Children’s health risk assessment based on the content of toxic metals Pb, Cd, Cu and Zn in urban soil samples of Podgorica, Montenegro

Procena rizika po zdravlje dece na osnovu sadržaja toksičnih metala Pb, Cd, Cu i Zn u gradskom zemljištu na teritoriji Podgorice, Crna Gora

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Abstract

Background/Aim. Due to their low tolerance to pollutants and hand-to-mouth pathways the health risk is very high in children’s population. The aim of this study was to evaluate risk to children's health based on the content of heavy metals in urban soil samples from Podgorica, Montenegro. This study included the investigation of several toxic metals such as Pb, Cd, Cu and Zn in soil samples from public parks and playgrounds. Methods. Sampling was conducted in a period October-November, 2012. Based on cluster analysis, soil samples were divided into two groups related to similarity of metal content at examined locations: the group I – near by recreational or residential areas of the city, and the group II – near traffic roads. Concentration of toxic metals, in urban soil samples were determined by a graphite furnace atomic absorption spectrometry (Pb and Cd) and by inductively coupled plasma optical emission spectrometry technique after microwave digestion. Due to exposure to urban soil, non-cancerogenic index hazardous index (HI) for children was estimated using 95th percentile values of total metal concentration. The value of the total (ingestion, dermal and inhalation) HI is calculated for maximum, minimum and the average concentration of metals for children. Results. Mean concentrations of Pb, Cd, Cu and Zn in the surface layer of the studied urban soils were 85.91 mg/kg, 2.8 mg/kg and 52.9 mg/kg and 112.5 mg/kg, respectively. Samples from group II showed higher metal content compared to group I. Urbanization and traffic are the main sources of pollution of the urban soils of Podgorica. Most of the samples (93.5%) had a high Pb content, 12.9% of the samples had a higher content of Cd, while Cu and Zn were within the limits prescribed by national legislation. At one location the level of security for lead is HI = 0.8 and very closed to maximum acceptable value of 1. It is probably the result of intensive traffic near by. Conclusion. All metals investigated showed relatively higher concentrations at sites that were close to industrial places and high ways. The mean concentrations of Pb and Zn and maximum concentrations of Pb, Cd, and Zn were higher than presented values in the National Regulation.

Key words: metals, heavy; soil; risk assessment; health; child.

Apstrakt


ma urbanog zemljišta odredena je primenom atomske apsorpncije spektrometrije pomoću grafitne kivete (Pb i Cd) i tehničke optičke emisije spektroskopije sa induktivno kupovlom plazmom (C u i Zn) nakon mikrotalaške digestije. Na osnovu stepena izloženosti uticaju gradskog zemljišta, nekancerogeni indeks opasnosti (zadget index – HI) za decu izračunat je na 95. procentu vrednosti ukupne koncentracije metala. Vrednost za ukupni (ingestion, dermalni i inhalacioni) HI izračunata je za maksimalne, minimum i srednje koncentracije ispitivanih metala za decu. Rezultati. Srednja koncentracija toksičnih metala u uzorcima površinskog sloja zemljišta iznosila je 85,91 mg Pb/kg tla, 2,8 mg Cd/kg tla, 52,9 mg Cu/kg tla i 112,5 mg Zn/kg tla. Sadržaj metala bio je značajno veći u uzorcima zemljišta iz grupe II nego u uzorcima grupe I. Ovo jasno ukazuje na izražen i uočljiv uticaj urbanizacije, a naročito saobraćaja, na zagađenje zem

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Introduction

Continual urbanization and industrialization induces metals emissions into the terrestrial environment which may greatly influence human health. Samples of soils become a very good diagnostic tool of environmental conditions that influence human health. Chemical composition of soil has been conducted in many studies during the last ten years. Special attention has been devoted to studies on urban park playgrounds. Dermal contact, ingestion and inhalation are the main route of exposure to toxic metals in urban environment. A high concentration of toxic metals in urban soils is an important source of human metal intake. Possibility of exposure to adverse effects of soil ingestion is higher in children than adults. Urban children come in contact with soil in parks and playgrounds. A significant amount of toxic metals children could ingest from soil, dust and air. Due to their low tolerance to pollutants and hand-to-mouth pathways the health risk is very high in this population.

