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## Geochemical investigation as a tool in the determination of the potential hazard for soil contamination (Kremna Basin, Serbia)

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**Abstract:** The geochemical composition of the soils and underlying sediments in the Kremna Basin was investigated. The aim was to assess whether the observed heavy metal concentrations in the soil samples represent geogenic or anthropogenic contamination. The second objective was to show that geochemical data of underlying sediments should be used as a tool in the determination of the potential hazard for soil contamination. For this purpose, the contents of As, Cr, Cu, Hg, Ni, Pb and Zn of soil samples were compared with standard values, a reference soil sample and local background values of the underlying sediments. The soil samples were unpolluted regarding the contents of As, Hg, Pb and Zn. All samples had higher contents of Cr and Ni, whereas three samples had higher contents of Cu than the limit standard values. Geochemical parameters showed that the higher concentrations of Cr, Cu and Ni in the soils could be attributed to geogenic impact. This conclusion was supported by the Chemical Proxy of Alteration and Chemical Index of Weathering values, which indicated intense weathering of the sediments. The obtained results showed that the Kremna area is under slight to moderate hazard if a land use change would occur, and proved the importance of the geochemical composition of underlying sediments in the interpretation of heavy metal pollution.

**Keywords:** soils; sediments; geochemistry; heavy metals; pollution; weathering.

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## INTRODUCTION

In natural systems, enrichment and depletion balance each other out. However, anthropogenic influences tend to enrichments in different parts of the system and the distribution function is skewed towards higher values.<sup>1</sup>

Heavy metals are one of the serious pollutants in the natural environment due to their toxicity, persistence and bioaccumulation problems.<sup>2,3</sup> Assessment of the contamination status is regularly based on the Quality Guidelines. Comparison of concentrations of heavy metals measured in samples and contents given by the Quality Guidelines provides data about the level of sample contamination. However, assessment of whether the measured heavy metal concentrations in samples represent geogenic or anthropogenic contamination is difficult based purely on such results. In order to overcome this problem, numerous geochemical parameters have been proposed. These indices are based on comparison of the contents of heavy metals in studied samples and a reference sample. It is very important to choose the most suitable reference sample for the studied area, which can be determined using geochemical or statistical methods.<sup>1,4</sup>

The geo-accumulation index ( $I_{geo}$ )<sup>5</sup> is expressed as follows:

$$I_{geo} = \log_2 \left( \frac{c_n}{1.5B_n} \right) \quad (1)$$

where  $c_n$  represents measured concentration of a heavy metal in the sediment or soil sample and  $B_n$  is the concentration of an element in the reference sample (background value). The factor 1.5 is incorporated in the equation to account for possible variation in the background data due to lithologic effects. The geo-accumulation index ( $I_{geo}$ ) scale<sup>5</sup> consists of seven grades ranging from unpolluted to very strongly polluted:

$I_{geo} < 0$ , unpolluted;

$I_{geo} = 0-1$ , unpolluted to moderately polluted;

$I_{geo} = 1-2$ , moderately polluted;

$I_{geo} = 2-3$ , moderately to strongly polluted;

$I_{geo} = 3-4$ , strongly polluted;

$I_{geo} = 4-5$ , strongly to very strongly polluted;

$I_{geo} > 5$ , very strongly polluted.

The pollution load index ( $PLI$ ) was introduced by Tomlinson *et al.* (1980).<sup>6</sup> The  $PLI$  is calculated using the following equation:

$$PLI = (CF_1 CF_2 CF_3 \dots CF_n)^{1/n} \quad (2)$$

where  $CF$  is the contamination factor and  $n$  is the number of determined metals.

The contaminant factor  $CF$  is defined as:

$$CF = \frac{c_{\text{metal}}}{c_{\text{background}}} \quad (3)$$

where  $c_{\text{metal}}$  is the concentration of a metal in the sample and  $c_{\text{background}}$  represents the background value for the same metal. A  $PLI$  value  $> 1$  implies pollution, whereas  $PLI < 1$  indicates no pollution.<sup>6</sup>

The enrichment factor,  $r$  is defined as the ratio:<sup>7</sup>

$$r = \frac{c_s - c_{\text{back}}}{c_{\text{back}}} \quad (4)$$

where  $c_s$  is the content of metal in the sample, while  $c_{\text{back}}$  is the concentration of the same metal in the reference sample. Metals with  $r > 1$  could be considered as indicators of anthropogenic metal pollution, whereas  $r < 1$  indicates no pollution.<sup>7</sup>

