METALS DISTRIBUTION AND PARTICLE SIZE ANALYSIS IN WATER AND SEDIMENT OF THE DJETINJA RIVER AND DRAGIĆA SPRING (SERBIA)

This paper reports the results on total metal concentration (Al, Fe, Cr, Cu, Ni and Zn) in water and sediment of the Djetinja river basin in the area of western Serbia. Samples were collected in spring season. Based on the comparison of the concentrations of all analyzed metals it is possible to differentiate two zones: zone I (sampling sites 1-4), affected by the discharge of the Dragića spring, and zone II (sites 5-8), affected by the confluence of the Dragića spring with the Djetinja river. The analysis of suspended solid particle size in water as well as in sediment samples was performed in size range 0.02-2000 μm and a positive correlation was found with the concentration of aluminium, zinc, iron and nickel in water samples. The study of particle size and metals distribution through the river basin of the Djetinja was a useful tool for getting information about the distribution degree of the polluting agents, and their possible evolution growth and pollution sources. The research of metals distribution and particle size analysis in water and sediment of the Djetinja river and Dragića spring (Serbia) was conducted for the first time.

Key words: metal distribution; sediment; water pollution; Djetinja river; Dragića spring.

The Djetinja Basin is located in the western part of Serbia, between 44°8' and 43°42'N and 19°27' and 20°06'E. The area of the Djetinja river basin is 1187.03 km², while the flow direction is parallel to the valley Djetinja [1]. The length of the river is 75.25 km. On the left side of the river Djetinja in Sevojno, there are sandstones, phyllite and argilosit, and on the right side are quartz conglomerates, sandstones, quartz breccias, alevrolits, sericit quartzite and massive, layered limestone [2]. The mineralogical description of the terrain, based on the location of Sevojno in the river valley, was documented in literature [3]. The south side of Sevojno is perpendicular to the river valley and limy, while the north one is silicate, away from the river, and milder [3].

Traditionally, the Djetinja river and Dragića spring (Užice, Serbia) receive pollution from two different sources, in the upper section of the Dragića stream from a primary metal manufacturing sector, Copper Mill Sevojno and, in its lower section, in the Djetinja river, from untreated urban wastes and intensive agricultural activities (Figure 1). Two major producers of semi-finished copper and aluminium in Serbia are located in Sevojno. During the copper and aluminium processing, large amounts of waste are generated in the form of: copper sediment in the process of wastewater neutralization, brass waste treated with mercury nitrate, waste copper oxides from the process of engraving, waste copper slag from the casting process, zinc oxide waste, oil concentrate in the process split emulsion, waste oil mixture, sulphuric acid solutions used for engraving copper brass products, dichromate solution used for copper and aluminium plating, oil-based rolling emulsions applied for cooling and lubricating the rollers and strips, pollution emission from the plants into the air, water, and sediment as metals: Pb, Cd, Hg, As, Cu, Fe, Zn, Ni and other pollutants [1].

The industries of the Užice and Sevojno settlements are the largest water polluters of the Djetinja river basin. Užice, with the suburban Sevojno settlements has an appropriately built sewerage system, covering mainly parts of the settlements. Wastewaters from the town's area are gravitationally dischar-

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ing into the Djetinja river, either directly or into the main collector. The main collector receives the greater part of the collected wastewaters, ending by a drain-pipe into the river towards Sevojno, upstream from the mouth of the Dragića stream. The main collector makes the framework of the sewerage network and from the left side, wastewaters of the lateral collectors flow into it from the direction of Sevojno. The extent to which a particular substance will be retained in the sediment depends on the composition of the medium through which the river flows, the speed and dynamics of the metal ions migration, the composition of the sediment in the river bed, the nature of the suspended substances contained in the water, and the equilibrium distribution process. The accumulation of pollutants, especially metals, in the river sediment has been insufficiently studied and their presence has increased with time above the maximum allowable concentration. These pollutants, through the food chain, represent a very serious hazard to humans. Therefore, there exists an urgent need to determine the ways of protecting the environment from uncontrolled spread of metals and its accumulation in the investigated region of Serbia.

Figure 1. Geographical map of Serbia.