So, the control of potentially harmful substances in soil is of high importance and has to be kept at low level in the areas frequented by children.

As heavy metals are nondegradable and there is no known homeostasis mechanism for them, any high level of this pollutant may affect the human health affecting the normal functioning of organs, liver, kidney, central nervous system, bones, etc., or acting as cofactors in other diseases.

The aim of this study was to evaluate risk assessment to children’s health based on the content of toxic metals in urban soil samples of Podgorica, Montenegro. This study included the investigation of several toxic metals such as Pb, Cd, Cu and Zn in surface soil samples from public parks, playgrounds and kindergartens of Podgorica. Children health risk due to children’s toxic metal exposure from urban soil according to hazardous indices (His) was estimated.

Method

Sampling and analysis

This study presents concentrations of four toxic metals, Pb, Cd, Cu and Zn, in surface soil samples from the city’s playgrounds in public parks, playgrounds and kindergartens of Podgorica, the capital of Montenegro. A total of 31 parks and playgrounds from the different location of the city were studied. Sampling was conducted during October and November, 2012. Samples of approximately 500 g weight, from top 10 cm layer, within 20 × 20 cm of surface soil, consisting of three sub-samples, were taken and mixed to obtain a bulk composite sample at each playground. Sampling was conducted near by playground equipment such as swings, slides, etc. Stainless trowel was used for sampling and samples are transferred to the laboratory in plastic bags. Stones and foreign objects were hand-removed, and the samples were air-dried for several days. After drying at room temperature samples were gently crushed and sieved to 2 mm and 1.0 ± 0.01 g was weighed for analysis. Microwave acid digestion based on US EPA 3052 method was used for sample preparation. The concentrations of Pb and Cd were determined by a graphite furnace atomic absorption spectrometry (GFAAS) (240Z AA Agilent Technologies-Netherlands) and Cu and Zn by inductively coupled plasma-optical emission spectrometry (ICP-OES) (AMETEC-SpectroArcos, Germany).

Reagents and standards

All chemicals used through the study were analytical grade chemicals. There was no further purification for preparation of all reagents and calibration standards. Deionized ultra pure water was used with conductivity < 1μS/cm. Certified metal stock solution of 1,000 mg/L (J.T. Baker) by successive dilution with deionized water was used for preparing standards for calibration. Each sample was carried out in triplicate.

Data analysis and risk assessment

Statistical package (SPSS 17.0 for Windows) was used for statistical data analysis. This software uses the upper limit of the 95 percent confidence interval (95 percent upper confidence limit – UCL) for the mean concentrations for risk estimation. For evaluation of the similarity of sampling sites with respect to contribution of metals in urban soils, cluster analysis (CA) was applied. Hierarchical CA was performed using the Ward’s method and Euclidean distances as a measure of similarity and the results are showed in a dendrogram. Before applying CA, the normality of all metals was checked using Shapiro-Wilk’s normality test (p < 0.05). In this study prior to CA all the data were log-transformed to reduce the influence of high values.

Input parameters (toxicity values) for estimation have been taken USEPAs exposure parameters. Children could be exposed to contaminants from soil via three different pathways oral intake (Ingestion), inhalation intake (Inhalation) and through skin exposure (Dermal). Based on this fact noncancer risk assessment in this study was estimated. For intake estimation via each exposure pathways the following equitations were used.
\[
\text{Intake}_{\text{ingestion}} = \frac{C \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6}
\]

where, \(C\) – concentration of a contaminant in soil (mg/kg), \(\text{IngR}\) – ingestion rate of soil (mg/day) = 200 \(^{14,15}\), \(\text{EF}\) – exposure frequency (days/year) = 360 \(^{13}\), \(\text{ED}\) – exposure duration (years) = 6 \(^{16}\), \(\text{BW}\) – average body weight (kg) = 20.3 \(^{17}\), \(\text{AT}\) – averaging time (days) = \(\text{ED} \times 365\) \(^{13}\)

\[
\text{Intake}_{\text{inhalation}} = \frac{C \times \text{InhR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}}
\]

where,
\(\text{InhR}\) – inhalation rate (m\(^3\)/day) = 7.6 \(^{18}\), \(\text{PEF}\) – particle emission factor = \(1.36 \times 10^9\) m\(^3\)/kg \(^{16}\).

\[
\text{Intake}_{\text{dermal}} = \frac{C \times \text{SA} \times \text{SAF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6}
\]

where,
\(\text{SA}\) – surface area of the skin that contacts the soil (cm\(^2\)) = 2,800 \(^{16}\), \(\text{SAF}\) - skin adherence factor for soil (mg/cm\(^2\)) = 0.2 \(^{16}\), \(\text{ABS}\) – dermal absorption factor (chemical specific) = 0.001 (for all metals) \(^{18-20}\).