The total enrichment factor ( $R$ ) for each sample averages the enrichment factor ( $r$ ) values of the all ( $n$ ) indicator-metals as follow:

$$R = \frac{\sum r}{n} \quad (5)$$

$R$  values exceeding 1.5 indicate high pollution,  $R$  values between 1.5 and 1 imply moderate pollution, whereas samples with  $R$  values below unity are considered as unpolluted or exposed to low pollution.<sup>7</sup>

Hakanson (1980)<sup>8</sup> suggested a contamination factor ( $C_f^i$ ) and the degree of contamination ( $C_d$ ) to describe the contamination by heavy metals.  $C_f^i$  is given by:

$$C_f^i = \frac{\bar{c}_n}{c_{Rn}} \quad (6)$$

where  $\bar{c}_n$  is the mean content of a heavy metal in the investigated samples and  $c_{Rn}$  is the reference value for a heavy metal.

$C_d$  represents the sum of contamination factors for all analyzed metals and is given by:<sup>8</sup>

$$C_d = \sum C_f^i \quad (7)$$

$C_f^i < 1$  and  $C_d < 7$  indicate a low degree of contamination;  $C_f^i$  in the range from 1 to 3 and  $C_d$  in range from 7 to 14 indicate a moderate degree of contamination;  $C_f^i$  in the range from 3 to 6 and  $C_d$  in range from 14 to 28 imply a considerable degree of contamination, whereas  $C_f^i > 6$  and  $C_d > 28$  reflect a very high degree of contamination.<sup>8</sup>

In this study, the geochemical composition of soils and underlying sediments in the Kremna Basin were investigated (Fig. S-1 of the Supplementary material to this paper). This location was chosen, due to its importance as a potential

evaporite (magnesite) deposit and boron occurrence, as well as because of its proximity to the Tara National Park. The aim was to assess whether the observed heavy metal concentrations in the soil samples represent geogenic or anthropogenic impact. The second objective was to show that geochemical data of underlying sediments should be used as a tool in the determination of potential hazard for soil contamination. For this purpose, comparison was performed of the contents of heavy metals (As, Cr, Cu, Hg, Ni, Pb and Zn) of seven soil samples with standard values, a reference soil sample and the local background values of the underlying sediments. The results of the chemical composition of sixty soil samples surrounding the Kremna Basin (Fig. S-1) were used for the calculation of the reference soil sample (Table I). The local background values of the underlying sediments were calculated based on the contents of heavy metals in forty-three sediment samples from the borehole ZLT-2 (depth from 11.5 to 343 m) of the Kremna Basin (Fig. S-1; Table S-I of the Supplementary material to this paper). For assessment of geogenic (natural) and anthropogenic pollution of the soils, numerous geochemical parameters, explained above, were used.

TABLE I. Contents of heavy metals in the reference soil sample (mg kg<sup>-1</sup>), investigated soil samples and reference standard values

| Sample No.                 | As   | Cr            | Cu           | Hg   | Ni             | Pb    | Zn    |
|----------------------------|------|---------------|--------------|------|----------------|-------|-------|
| The reference soil sample  | 3.87 | 89.21         | 16.76        | 0.14 | <b>423.27</b>  | 48.10 | 52.28 |
| 1                          | 2.59 | <b>365.74</b> | 19.84        | 0.00 | <b>1261.02</b> | 4.41  | 53.79 |
| 2                          | 2.18 | <b>221.15</b> | 35.86        | 0.00 | <b>351.81</b>  | 4.12  | 39.57 |
| 3                          | 2.42 | <b>186.64</b> | <b>50.51</b> | 0.00 | <b>299.66</b>  | 4.28  | 92.47 |
| 4                          | 2.07 | <b>143.91</b> | <b>44.22</b> | 0.00 | <b>240.50</b>  | 3.88  | 59.54 |
| 5                          | 2.15 | 61.083        | 19.10        | 0.00 | <b>108.10</b>  | 4.20  | 49.75 |
| 6                          | 2.10 | <b>225.59</b> | 27.26        | 0.00 | <b>461.76</b>  | 4.07  | 51.06 |
| 7                          | 2.37 | <b>296.07</b> | <b>81.44</b> | 0.00 | <b>579.69</b>  | 4.37  | 54.15 |
| Mean value                 | 2.27 | <b>214.31</b> | 39.75        | 0.00 | <b>471.79</b>  | 4.19  | 57.19 |
| Standards                  |      |               |              |      |                |       |       |
| RS 88/2010 <sup>9</sup>    | 29   | 100           | 36           | 0.3  | 35             | 85    | 140   |
| FBIH 72/09 <sup>10</sup>   | 15   | 100           | 65           | 1.0  | 40             | 80    | 150   |
| ÖNORM L 1075 <sup>11</sup> | 20   | 100           | 50           | 1.0  | 40             | 100   | 150   |

