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Heavy metals concentration in soils from parks and green areas in Belgrade

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Abstract: The current study included the investigation of several metals and their distribution in urban soils from parks and green areas in the city of Belgrade. The soils were sampled in January and February 2008. The concentrations of Cd, Co, Cu, Pb, Mn and Zn were measured, as well as the pH values and organic matter contents. The obtained results showed that there was a significant level of contamination in some samples, especially with lead, and that it was most probably caused by anthropogenic activities, mostly from traffic. The results were compared with the National legislation and Netherlands standards. Also, the recent results were compared with the data from previous work and it was concluded that there has been a certain increase of the Pb concentration in the past three years. The level of pollution in playground soil was very high and each analyzed sample exceeded the Dutch target value for Cd, Co and Pb.

Keywords: pseudo-total metal contents; urban soil; parks; green areas; pollution.

INTRODUCTION

Trace elements, especially heavy metals, are considered to be one of the main pollutants in the environment, since they have a significant effect on its ecological quality.[1]

Expanding interest in the field of heavy metal research is associated with an increasing world production of metals and their common usage in the past century and, consequently, with their increasing emissions into the environment. This has resulted in a growing hazard to human health posed by elevated metal concentrations in the air, water and food.[2] The problem with heavy metals is their persistence, making it impossible to eliminate them from the environment.[3]

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The majority of the studies[4–10] agreed that urban soils contained enriched levels of trace elements relative to the natural background levels.[11] While usually natural forms are presented in relatively low concentrations, in recent years a number of anthropogenic sources, such as emissions of industrial plants, vehicle exhausts, thermal power stations and commercial product waste, have made notable contributions to the increase of environmental metal concentrations.[4, 12–14]

The heavy metal contents of urban soils may influence public health *via* direct contact with contaminated dust or soil or by inhalation.[3] Children are the most sensitive target group of exposure.[15,16] Due to their higher sensitivity, as well as characteristic behaviors (outdoor activities, hand–mouth activity, deficient hygienic habits, *etc*.), children are at greater risk of exposure to the toxic elements from contaminated soils than adults.[12] Bearing in mind that children are more susceptible to metals, since they are in the early stage of development, determining the heavy metal contents in playground soils is of particular importance.

The aim of the current study was to investigate the metal contents in urban soil in Belgrade and to obtain some knowledge about possible changes of the metal concentrations with time. The current study included the investigation of several metals and their distribution in urban soils in Belgrade. Special attention was paid to playground sampling in parks where children spend most of their time.

EXPERIMENTAL

Sites of investigation

Belgrade is the capital and the largest city in Serbia, located in southeastern Europe, between 44 and 49° of the northern latitude and 20 and 27° of the eastern longitude, 90–120 m above sea level. Belgrade has a moderate continental climate, with an average annual air temperature of 11.9 °C. January is the coldest month with an average temperature of 0.1 °C and July is the hottest month with an average temperature of 22.1 °C. A characteristic of the Belgrade climate is the Košava, a southeast–east wind which brings clear and dry weather. It blows mostly in autumn and winter, in 2–3 days intervals. The average annual rainfall on Belgrade and its surroundings is 669.5 mm. The months with the most rainfall are May and June.

Belgrade is situated at the confluence of the Sava and the Danube Rivers. It is an important intersection of roads and industry and the commercial center of the country. With a growing population (around 1.8 million citizens) and economic development, the environmental quality of the urban soils is becoming more important considering human health. Numerous heating plants, coal or crude oil used for domestic heating, leaded gasoline and diesel vehicle exhaust, are some of the potential sources of pollutions in urban soils and they are major problems in Belgrade.[17,18]

Sampling strategy

In the study areas, there are no specific point-sources of heavy metals and therefore, heavy metal contamination of the soils is derived from continuous urbanization and development, which can adversely affect human health in the contaminated area.

Soil samples were taken from 15 locations from parks and green areas in the urban parts of Belgrade (Fig. 1) in January and February 2008. Most of the locations were chosen within the main public parks and green areas in the central zone of Belgrade. Each location was represented with 2 or 3 samples, one sample from the children's playground and one or two samples near a street or crossroad. At each sampling point, three sub-samples, from top 10 cm layer, within a 20 cm×20 cm surface, were taken and mixed to obtain a bulk composite sample. Such a sampling strategy was adopted in order to reduce the possibility of random influence of urban waste not clearly visible.[5] Samples were collected with a stainless trowel and transferred to the laboratory in plastic bags. Stones and foreign objects were hand-removed, and the samples were air-dried for seven days.

