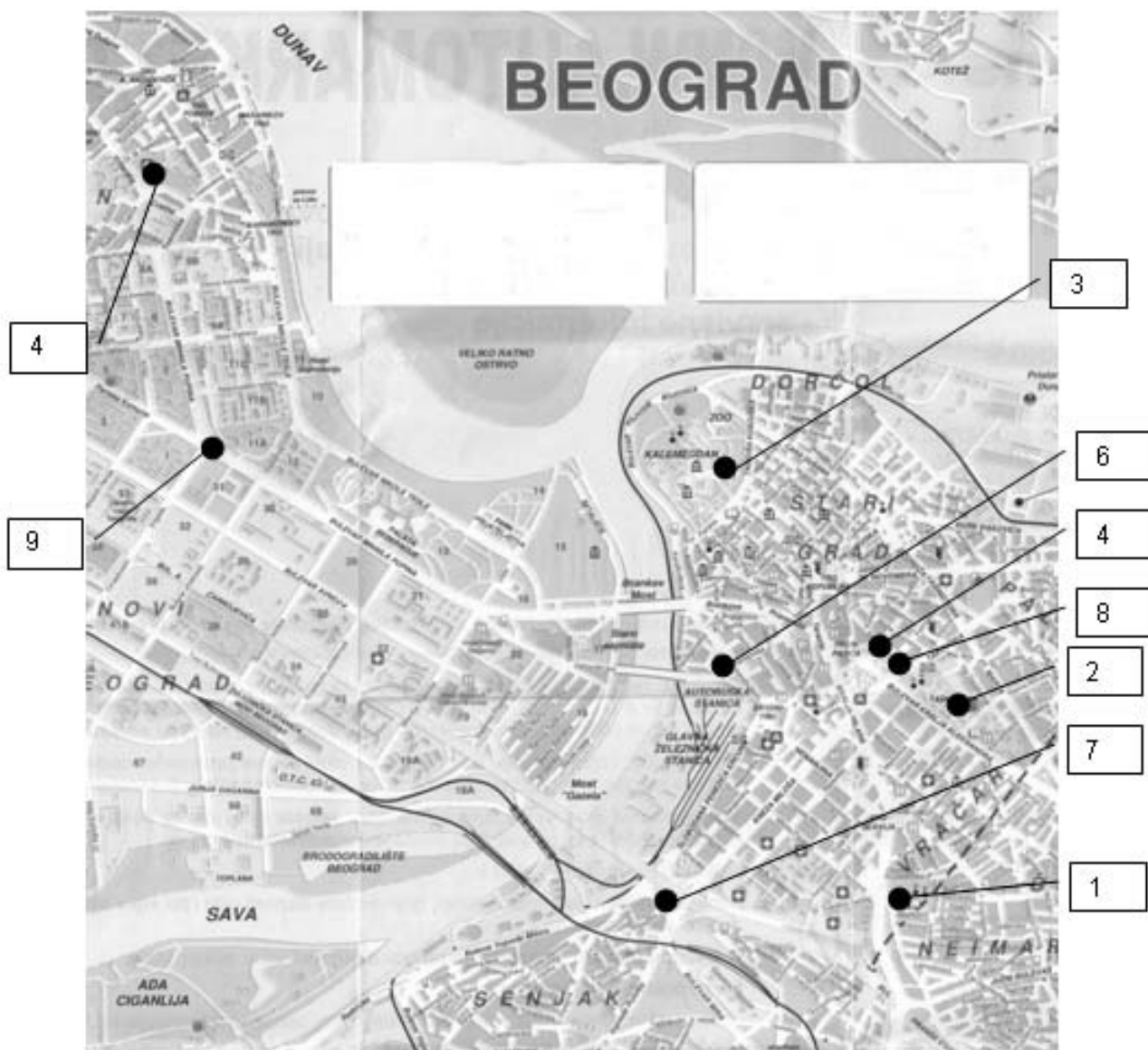


Figure 1. Location of the sampling sites  
 Parks: Karadjordje's park (1), Tašmajdan (2), Kalemegdan (3), Pioneer park (4), City park Zemun (5), Central bus station park (6)  
 Green areas: Mostar square (7); Parliament (8); New Belgrade community square (9)

direct intake of metals from soils by children and animals [15].

The organic matter content and pH of the aqueous water extract were determined for soil samples collected in June, 2005. The organic matter content was determined as the weight loss after heating at 500°C for 2 h; pH measurements were carried out in deionized water (100 ml), after stirring a 20 g the air-dried sample for one hour.

**RESULTS**

The values of the pH and organic matter content determined in the samples taken in June, 2005 are presented in Table 1.

Tabela 1. Organic matter determined by loss-on-ignition (O.M.) and pH

Sample	1	2	3	4	5	6	7	8	9
O.M.(%)	9.4	18.2	13.1	12.5	13.0	12.6	8.8	10.1	11.6
pH	7.0	5.0	6.8	7.5	7.1	6.3	7.0	7.6	6.3

The pH-H<sub>2</sub>O was generally neutral or subalkaline. Only one sample (No 2) from the central urban district had a pH value lower than 6.0. The range of organic matter in the investigated soil samples was 8.8–18.2%.