#### EXPERIMENTAL

The soils were sampled at seven locations (see Supplementary material). From each location, soil samples were taken with a small shovel from a surface area of 40 cm×40 cm×10 cm. Each sample originally weighed 2.5 kg. In the laboratory, after removing vegetation and root remains, the samples were air dried at room temperature. Soil samples were then mixed thoroughly and the quartering procedure was used to obtain a representative sample for analyses. The obtained representative samples were gently ground in an agate mortar and finally sieved through a 63-µm sieve.

Sediment samples were dried at 105 °C. In the next step, the samples were successively crushed to 2.36 mm in three stages using a jaw crusher, cone crusher and roller crusher,

respectively. Then, the samples were homogenized. The rough milled fragmented sample was subsequently finely pulverized and sifted through a 63- $\mu\text{m}$  sieve.

About 0.1 g of soil or sediment sample was precisely weighed on an analytical balance. A mixture of 4 cm<sup>3</sup> nitric acid (HNO<sub>3</sub>, 65 %), 15 cm<sup>3</sup> hydrochloric acid (HCl, 37 %), 3 cm<sup>3</sup> orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85 %) and 1 cm<sup>3</sup> hydrofluoric acid (HF, 50 %) was used for digestion of the samples. Digestion was performed in an Advanced Microwave Digestion System (ETHOS 1, Milestone, Italy) using an HPR-1000/10S high pressure segmented rotor. The temperature was controlled with a predetermined power program. The temperature was typically increased to 220 °C in the first 15 min. The temperature of 220 °C was maintained for an additional 20 min. and then cooled down rapidly. The contents of major elements and heavy metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Thermo Scientific iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, UK) spectrometer equipped with an RACID86 Charge Injector Device (CID) detector, a pneumatic cross-flow type nebulizer, a quartz torch, and an alumina injector, which enabled samples containing HF in a small amount to be detected. The optical system was purged with argon and the Echelle polychromator was thermostated at 38 °C. Two multi-elemental plasma standard solutions (Multi-Element Plasma Standard Solution 4, Specpure<sup>®</sup>, 1000  $\mu\text{g ml}^{-1}$  and a Semi-Quantitative Standard 1, Specpure<sup>®</sup>, 10  $\mu\text{g ml}^{-1}$ ) and two single plasma standard solutions (Silicon, Specpure<sup>®</sup>, 1000 $\mu\text{g ml}^{-1}$  and Titanium, Specpure<sup>®</sup>, 1000 $\mu\text{g ml}^{-1}$ ) certified by Alfa Aesar GmbH & Co KG, Germany, were used to prepare the calibration solutions for the ICP-AES measurements. Two types of blanks were required for the analysis of the prepared samples. The calibration blank was used for establishing the analytical curve and the method blank was used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing. For each run, the samples were prepared in duplicate, and the ICP-AES measurement for each digested sample was performed in triplicate.

## RESULTS AND DISCUSSION

### *Heavy metal content in the reference soil sample*

The contents of trace elements in the reference soil sample are given in Table I. The concentrations of all elements in the reference soil sample, with the exception of Ni, were notably lower in comparison to the Serbian Regulation about the program of systematic monitoring of soil quality, indicators for risk assessment of soil degradation and methodology for development of remediation programs, RS 88/2010,<sup>9</sup> The Bosnian and Herzegovinian Regulation for the determination of permitted quantities of harmful and hazardous substances in the soil and methods of their investigation, FBiH 72/09<sup>10</sup> and the Austrian Standard, ÖNORM L 1075<sup>11</sup> values (Table I). The obtained concentration of Ni was higher than all the values given in the considered standard. However, the local background value of 165.69 mg kg<sup>-1</sup> for Ni (Table S-I), discussed below, is also higher than the standard values<sup>10,12-15</sup> (Table S-I), indicating that a high amount of Ni in the reference soil sample is of geogenic origin. Therefore, the reference soil sample could be considered as native and unpolluted and be used for an estimation of the difference between geogenic and anthropogenic impacts in the