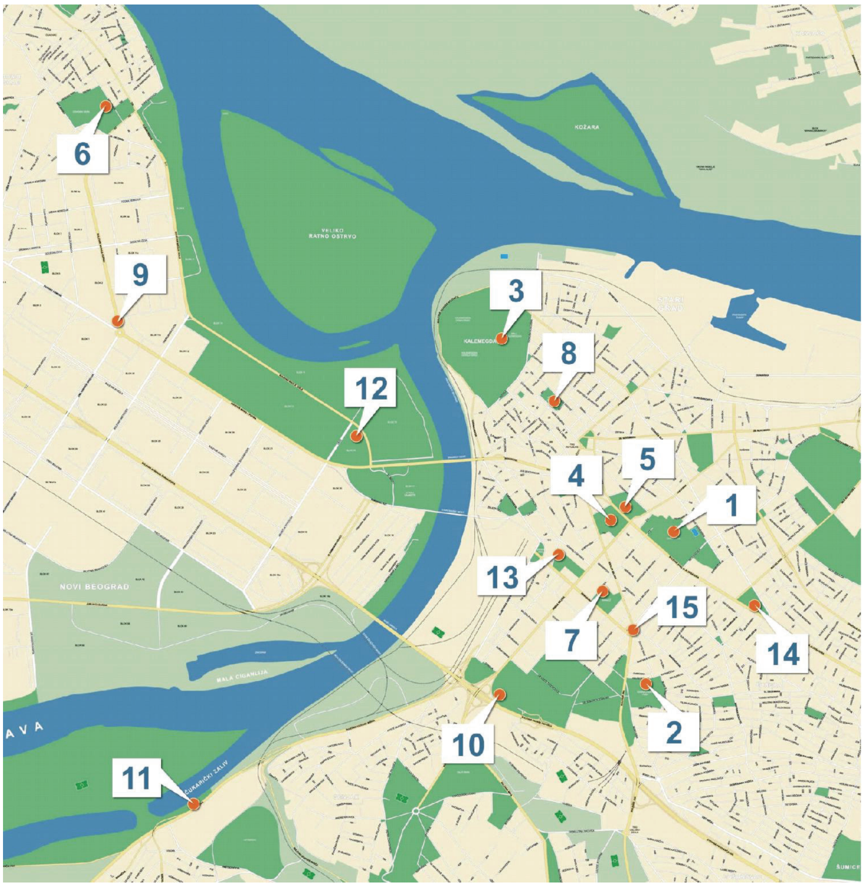

Fig. 1. The study area and sampling locations. Legend: 1. Tašmajdan, 2. Karađorđev park, 3. Kalemegdan, 4. Pionirski park, 5. Skupština, 6. Zemun, 7. Manjež, 8. Studentski park, 9. Novi Beograd, 10. Mostarska petlja, 11. Ada Ciganlija, 12. Ušće, 13. Finansijski park, 14. Vukov spomenik, 15. Slavija.

Analytical procedure

The dry samples were gently crushed and sieved to 2 mm and 1.00±0.02 g was weighed for analysis. Measurements of the pH values were realized on a 1:5, soil:deionized water suspension.[19] The content of organic matter was determined as the weight loss after heating 1 g soil at 550 °C for 2 h.

"Pseudo-total metal contents" were obtained by digesting soil samples in *aqua regia*. The term pseudo-total accounts for the *aqua regia* digestion not completely destroying silicates. This method is widely used in environmental studies and, for example, recommended by the National Government Regulation of Italy.[5]

One gram of dried and homogenized portion of the soil fraction smaller than 2 mm was digested with 18 ml HCl and 6 ml HNO_3 by heating under reflux until most of the solvent was removed. After cooling, the digestion was repeated. Cool suspension was filtered into 50 ml volumetric flask and made up to the volume with deionized water. The concentrations of Cd, Co, Cu, Pb, Mn, and Zn were measured using a Pye Unicam SP9 atomic absorption spectrometer.