The main polluting agents of the investigated water and sediment are metals. The total concentration of a metal provides base information about the negative effects on environmental processes and the toxicity of the sediment samples. A more sophisticated fractionation of the sediment samples based on chemical species (metals) distribution can help to understand the behaviour and the fate of the metals involved. The pollution source contained significant amounts of metals (Fe, Zn, Pb, Cd, Cu, Mn, etc.) [4]; the high pH of the medium rendered the metallic forms readily available and, therefore, easy to propagate through the river basin. Vertical transport of metals and other contaminants into sediment seems to be associated with the mobile aqueous phase or immobile solid sediment phase [5]. Regarding this, some pollutants with a strong tendency to adsorbed to the solid suspended phase and with low solubility in water are assumed to be almost immobile and, therefore, exhibit low risk to the deeper sediment layers, or even the groundwater [6]. On the contrary, colloids that are easily dispersible in the solid phase may be also mobile in the subsurface water [6, 7]. Metal mobility and transport capacity of the readily dispersible colloids that enter deeper bed loaded layers depends on the solution phenomena and, to a greater extent, on the colloids’ physical, chemical, mineralogical, and electro-kinetic properties [5].

The metal pollution in the area of river Djetinja was studied by determining total metal levels. Although these data are very useful for immediate actions to prevent the spread of the pollutants, they do not, however, provide enough information about their impact on the environment. There is a direct relationship between the physico-chemical properties of a metal and its toxicity, biological activity, bioavailability, solubility, etc. [8-11].

Particle size analysis, more specifically, particle size distribution (PSD) analysis, is very important for wastewater and sediment characterization. Physical and chemical properties of metals are closely correlated to the PSD. Smaller suspended pollutant particles are of more concern than larger particles because they have relatively high surface area, which facilitates their adsorption [12,13].

The objectives of this research were: to assess the metal distribution in sediment profiles to determine PSD and find out the correlation between the metal concentration and the PSD parameters. The study was focused on the behaviour of Al, Cr, Cu, Fe, Ni and Zn in some sediment profiles of the Djetinja river basin from the western area of Serbia. These metals are characterized by distribution under alkaline conditions, which could increase the risk of their leaching, whereby silica is leached out to leave iron and aluminium hydroxides behind caused by the alkalinity of wastewaters.
EXPERIMENTAL

Material and procedure

Water and sediment sampling. Water and sediment samples were taken from the Dragiča spring and Djetinja river in 2008. Locations of sampling sites, named 1W–8W for water and 1S–8S for sediment are shown in Figure 2. Sampling sites 1 to 4 are located on the Dragiča spring, upstream from the sites of the industrial wastewater discharge to the stream, every 50 m. The site of the confluence of the Dragiča stream with the Djetinja river is the sampling site 5, while the sampling sites 6–8 are located downstream the confluence, every 500 m, Figure 2.

The water samples were collected according to the EPA method No. 600482029 [14], in 1-L polyethylene flasks, pre-cleaned with 10% nitric acid (v/v) solution, and stored frozen at –30 °C until analysis.

For the digestion of sediment samples, according to the EPA 3050B method, a representative amount of 1-2 g (wet weight) or 1 g (dry weight) of sample was digested with repeated additions of nitric acid and hydrogen peroxide [15]. For direct energy coupling devices, such as a microwave, digest samples were prepared for the analysis by ICP-MS by adding 10 mL of 1:1 HNO₃, mixing the slurry and then covering it with a vapour recovery device. The sample was heated to 95±5 °C, refluxed for 5 min at 95±5 °C without boiling and was cooled for 5 min. Then, 5 mL of concentrated HNO₃ was added to the sample and heated to 95±5 °C and refluxed for 5 min at 95±5 °C. If brown fumes are generated, indicating oxidation of the sample by HNO₃, this step must be repeated (addition of 5 mL concentrated HNO₃) until no brown fumes are given off by the sample indicating complete reaction with HNO₃. Using a vapour recovery system, the sample was heated to 95±5 °C and refluxed for 10 min at 95±5 °C without boiling. After this step, the digestion is completed and the sample cooled, and 2 mL of water and 3 mL of 30% H₂O₂ was added. The vessel was covered with a watch glass or vapour recovery device and returned to the heat source for warming and starting the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cools the vessel. After the digestion step has been completed and the sample was cooled for 5 min, 30% H₂O₂ up to 10 mL were added. Care must be taken to ensure that losses do not occur due to excessive vigorous effervescence. 30% H₂O₂ in 1-mL aliquots was added with heating until the effervescence was minimal or until the general sample appearance was unchanged. The acid-peroxide digestate was heated to 95±5 °C in 6 min and remained at 95±5 °C without boiling for 10 min. After cooling, the digestate was diluted to 100 mL with water.