investigated soil samples. The elevated content of Ni in the reference unpolluted soil sample (Table I) shows the importance of the mineral and geochemical composition of the underlying sediments, which should be determined prior to any land use change, particularly in areas exposed to intense weathering. Elevated Cr and Ni contents may result from ophiolites (ocean floor on land, which is usually rich in some heavy metals, such as Cr and Ni) occurring in the neighborhood (Dinaric ophiolite belt).<sup>16</sup> The same result was obtained in a recent investigation of sediments from the eastern Posavina region.<sup>17</sup>

#### *Heavy metal content in background sediments*

The background levels of heavy metals in the underlying sediments were relatively uniformly distributed within borehole ZLT-2, with exception of Cr and Ni, which were generally higher in the lower sedimentary sequence (below 200 m; Table S-I). The contents of almost all heavy metals were lower compared to the limit standard values,<sup>10,12–15</sup> with exception of Cr and Ni which were higher than the standard values (Table S-I). Elevated contents of Cr and Ni in the sediments are of geogenic origin and originated from the ultrabasic source rocks and serpentinites. According to the relatively uniform distribution of almost all the analyzed trace elements and their relatively low content (Table S-I), it could be concluded that the sediments are unpolluted, derived predominantly from natural sediment sources. Therefore, they could be used as local background levels for soil in this area to estimate the difference between geogenic and anthropogenic impacts, and to assess the enrichment of soil in heavy metals, which originate from the underlying sediments. Despite the relatively low contents of almost all the heavy metals (Table S-I), bearing in mind that the base and the edge of the Kremna Basin consist of ultrabasic rocks, serpentinite and ophiolitic mélange, which are all prone to weathering, the high concentrations of Cr and Ni, and the presence of As, Cu, Hg and Pb in the borehole ZLT-2 could be highly negative to the soil and water quality. This was confirmed by the very high values of the Chemical Proxy of Alteration, *CPA*<sup>18</sup> and the Chemical Index of Weathering, *CIW*<sup>19,20</sup> (> 80 and > 70 %, respectively), which remain continuously high even up to the depths of 150 m (Table S-I).

#### *Distribution of heavy metals in the soil samples from the Kremna Basin*

Relatively thin soil (≈40 cm) developed over Miocene sediments in the Kremna Basin. Seven samples at different locations (Fig. S-1) were taken from the surface soil horizon.

The contents of heavy metals in the soils are listed in Table I. Comparison of these results with the limit standard values<sup>9–11</sup> indicates that all samples have higher contents of Cr (sample 5 being the exception) and Ni (Table I). Moreover, three samples (3, 4 and 7; Table I) show a higher content of Cu than the limit

standard value indicated in the Serbian Regulation about the program of systematic monitoring of soil quality, indicators for risk assessment of soil degradation and methodology for the development of remediation programs, RS 88/2010<sup>9</sup> (Table I). The contents of the other trace elements were below the standard values<sup>9–11</sup> (Table I). The obtained results are in a concordance with the observation of Alexander (2013),<sup>21</sup> that strong weathering of ultramafic rocks and leaching of elements from serpentinites result in high to very high concentrations of Cr, Cu, and Ni in overlying soils, compared to the average data for world soils. The elevated contents of Cr, Cu and Ni (Table I) confirmed the notable influence of the geochemical composition of the underlying sediments on the heavy metal levels in soil.

#### *Determination of geogenic and anthropogenic impact in soils*

For more precise estimations of the geogenic and potential anthropogenic impacts on the investigated soil samples, several indices, geo-accumulation index ( $I_{geo}$ ),<sup>5</sup> pollution load index ( $PLI$ ),<sup>6</sup> enrichment factor ( $r$ ),<sup>7</sup> total enrichment factor ( $R$ ),<sup>7</sup> contamination factor ( $C_f^i$ )<sup>8</sup> and degree of contamination ( $C_d$ )<sup>8</sup> were used. The values of mentioned indices were calculated related to both, the reference soil sample (Table I) and background sediment levels (borehole ZLT-2; Table S-I). The results are presented in Tables II–V.