RESULTS AND DISCUSSION

The obtained results for pH values of soil–deionized water suspension and organic matter content determined by loss-on-ignition are presented in Table I. The results are given as mean value for each location, which included 2 or 3 samples. The range for the acquired values at the locations is also given. The measured pH values indicated that all the analyzed samples were sub-alkaline or alkaline, which could affect a lower solubility and greater retention of metals in soils.[20] The range of the organic matter content was generally 6.11–13.11 %, with two exceptions: an extremely low value at location 12 (3.38 %) and an extremely high value at location 11 (23.65 %).

TABLE I. Mean and range of pH values and organic matter content (*OM*)

Location	pH		*OM* / %	
	Range or value	Mean	Range or value	Mean
1	8.07–8.57	8.31	6.11–9.09	9.49
2	8.44–8.75	8.60	8.27–8.93	8.60
3	8.00–8.62	8.36	8.72–11.69	10.22
4	8.38–8.58	8.45	7.17–11.22	8.65
5	8.72–9.32	9.02	9.55–11.26	10.41
6	8.32–8.57	8.41	7.09–11.19	9.11
7	8.23–8.44	8.35	7.44–9.46	8.77
8	8.63–9.01	8.82	8.95–9.72	9.34
9	8.64–9.00	8.82	7.53–7.69	7.61
10	8.35–8.38	8.36	12.13–13.1	12.62
11	8.55–9.21	8.83	8.13–23.65	13.37
12	8.56–9.72	8.97	3.38–8.42	6.11
13	8.34–8.62	8.50	7.54–10.92	9.17
14	8.58	–	8.93	–
15	8.18–8.30	8.24	6.52–7.23	6.88

The minimum, maximum, and average metal concentrations are summarized in Table II. The average heavy metal concentrations for each of the 15 locations are shown in Fig. 2.

All of the investigated metals had a wide range of concentration values, depending on location and sampling point at a specific location. High concentrations coupled with wide range of values suggests anthropogenic sources for these elements.[21]

TABLE II. Minimum, maximum and average metal concentrations (mg/kg soil)

Concetration	Cd	Co	Cu	Pb	Mn	Zn
Min	1.1	4.4	8.8	≤ *LOD*[a]	281.8	63.2
Max	3.1	36.0	251.3	785.7	688.9	691.1
Average	1.8	16.5	46.3	298.6	417.6	174.2