Table 2 summarizes the results for examined metals by both extracting solutions.

Table 2. Mean values and ranges for metal contents extractable by HCl and aqua regia ( $\text{mg kg}^{-1}$ )

Extractant	Metal	Sampling 2003		Sampling 2005	
		Mean	Range	Mean	Range
HCl	Cu	32.5	14.9–66.3	61	27.8–145
	Zn	86	4.5–174	147	43.2–504
	Cd		n.d.*	1.3	n.d.–2.5
	Pb	113	55.7–199	89.6	46.6–145
Aqua regia	Cu	53.3	28.7–99.4	95.7	50.7–214
	Zn	152	55.2–229	214	121–515
	Cd	1.3	n.d.–2.6	1.9	n.d.–3.3
	Pb	151	44.7–238	125	54.3–189

\*not detected

## DISCUSSION

The concentrations of Cu, Zn, Cd and Pb in urban soils of Belgrade have a wide range of values and have a marked spatial variability. Concerning the total soil content, it was found that the elements were arranged in the order  $\text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$  in the samples collected in the examined area.

The total soil Zn content ranged from 55.2 to 515  $\text{mg kg}^{-1}$ , and only two samples taken in 2005 from green areas (7 and 8; Fig. 2) exceeded the regulatory limit of 300  $\text{mg kg}^{-1}$  [16]. The total soil Pb content ranged between 44.7 and 238  $\text{mg kg}^{-1}$ ; 8 samples from 2003 and 6 samples taken in June 2005 exceeded the regulatory limit (100  $\text{mg kg}^{-1}$ ) [16]. The Pb content decreased between two sampling campaigns. This effect is probably caused by the high mobility of Pb in comparison with other metals and the utilization of unleaded fuel in the last few years. The total Cu content ranged from 28.7 to 214  $\text{mg kg}^{-1}$ . Approximately 83% of the analyzed soils contained from 6.2 to 100  $\text{mg kg}^{-1}$  total Cu, and only 3 samples, those from 2005, exceeded the maximum concentration (100  $\text{mg kg}^{-1}$ ) established by national legislation [16]. The total Cd content ranged between less than the LOD (limit of detection, 0.5  $\text{mg kg}^{-1}$ ) and 3.3  $\text{mg kg}^{-1}$ . Only soil sample No 6 (2005 campaign) was polluted by Cd, with a concentration in excess of the 3  $\text{mg kg}^{-1}$  limit set by national regulations [16].

Cadmium was detected in seven samples, those taken in 2005. The application of Cd-containing phosphate fertilizers may be an important source of Cd in urban park soils. Comparison between the 2005 data and those of 2003 revealed a decrease of the mean Pb content (17%) and an increase of the Cu, Zn and Cd contents of the urban soils. The Pb content decreased from 9% (sample 2–Tasmajdan) to 46% (sample 6–Central bus station park).

The Zinc content increased from 1% (sample 1–Karadjordje's park), to 245% (sample 8–Parliament),

Table 3. Target values and soil remediation intervention values for selected metals in soils from the Dutch Ministry of Housing, Spatial Planning and Environment [17]

	Zn	Cu	Pb	Cd
Target value ( $\text{mg kg}^{-1}$ )	140	36	85	0.8
Intervention value ( $\text{mg kg}^{-1}$ )	720	190	530	12

with a mean increase of 41%, due to the possible accumulation of Zn from garden fertilizing activities and traffic inputs. Presumably, the increases in the Zn content in urban soils can be related to a continuous input of the metal in the urban environment principally as a consequence of vehicle emissions and tyre and brake abrasion [4]. The Cu content increased from 14.7% (sample 3–Kalemegdan) to 193% (sample 4–Pioneer park), with a mean increase of 80%. Tyre and line abrasion processes in the rail and tram-ways may be responsible for the soil Cu pollution.

The possible pollution can also be evaluated according to Dutch guidelines [17], due to the fact that national legislation was established more than ten years ago. We chose to use the latest (2000) Dutch Ministry of Housing, Spatial Planning and Environment target and intervention values for soil remediation (Table 3) on the basis that it is a long established (first introduced in the early 1980's), tried and tested scheme, where the intervention values are based on extensive studies of both the human and eco-toxicological effects of soil contaminants. The Dutch intervention values for soil/sediment remediation are considered to be numeric manifestations of the concentrations above which it may be said that there is a case of serious contamination. These values indicate the concentration levels of metals above which the functionality of the soil for human, plant and/or animal life may be seriously compromised or impaired. Target values indicate the level at which there is a sustainable soil quality and gives an indication of the benchmark for environmental quality in the longterm on the assumption of negligible risk to the ecosystem.

The mean metal concentrations in the soils did not exceed the intervention values which led to the conclusion that the soil from Belgrade was unpolluted. However, 89% of the soil samples from 2003 and 67% from 2005 had lead contents higher than the Dutch target value. Concerning copper all the examined samples had copper contents higher than the target value. The zinc content was higher than the target value in 67% of the samples for both samplings. Obviously, the contamination is not sufficiently high to require remediation/intervention, but does not exclude risk to the ecosystem.