TABLE II. Values of geo-accumulation index ( $I_{geo}$ ) for the investigated soils, related to the reference soil sample and local background sediment level; N.D.: not determined due to concentration of Hg being below detection limit

| Soil sample No.  | As    | Cr          | Cu          | Hg   | Ni          | Pb    | Zn          |
|--|-------|-------------|-------------|------|-------------|-------|-------------|
| $I_{geo}$ , related to the reference soil sample       |       |             |             |      |             |       |             |
| 1  | -1.17 | <b>1.45</b> | -0.34       | N.D. | <b>0.99</b> | -4.03 | -0.54       |
| 2  | -1.41 | 0.72        | 0.51        | N.D. | -0.86       | -4.13 | -0.99       |
| 3  | -1.26 | 0.48        | <b>1.01</b> | N.D. | -1.08       | -4.08 | 0.24        |
| 4  | -1.49 | 0.10        | 0.81        | N.D. | -1.40       | -4.22 | -0.40       |
| 5  | -1.43 | -1.13       | -0.40       | N.D. | -2.55       | -4.10 | -0.66       |
| 6  | -1.47 | 0.75        | 0.12        | N.D. | -0.46       | -4.15 | -0.62       |
| 7  | -1.29 | <b>1.15</b> | <b>1.70</b> | N.D. | -0.13       | -4.05 | -0.53       |
| Mean value   | -1.36 | 0.50        | 0.49        | N.D. | -0.78       | -4.11 | -0.50       |
| $I_{geo}$ , related to local background sediment level |       |             |             |      |             |       |             |
| 1  | -1.74 | <b>1.11</b> | 0.87        | N.D. | <b>2.34</b> | 0.21  | <b>1.53</b> |
| 2  | -1.99 | 0.38        | <b>1.73</b> | N.D. | 0.50        | 0.11  | <b>1.09</b> |
| 3  | -1.84 | 0.14        | <b>2.22</b> | N.D. | 0.27        | 0.17  | <b>2.32</b> |
| 4  | -2.07 | -0.24       | <b>2.03</b> | N.D. | -0.05       | 0.03  | <b>1.68</b> |
| 5  | -2.01 | -1.47       | 0.82        | N.D. | -1.20       | 0.14  | <b>1.42</b> |
| 6  | -2.05 | 0.41        | <b>1.33</b> | N.D. | 0.89        | 0.09  | <b>1.46</b> |
| 7  | -1.87 | 0.80        | <b>2.91</b> | N.D. | <b>1.22</b> | 0.20  | <b>1.54</b> |
| Mean value   | -1.94 | 0.16        | <b>1.70</b> | N.D. | 0.57        | 0.14  | <b>1.58</b> |

The  $I_{\text{geo}}$  values of the investigated sediments, related to both the reference soil sample and background levels from borehole ZLT-2, are given in Table II. Comparison of the  $I_{\text{geo}}$  values calculated using the reference soil sample with the geo-accumulation index ( $I_{\text{geo}}$ ) scale<sup>5</sup> (Table II) showed that the investigated samples were unpolluted regarding As, Hg, Ni, Pb and Zn. Slight enrichment in almost all soil samples, in relation to the reference soil sample, was observed for Cr and Cu ( $I_{\text{geo}}$  in range 0.1–1.45 and 0.12–1.70, respectively; Table II). The  $I_{\text{geo}}$  values related to background sediment levels indicated that the investigated soil samples were unpolluted regarding As and Hg. For samples 4 and 5, no pollution with Cr and Ni was detected. Generally, the low mean values of  $I_{\text{geo}}$  for Cr and Ni (0.16 and 0.57; Table II) imply a geogenic origin of these elements. Slight enrichment was observed for Pb, whereas moderate pollution is noticed for Cu and Zn in all samples, as well as for Cr and Ni in several samples (Table II). These results show the importance of recognition of the biochemical and mineral composition of the underlying sediments for further land usage and prevention of risk for serious soil and water contamination.