In this study, the body weight of 20.3 kg was taken from World Health Organization – WHO reference value \(^{17}\). After the three exposure pathways intake\(_{\text{ingestion}}\), intake\(_{\text{inhalation}}\) and intake\(_{\text{dermal}}\) were calculated, hazard quotient (HQ) and HI based on non-cancer toxic risk can be calculated as follows \(^{13}\):

\[
\text{HQ} = \frac{\text{Intake}}{\text{RfD}}
\]

\[
\text{HI}_{\text{exP}} = \sum \text{HQ}_{\text{exP}}
\]

where, \(\text{exP}\) are different exposure pathways, respectively.

Reference dose (RfD) (mg/kg/day) is an estimate value of the daily exposure, maximum permissible risk, to the human population, including sensitive subgroups (children) during a lifetime. The values of RfD are showed in Table 1 \(^{19}\).

<table>
<thead>
<tr>
<th>Metals</th>
<th>RfD(_{\text{ingestion}})</th>
<th>RfD(_{\text{inhalation}})</th>
<th>RfD(_{\text{dermal}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4E-02</td>
<td>1.2E-02</td>
<td>4E-0</td>
</tr>
<tr>
<td>Pb</td>
<td>3.5E-03</td>
<td>5.25E-04</td>
<td>3.5E-03</td>
</tr>
<tr>
<td>Cd</td>
<td>1E-03</td>
<td>1E-05</td>
<td>1E-03</td>
</tr>
<tr>
<td>Zn</td>
<td>3E-01</td>
<td>6E-02</td>
<td>3E-01</td>
</tr>
</tbody>
</table>

In this study it was assumed that after inhalation, all toxicants bonded to particular matter will have similar health effect as if they are ingested. It was assumed that absorption factor for inhalation and ingestion is 100 and this value was used in this study \(^{12,19-21}\).

Each HQ for different pathways could be calculated and summed to generate HI (Eq.5). If the value of HI < 1, there is no significant risk of noncancerogenic effect. But if the HI > 1, there is probability of occurrence of noncancerogenic effect and it will be increased if HI increases \(^{22}\).

**Results**

Based on metal concentrations after cluster analysis, urban soils, collected from 31 locations, were classified into two groups and results are presented in Figure 1. The group I con-
sisted of samples Vr1, Pr2, Pr1, Vr4, Vr5, Vr2, Vr3, Vr9, Vr10, Pr5, Vr8, Pr4, Vr7, Vr6, and Pr3 from locations that were near recreational or residential places. The group II consisted of samples Vr25, Vr26, Vr23, Vr24, Vr21, Vr22, Vr19, Vr20, Vr17, Vr18, Vr15, Vr16, Vr13, Vr14, Vr11, and Vr12 and these sites were near traffic roads and some small building materials facilities such as Vr11 location. Descriptive statistics of the two groups are shown in Table 2. Figure 1 shows the dendrogram of clustering of monitoring sites.

All mean metal concentrations in the group II were higher, except of Cd, compared to the group I. The mean concentration of Pb in the group II was 30% higher than in the group I, while the mean Zn concentration in the group II was 50% higher than in the group I. There is no significant difference between mean concentrations of Cd and Cu in these two groups.

Correlation analysis

Pearson’s correlation analysis was applied for each group to analyze the relationships of metal concentrations, and the results are showed in Table 3. Pb, Cd, Cu and Zn were among significantly positively correlated with each other in the group II. Cu and Zn showed very strong positive correlation (0.85) indicating that also natural source together with traffic and industry contribute to contamination. In the group I, there were no statistically significant correlations among metals, and this might be due to natural content and lower pollution of these sites. Concentrations of Cd and Zn were negatively correlated, but not statistically significant, probably indicating different sources of pollution by these two metals.