Because there is no database to compare the metal contents in the studied samples with other

Table 4. Average metal concentrations in urban soils from different cities across the world (mg kg<sup>-1</sup>)

City	Pb	Cu	Zn	Reference
Sevilla	161	65	107	[2]
Naples city	262	11	251	[5]
Madrid	161	72	210	[6]
Palermo	253	77	151	[18]
Belgrade (2003)	151	53	152	
Belgrade (2005)	125	96	214	

findings in the region, the contents of the examined metals were compared with those reported for urban soils in Italy and Spain. The average contents for *aqua regia* are compared to those found in different cities in Table 4. In comparison with industrialized cities from developed countries, the Cu and Zn concentrations in urban soils of Belgrade are generally similar or higher, while the Pb concentration is similar or lower.

The labile phase concentration (Table 2), determined as the amount of metal extracted with HCl, was in the order Pb>Zn>Cu>Cd for samples from 2003 and Zn>Pb>Cu>Cd for samples from 2005. The decrease in Pb extracted by both methods between two samplings suggests that some of this metal was removed by rain or irrigation. Among all metals the more readily available pool was particularly consistent for Pb and Zn (70% and 65% of the total, respectively), indicating these elements are potentially bioavailable and may leach through the soil.

## CONCLUSIONS

The soils of the urban area of Belgrade have been hardly studied, especially the concentrations of potentially toxic metals. The obtained results indicate that urban soils in Belgrade have elevated concentrations of Pb, Zn and Cu. Parks with high metal concentrations are located in areas with high traffic flow, indicating that the major contamination sources in these soils are traffic emissions. Comparison between the 2005 data and those of 2003 revealed a decrease of the Pb content (17%) and an increase of the Cu, Zn and Cd contents of the urban soils. The mobility of the four metals declined in the following order: Pb, Cu, Zn and Cd. The Pb content between two samplings decreased, probably because it is more mobile than the other metals studied. Also a progressive shift in the last few years towards the use of unleaded petrol should have some influence.

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## IZVOD

### ZAGAĐENJE METALIMA URBANOG ZEMLJIŠTA U PARKOVIMA I ZELENIM POVRŠINAMA U BEOGRADU (SRBIJA)

(Naučni rad)

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Zemljište u urbanim delovima gradova, naročito kada je reč o parkovima ili zelenim površinama, direktno utiče na zdravlje ljudi, iako se ne nalazi u lancu produkcije hrane. Razlog tome je kontakt ljudi sa delovima zemljišta koje je u obliku suspendovanih čestica u vazduhu ili direktni kontakt ljudi, posebno dece sa zemljištem. Čest je slučaj da zemljište u parkovima sadrži povećane koncentracije zagađujućih materija koje potiču iz saobraćaja ili industrije.

Primarni izvor zagađenja zemljišta metalima su razna sredstva koja se direktno dodaju zemljištu: fosfatna đubriva (Cd, Pb, As), krečnjak (Pb, As), pesticidi (Pb, As, Hg) i drugo. Sekundarni izvori zagađenja, odakle metali u urbanim sredinama dospevaju kako u hidrosferu tako i u litosferu, su: automobilski izduvni gasovi (Pb), trošenje guma (Cd, Zn), ispiranje boja (Pb, Cd), spaljivanje otpada.

Većina parkova u Beogradu se nalazi u urbanom delu grada zbog čega su izloženi potencijalnom zagađenju, u koje spada i emisija zagađujućih materija iz saobraćaja i industrije. Izloženi rad je rezultat ispitivanja distribucije metala na javnim površinama u Beogradu. Bakar, cink, olovo i kadmijum su izabrani kao dobri pokazatelji zagađenja koji se najčešće javljaju u urbanim sredinama.

U okviru ovog rada ispitivano je devet uzoraka zemljišta uzetih iz parkova i sa zelenih površina u Beogradu. Uzorci zemljišta su uzimani i analizirani 2003. i 2005. godine da bi se ustanovilo da li je u tom periodu došlo do akumulacije metala na ispitivanim lokacijama. Ukupna koncentracija metala u ispitivanim uzorcima određivana je digestijom sa carskom vodom, dok je lako dostupna, mobilna frakcija određivana izluživanjem sa razblaženim rastvorom HCl ( $0,5 \text{ mol/dm}^3$ ).

Uočeno je da ukupna koncentracija ispitivanih metala opada u nizu  $\text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$ . Poređenjem rezultata iz 2005 i 2003 može se zaključiti da ukupni sadržaj olova predstavljen kao srednja vrednost devet uzoraka opada (17%), dok se koncentracija Cu, Zn i Cd povećava. Praćenjem ukupne i mobilne frakcije utvrđeno je da su metali u ispitivanim uzorcima uglavnom antropogenog porekla i da je došlo do akumulacije bakra, cinka i kadmijuma u ispitivanom periodu. Koncentracija olova se smanjila, verovatno zbog migracije i ispiranja.

Ključne reči: Metali, Zemljište, Zelene površine, Zagađenje, Beograd.