TABLE III. Values of pollution load index ( $PLI$ ) for the investigated soils, related to the reference soil sample and local background sediment level

| Sample   | As          | Cr          | Cu          | Hg   | Ni          | Pb          | Zn          |
|--|-------------|-------------|-------------|------|-------------|-------------|-------------|
| <i>PLI, related to the reference soil sample</i>       |             |             |             |      |             |             |             |
| Soil samples   | 0.58        | <b>2.13</b> | <b>2.10</b> | 0.00 | 0.87        | 0.09        | 1.06        |
| Mean value   | 0.98        |             |             |      |             |             |             |
| <i>PLI, related to local background sediment level</i> |             |             |             |      |             |             |             |
| Soil samples   | 0.39        | <b>1.68</b> | <b>4.89</b> | 0.00 | <b>2.23</b> | <b>1.65</b> | <b>4.48</b> |
| Mean value   | <b>2.18</b> |             |             |      |             |             |             |

The values of the pollution load index ( $PLI$ ) higher than 1 (Table III) confirmed that the investigated soil samples were enriched in Cr and Cu in comparison to the reference soil sample, whereas no contamination with As, Hg, Ni, Pb and Zn was observed.<sup>6</sup> On the other hand, the values of  $PLI$  calculated in relation to the background sediment values showed moderate contamination with Cr and Pb and significant enrichment in Cu, Ni and Zn, whereas pollution with As and Hg was not detected (Table III).<sup>6</sup>

Values of the enrichment factor ( $r$ ),<sup>7</sup> calculated using the reference soil sample showed the same result as the  $I_{\text{geo}}$  and  $PLI$  values (Table IV). The soil samples were unpolluted regarding As, Hg, Ni, Pb and Zn, whereas slight enrichment was observed of the contents of Cr and Cu in almost all samples (Table IV). In comparison to background sediment levels, significant increases were noticed for Cu and Zn in all samples and for Cr and Ni in a few samples (Table IV). Values of  $r$  below 1 indicated no pollution with As, Cr (samples 2–6), Hg and Pb.<sup>7</sup>



TABLE IV. Values of enrichment factor ( $r$ ) and total enrichment factor ( $R$ ) for the investigated soils, related to the reference soil sample and local background sediment level

| Soil sample No.                                  | As    | Cr                      | Cu           | Hg          | Ni          | Pb    | Zn          |
|--|-------|-------------------------|--------------|-------------|-------------|-------|-------------|
| $r$ , related to the reference soil sample       |       |                         |              |             |             |       |             |
| 1  | -0.33 | <b>3.10<sup>a</sup></b> | 0.18         | -1.00       | <b>1.98</b> | -0.91 | 0.03        |
| 2  | -0.44 | <b>1.48</b>             | <b>1.14</b>  | -1.00       | -0.17       | -0.91 | -0.24       |
| 3  | -0.38 | <b>1.09</b>             | <b>2.01</b>  | -1.00       | -0.29       | -0.91 | 0.77        |
| 4  | -0.47 | 0.61                    | <b>1.64</b>  | -1.00       | -0.43       | -0.92 | 0.14        |
| 5  | -0.44 | -0.32                   | 0.14         | -1.00       | -0.74       | -0.91 | -0.05       |
| 6  | -0.46 | <b>1.53</b>             | 0.63         | -1.00       | 0.09        | -0.92 | -0.02       |
| 7  | -0.39 | <b>2.32</b>             | <b>3.86</b>  | -1.00       | 0.37        | -0.91 | 0.04        |
| Mean value                                       | -0.41 | <b>1.40</b>             | <b>1.37</b>  | -1.00       | 0.11        | -0.91 | 0.09        |
| $r$ , related to local background sediment level |       |                         |              |             |             |       |             |
| 1  | -0.55 | <b>2.23</b>             | <b>1.75</b>  | -1.00       | <b>6.61</b> | 0.74  | <b>3.35</b> |
| 2  | -0.62 | 0.95                    | <b>3.97</b>  | -1.00       | <b>1.12</b> | 0.62  | <b>2.20</b> |
| 3  | -0.58 | 0.65                    | <b>6.00</b>  | -1.00       | 0.81        | 0.69  | <b>6.47</b> |
| 4  | -0.64 | 0.27                    | <b>5.13</b>  | -1.00       | 0.45        | 0.53  | <b>3.81</b> |
| 5  | -0.63 | -0.46                   | <b>1.65</b>  | -1.00       | -0.35       | 0.65  | <b>3.02</b> |
| 6  | -0.64 | 0.99                    | <b>2.78</b>  | -1.00       | <b>1.79</b> | 0.60  | <b>3.13</b> |
| 7  | -0.59 | <b>1.62</b>             | <b>10.29</b> | -1.00       | <b>2.50</b> | 0.72  | <b>3.38</b> |
| Mean value                                       | -0.61 | 0.89                    | <b>4.51</b>  | -1.00       | <b>1.85</b> | 0.65  | <b>3.62</b> |
| $R$ , related to the reference soil sample       |       |                         |              |             |             |       |             |
| 1  |       |                         |              | 0.68        |             |       |             |
| 2  |       |                         |              | 0.14        |             |       |             |
| 3  |       |                         |              | 0.38        |             |       |             |
| 4  |       |                         |              | 0.10        |             |       |             |
| 5  |       |                         |              | -0.39       |             |       |             |
| 6  |       |                         |              | 0.14        |             |       |             |
| 7  |       |                         |              | 0.88        |             |       |             |
| Mean value                                       |       |                         |              | 0.28        |             |       |             |
| $R$ , related to local background sediment level |       |                         |              |             |             |       |             |
| 1  |       |                         |              | <b>2.35</b> |             |       |             |
| 2  |       |                         |              | <b>1.37</b> |             |       |             |
| 3  |       |                         |              | <b>2.34</b> |             |       |             |
| 4  |       |                         |              | <b>1.59</b> |             |       |             |
| 5  |       |                         |              | 0.65        |             |       |             |
| 6  |       |                         |              | <b>1.44</b> |             |       |             |
| 7  |       |                         |              | <b>2.98</b> |             |       |             |
| Mean value                                       |       |                         |              | <b>1.82</b> |             |       |             |