[a]Limit of detection for Pb is 5 mg/kg dry sample

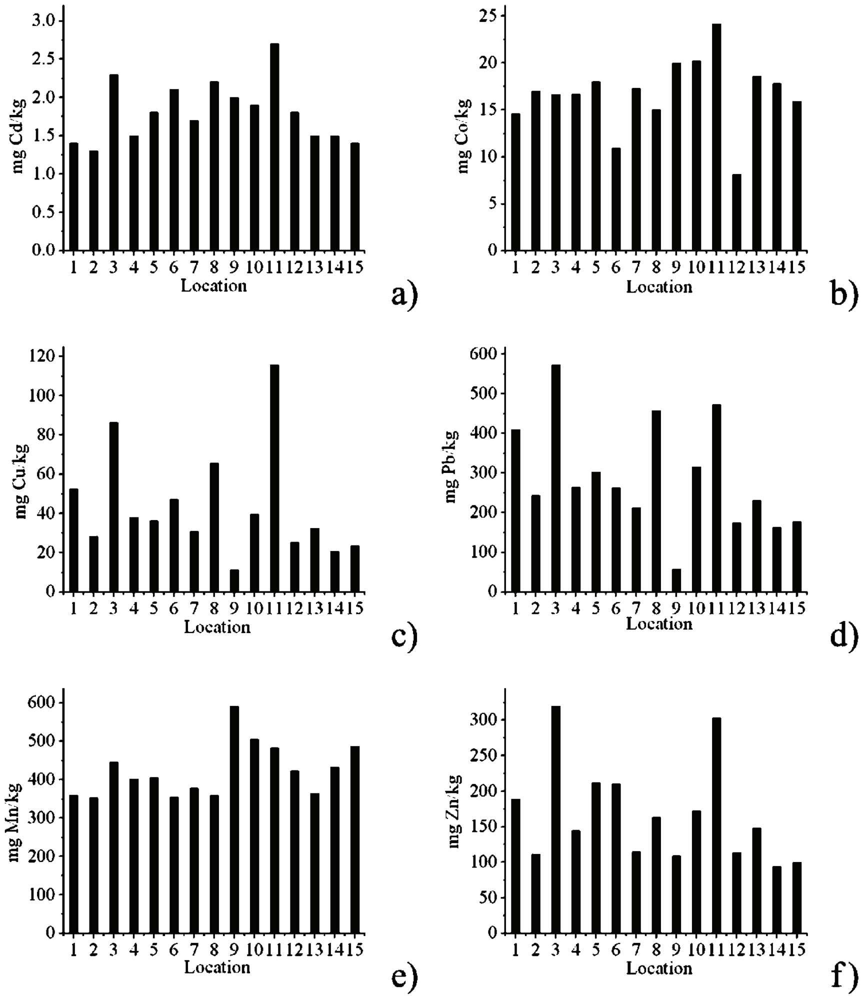

Fig. 2. Mean values of a) Cd, b) Co, c) Cu, d) Pb, e) Mn and f) Zn concentrations (mg/kg).

According to the National legislation,[22] 93.3 % of the analyzed samples were contaminated with lead (maximum allowed concentration for lead in soil is

100 mg/kg); 13.3 % of the samples were contaminated with zinc (maximum allowed concentration for zinc in soil is 300 mg/kg); 6.7 % of samples were contaminated with copper (maximum allowed concentration for copper in soil is 100 mg/kg). There was no soil contamination with cadmium (maximum allowed concentration for cadmium in soil is 3 mg/kg). Manganese and cobalt are not regulated with the National legislative.

The possible contamination can also be estimated according to the Netherlands Soil Quality Standard,[23] an often cited standard in similar studies.[4,24–26] The Dutch target values (Table III) indicate the level at which there is a sustainable soil quality. This means that soils are relatively unpolluted if they meet the target values. According to the Netherlands Standard, 93.3 % of the examined samples were polluted with Pb and Co, 60 % were polluted with Zn and 53.3 % were polluted with Cu. The soil intervention values are representative of the level of contamination above which there is a serious case of soil contamination. According to this, 6.7 % of analyzed soil samples exceeded the intervention value for the concentration of Pb, which means that these locations require remediation. Comparing the obtained Zn, Cd, Cu, and Co concentrations with the intervention values, the contamination was not sufficiently high to require remediation. The manganese concentration is not defined with this standard.

TABLE III. Target and intervention values for selected metal concentrations (mg/kg) in soils from the Ministry of Housing, Spatial Planning and Environment Directorate, Netherlands[23]

Value	Cd	Co	Cu	Pb	Zn
Target	0.80	9.0	36	85	140
Intervention	12	240	190	530	720

Comparing results obtained in this study and the results from the previous study,[27] it could be concluded that there was a significant increase in average concentrations for Pb in urban soils of Belgrade. The mean concentration for Pb was 299 mg/kg in the year 2008, which was approximately twofold higher than the mean concentrations in 2003 and 2005, 151 and 125 mg/kg, respectively. It is also worth noting that the maximum Pb concentration from the previous study[27] was 238 mg/kg, which was more than three times lower than the maximum concentration obtained in 2008. Possible explanations for the obtained data could be the growing density of the traffic in the past few years or the fact that sampling was performed during the winter season, when heating plants could be a potential source of pollution. On the other hand, the concentration of Cu was more than twofold lower than the concentration acquired in 2005 (95.7 mg/kg) and almost the same as the concentration in 2003 (53.3 mg/kg). The decrease in the concentration of Cu suggests that some of this metal was removed by rain or irrigation. The mean concentrations for Zn and Cd were similar as in the previous study (mean concentrations for Zn were 152 and 214 mg/kg; and for Cd they were 1.3 and 1.9 mg/kg for the years 2003 and 2005, respectively).

It is a common practice to compare mean concentrations of trace metals in urban soils from different urban settings.[28] It is obvious that the existing level of contamination in Belgrade with Cd, Co, Cu, Pb, Mn, and Zn is significantly higher than comparable levels in several other cities over the world (Table IV). Considering that all the studies were published in the last year or two, the only explanation for extremely high Pb contamination is the use of leaded gasoline, which is still available in Belgrade and is more often in use than unleaded gasoline.[17] The other investigated metals (Cd, Co, Cu, and Zn) were also present in higher concentrations than in other cities, but they were similar or lower than the concentrations measured in the previous study.