The obtained results of noncancerogenic children health risk, based on metal concentrations in urban soils and exposure by three different pathways (ingestion, inhalation and dermal) are shown in Table 4. The results for HI for Pb at all investigated locations are showed in Figure 2. In soil sample at the location Vr11 HI for Pb was 0.8 and it is very close to the upper limit of the safe level. HI for Pb (0.68) at the location Vr22, in children was also lower than the upper limit of the safe level. HI for Pb at the 29 investigated locations is lower than 0.4. A high Pb concentration in urban soil

<table>
<thead>
<tr>
<th>Metal</th>
<th>0.07</th>
<th>0.8</th>
<th>0.24</th>
<th>1.8E-06</th>
<th>2.3E-05</th>
<th>7E-06</th>
<th>1.2E-03</th>
<th>1.5E-04</th>
<th>4.5E-03</th>
<th>0.071</th>
<th>0.8</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>8.6E-03</td>
<td>3.5E-02</td>
<td>2.7E-02</td>
<td>2.4E-07</td>
<td>1.0E-06</td>
<td>7.6E-07</td>
<td>2.4E-03</td>
<td>1.0E-02</td>
<td>7.6E-03</td>
<td>0.011</td>
<td>0.05</td>
<td>0.035</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0006</td>
<td>0.024</td>
<td>0.004</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

HQ – hazard quotient; HI – hazard index; UCL – upper confidence limit.
at the location Vr11 is the result of the vicinity of building materials facility and intensive traffic. Noncancer lead risk (HI) for children at the examined locations of Podgorica is shown in Figure 2.

![Graph showing noncancer lead risk (HI) for children at examined locations of Podgorica, Montenegro.](image)

**Fig. 2** – Noncancer risk for lead (HI) for children at examined locations of Podgorica, Montenegro.

- Group I (Vr1, Pr2, Pr1, Vr4, Vr5, Vr2, Vr3, Vr9, Vr10, Pr5, Pr8, Pr4, Vr7, Vr6, Pr3) – samples from locations that were near recreational and residential places;
- Group II (Vr25, Vr26, Vr23, Vr24, Vr21, Vr22, Vr19, Vr20, Vr17, Vr18, Vr15, Vr16, Vr13, Vr14, Vr11, Vr12) – samples from locations that were near traffic rods.

**Discussion**

Metals concentrations were compared with maximum allowed concentrations (MAC) values, recommended by the National Regulation 22 and the Italian intervention criteria for soils (the residential/recreational intervention limits fixed by the Italian Environmental Law DM 471/99) 24. According to the National Regulation, the mean concentration of Pb in both groups was higher than the prescribed value. The mean concentrations of Cd exceeded the Italian residential/recreational intervention limits. The maximum concentrations of Pb and Cd in urban soils, in both groups exceeded the National Regulation limits and Italian residential/recreational intervention limits. In the group II the maximum Zn values were above the National Regulation limits and residential/recreational intervention limits, while in the group I they were above residential/recreational intervention limits. Higher concentration of all investigated metals in the group II could be explained to its proximity to traffic roads and some industrial locations. Podgorica has been under high urbanization in the past few decades. In the study areas, there were no specific pollution sources of toxic metals, because of that, the toxic metal contamination of the soils was derived from continuous urbanization and development, which can influence human health in the contaminated area. It is important to emphasize that the main road that connects south and east part of Montenegro, goes through the city center, with very intensive and heavy traffic. It is common practice to compare the mean concentration of toxic metals in some urban soils from different urban cities 1. It can be concluded that the existing level of Cd and Cu soil contamination in Podgorica is significantly higher than comparable levels in some other cities over the world. Zinc concentrations vary from city to city, while Pb content is the lowest except in the city of Madrid, Spain.

The major path of children exposure to urban soil that adverse human health by Pb, Cd, Cu and Zn is ingestion, followed by dermal exposure. Contribution of inhalation exposure to HI is the smallest. For noncancer risk HI for chil-

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ченні здоров'я необхідно прийняти дії для дезамонізації цих сайтів і захистити здоров’я дітей. Цей інтегрований підхід, що базується на статистичних та імуногеномічних пробах риску, може допомогти в прийнятті рішення, що має вплив на розвиток кожного європейського міського регіону.

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