Furthermore, the  $r$  values were used for the calculation of the total enrichment factor ( $R$ ).<sup>7</sup> The values of  $R$  related to the reference soil sample were notably lower than unity, indicating no anthropogenic impact.<sup>7</sup> However, the  $R$  values related to the background sediment level indicated moderate to high enrichment, with the exception of sample 5 (Table IV). This result is primarily caused by sig-

nificantly elevated contents of Cu and Zn in the soil samples in comparison to the underlying sediments.

The values of contamination factor ( $C_f^i$ )<sup>8</sup> in the investigated soil related to the reference soil sample indicated a moderate degree of contamination in Cr and Cu and a slight enhancement in Ni and Zn, whereas no pollution with As, Hg and Pb was observed (Table V). The contamination degree ( $C_d$ )<sup>8</sup> that summarizes all contamination factors for all investigated soil samples reached 7.65, implying a low to moderate enrichment in heavy metals in relation to the reference soil sample (Table V).

TABLE V. Values of contamination factors ( $C_f^i$ ) and contamination degree ( $C_d$ ) for the investigated soils, related to the reference soil sample and local background sediment level

| Sample   | As           | Cr          | Cu          | Hg   | Ni          | Pb          | Zn          |
|--|--------------|-------------|-------------|------|-------------|-------------|-------------|
| $C_f^i$ , related to the reference soil sample       |              |             |             |      |             |             |             |
| Soil samples   | 0.59         | <b>2.40</b> | <b>2.37</b> | 0.00 | 1.11        | 0.09        | 1.09        |
| Mean value   | 1.09         |             |             |      |             |             |             |
| $C_f^i$ , related to local background sediment level |              |             |             |      |             |             |             |
| Soil samples   | 0.39         | <b>1.89</b> | <b>5.51</b> | 0.00 | <b>2.85</b> | <b>1.65</b> | <b>4.62</b> |
| Mean value   | <b>2.41</b>  |             |             |      |             |             |             |
| $C_d$ , related to the reference soil sample         |              |             |             |      |             |             |             |
| Soil samples   | 7.65         |             |             |      |             |             |             |
| $C_d$ , related to local background sediment level   |              |             |             |      |             |             |             |
| Soil samples   | <b>16.91</b> |             |             |      |             |             |             |

The contamination factors ( $C_f^i$ ) related to the background sediment values showed moderate pollution with Cr, Ni and Pb, considerable degrees of pollution by Cu and Zn and no pollution with As and Hg. This resulted in a relatively high value of  $C_d$  of 16.91, which indicates a considerable degree of contamination (Table V).<sup>8</sup>

Combining the results of all the mentioned parameters (Tables II–V), which showed very good agreement, it could be concluded that the investigated soil samples were unpolluted in terms of As, Hg, Ni, Pb and Zn, whereas slight enrichments in Cr and Cu were observed in comparison to the reference soil sample. Considering the geological origin and geochemical composition of underlying sediments, which had been exposed to intense weathering, this result is rather related to geogenic than to anthropogenic impacts.