TABLE IV. Average metal concentrations (mg/kg) in urban soils from different cities across the world

City	Cd	Co	Cu	Pb	Mn	Zn	Reference
Galway	–	6	27	58	539	85	8
Hong Kong	0.36	3.55	16.2	88.1	–	103	7
Madrid	0.14	–	14	22	249	50	29
Hangzhou	–	9.25	36.57	46.15	415.27	116.07	21
Belgrade	1.8	16.5	46.3	298.6	417.6	174.2	This paper

The results obtained by analyzing the playground soil samples are presented separately because high amounts of the examined metals were found in some of them. The results obtained for the concentrations of Cd, Co, Cu, Pb, Mn and Zn are shown in Table V.

TABLE V. Heavy metal concentrations (mg/kg) in soils from playgrounds

Location[a]	Cd	Co	Cu	Pb	Mn	Zn
1	1.20	10.21	17.17	151.52	282.51	90.86
2	1.31	14.04	15.11	221.43	299.59	101.83
3	1.55	16.01	71.01	535.71	372.22	122.02
4	1.41	13.91	26.78	190.95	365.58	146.68
5	1.53	17.80	20.56	176.80	443.41	97.29
6	1.67	12.08	23.91	192.86	372.22	119.64
7	1.80	14.19	15.27	180.38	352.86	98.06
8	2.14	12.08	50.92	550.00	331.43	157.65
9	1.89	20.02	8.79	99.01	506.54	121.67
10	1.90	24.16	36.51	157.14	471.81	156.14
11	3.10	35.96	251.32	300.00	563.35	495.82
13	1.07	17.98	22.65	207.14	388.14	113.70
15	1.53	15.85	19.94	190.95	425.68	109.05

[a]No playgrounds were at Locations 12 and 14

According to the National Legislation, 12 of the 13 playground soils were polluted with Pb and one of them (Location 11) was also polluted with Zn, Cd and Cu. On Location 9, the concentration of lead was almost the same as the maximum allowed by the National Legislation. In all the analyzed playground soil samples, the Dutch target values for Pb, Cd and Co were exceeded and in 4 of the 13 playground soil samples, the target values were exceeded for Zn and Co. Locations 3, 8 and 11 should be remediated since the intervention values for Pb (Locations 3 and 8) and Cu (Location 11) were exceeded. High levels of investtigated metal concentrations at Location 11 could be related to the high level of organic matter (23.65 %), as soils high in organic matter adsorb and bind heavy metals by forming complexes with organic acids, which increases the retention of metals in soils.[3] Children playing in parks could come in contact with soil polluted with metals, especially with lead. This could have negative effect on children's health, particularly for six-year olds and younger children.[15]

CONCLUSIONS

Cadmium, cobalt, copper, lead, manganese, and zinc are good indicators of contamination in soil because they appear in gasoline, vehicle exhausts, car components, industrial emissions, *etc*. According to the National Legislation, 93.3 % of the analyzed samples were contaminated with lead, 13.3 % of the samples were contaminated with zinc and 6.7 % of samples were contaminated with copper. A comparison between the obtained results with those from the previous study indicated that there was a significant increase in concentrations of Pb in the urban soils. Target values for Cd, Cu Pb and Zn in the analyzed soil samples from playgrounds were exceeded and also intervention values for Pb and Cu in some of the samples were exceeded. Furthermore, according to the National Legislation, 92.3 % of playgrounds were polluted with Pb and 7.7 % were polluted with other metals.

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И З В О Д

КОНЦЕНТРАЦИЈА ТЕШКИХ МЕТАЛА У ЗЕМЉИШТУ ПАРКОВА И ЗЕЛЕНИХ ПОВРШИНА У БЕОГРАДУ

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Циљ овог рада био је испитивање дистрибуције тешких метала у земљишту паркова и зелених површина у Београду. У узорцима земљишта, прикупљеним током јануара и фебруара 2008. године, одређиване су концентрације кадмијума, кобалта, бакра, олова, мангана и цинка, као и pH вредност и садржај органске материје. Добијени резултати показују значајан степен загађења код појединих узорака. Изузетно висок садржај олова забележен је код свих

испитиваних узорака, и највероватније је последица антропогених активности, пре свега саобраћаја. Поређењем резултата са ранијим испитивањима примећено је знатно повећање садржаја олова у земљишту у протекле три године. Изузетно забрињавајућа је и чињеница да је земљиште узорковано у дечијим игралиштима загађено тешким металима. Такође, поређењем добијених резултата са холандским стандардом, закључено је да су код свих узорака концентрације испитиваних метала више од концентрација дефинисаних тим стандардом.

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