Numerous geochemical parameters calculated in relation to the background values of the underlying sediments also showed very consistent results (Tables II–V). No pollution of the soil samples with As, Hg and Pb were observed. A slight enrichment of the soils in comparison to the underlying sediments was registered for the Cr content. Significant increases in the concentrations of Cu and Zn were detected in all soil samples and of Ni in samples 1 and 7. The ele-

vated content of Ni in these two samples could be attributed to their higher amount of organic matter. Namely, sample 1 was taken from a thin soil layer developed over an outcropping coal layer, while sample 7 was taken from a more developed soil, dark in color, indicating a higher presence of organic matter. Therefore, it could be assumed that in the Kremna Basin, Cu and Zn are the most prone to be readily incorporated into soils as result of weathering and leaching of ultramafic rocks and serpentinites. The obtained results showed the importance of the determination of the mineral and geochemical composition of underlying sediments prior to any land use change in order to prevent potential serious contamination of soil and water.

#### CONCLUSIONS

Soil samples from the Kremna Basin could be considered as unpolluted regarding the contents of As, Hg, Pb and Zn. All the investigated samples had higher contents of Cr and Ni, whereas three samples showed higher contents of Cu than the limit standard values given by the Serbian Regulation about the program of systematic monitoring of soil quality, indicators for risk assessment of soil degradation and methodology for the development of remediation programs. Values of numerous geochemical parameters calculated in relation to the reference soil sample from this area and background values of the underlying sediments in the Kremna Basin (borehole ZLT-2) indicated that the elevated concentration of Cr and Ni in the analyzed soils could be attributed to geogenic rather than to anthropogenic impact. This conclusion was support by the high values of Chemical Proxy of Alteration (*CPA*) and Chemical Index of Weathering (*CIW*), which indicated very intense weathering of the underlying rocks.

Values of the geo-accumulation index ( $I_{geo}$ ), pollution load index (*PLI*), enrichment factor (*r*), total enrichment factor (*R*), contamination factor ( $C_f^i$ ) and degree of contamination ( $C_d$ ), which indicated slight enrichment in Cr and Cu in comparison to the reference soil sample, and significant enrichment in Cu and Zn in comparison to sediment background values, imply that the Kremna area is under slight to moderate hazard risk if a land use change would occur. Physical deterioration and runoff that could easily occur would enhance the chemical weathering of deeper samples (below a depth of 10 m). In this way, heavy metals could get into soil and water. Therefore, erosion control should be mandatory in this area. This study proved that besides topographic characteristics, climatic data, and soil properties, the mineral and geochemical composition of underlying sediments play an important role in the interpretation of the level of geogenic hazard in the investigated area and should be determined prior to any land use change.

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## ИЗВОД

## ГЕОХЕМИЈСКО ИСПИТИВАЊЕ КАО ОСНОВА ЗА УТВРЂИВАЊЕ ПОТЕНЦИЈАЛНОГ РИЗИКА ОД ЗАГАЂИВАЊА ЗЕМЉИШТА (БАСЕН КРЕМНА)

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Испитиван је геохемијски састав земљишта и одговарајућих подинских седимената у басену Кремна. Циљ рада је био да се утврди да ли су концентрације тешких метала у узорцима земљишта последица природног или антропогеног загађења. Други циљ рада је био да се покаже да геохемијски подаци о подинским седиментима морају бити разматрани при утврђивању ризика од загађивања земљишта. У ту сврху изведено је поређење садржаја As, Cr, Cu, Hg, Ni, Pb и Zn у земљишту са граничним стандардним вредностима, концентрацијама ових елемената у референтном нативном узорку земљишта и загађеним подинским седиментима. Узорци земљишта нису контаминирани As, Hg, Pb и Zn. Сви испитивани узорци земљишта имају већи садржај Cr и Ni, док је у три узорка запажен повећан садржај Cu у односу на граничне стандардне вредности. Геохемијски параметри су показали да су повишене концентрације Cr, Cu и Ni у земљишту највероватније последица природног утицаја. Овом закључку у прилог иду вредности хемијског индекса промена и хемијског индекса распадања које указују на интензивно физичко и хемијско распадање седимената. Добијени резултати показују да се подручје Кремне налази под благим до умереним ризиком од било какве промене начина коришћења земљишта, и потврђују значај геохемијског састава подинских седимената при интерпретацији загађивања тешким металима.

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