Particle size analysis

Prior to chemical analysis, the PSD analysis of the water and sediment samples was performed using a Malvern Mastersizer 2000 Particle Size Analyzer capable of analyzing particles between 0.02 and 2000

Figure 2. Location of the eight sampling sites.
μm. The Malvern Mastersizer 2000 records the light pattern scattered from a field of particles at different angles. An analytical procedure is then used to determine the size distribution of spherically shaped particles that created the patterns. The result of the analysis is the relative distribution of volume (number) of particles in the range of size classes. Measurement parameters were: pump speed, 2500 rpm; ultrasonic, off. Water samples required 100-fold preconcentration by evaporation before the analysis.

**Metal determination**

The analyzed metals, Al, Fe, Cr, Cu, Ni and Zn, were determined by inductively coupled plasma atomic emission spectrometry on a Thermo Scientific, Thermo ICAP 6500 Duo instrument, after applying the procedure according to EPA 200.7 [16]. For total recoverable analysis of a solid or aqueous sample containing undissolved material, analytes are solubilized by gentle refluxing with HNO3 and HCl. After cooling, the sample is made up to appropriate volume, mixed and then centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in an aqueous sample aliquot total recoverable determination of analytes in water sample where sample turbidity is <1 NTU, the sample is made ready for analysis by the addition of the appropriate volume of HNO3, and then diluted to a predetermined volume and mixed before analysis. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosols are transported to the plasma torch. Element specific emission spectra are produced by inductively coupled plasma. The spectrometer has Echelle type grating with 52.91 grooves/mm. Photocurrent from the photosensitive device is processed and controlled by a computer system.

**RESULTS AND DISCUSSION**

Table 1 shows the total contents of Al, Fe, Cr, Cu, Ni and Zn in the sediment and surface water from the Dragiča stream and Djetinja river along with the water pH.

The lowest pH values of the surface water were measured in the sites nearby to the source of waste inflow, due to the copper milling contamination in the area of the river Djetinja. The variations of the contents of metals (Al, Fe, Cr, Cu, Ni and Zn) in the unfiltered surface water samples are in very high corresponding patterns to the characteristic metals of copper milling processes (Figure 3) in the investigated area.

The highest concentrations of the metals in surface water were found for sampling site 3, closest to the discharge of copper mill wastewater, with a tendency to decrease at the downstream sites (Figures 3a, 3b and 3c). Nickel and chromium were found at lower concentration levels than the other metals (Figure 3b). These metals presented different evolutionary trends in sediments compared to the trends in surface waters. The concentration levels of nickel and chromium were ten times higher in the sediments than in the surface water, especially in the area of merging of the Dragiča stream with the Djetinja river, sampling site 5 (Figures 3d and 3e). The concentration levels of all the metals presented similar and parallel trends to those observed for surface waters, with a general tendency to decrease in concentration downstream (Figure 3d, 3e and 3f). The highest concentrations of Zn and Cu were found in the sites nearby to the waste discharge and as expected concentration tended to decrease downstream. Based on the comparison of the concentrations of all analyzed metals it is possible to differentiate two zones: zone I (sampling sites 1-4), affected by the discharge of the Dragiča spring, and zone II (sites 5-8), affected by the confluence of the Dragiča spring with the Djetinja river.

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**Table 1. Comparison of metal contents in sediment (mean concentration ± SD, n = 5) and surface water from the Dragiča spring and Djetinja river**

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Water pH</th>
<th>Surface Water Al mg/L</th>
<th>Sediment Al mg/kg</th>
<th>Surface Water Fe mg/L</th>
<th>Sediment Fe mg/kg</th>
<th>Surface Water Cu mg/L</th>
<th>Sediment Cu mg/kg</th>
<th>Surface Water Cr mg/L</th>
<th>Sediment Cr mg/kg</th>
<th>Surface Water Ni mg/L</th>
<th>Sediment Ni mg/kg</th>
<th>Surface Water Zn mg/L</th>
<th>Sediment Zn mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.3</td>
<td>0.12</td>
<td>1102±331</td>
<td>0.21</td>
<td>1352±81</td>
<td>12.21</td>
<td>649000±32450</td>
<td>0.04</td>
<td>112.3±11.4</td>
<td>0.01</td>
<td>112.3±11.4</td>
<td>4.23</td>
<td>8948±2684</td>
</tr>
<tr>
<td>2</td>
<td>8.3</td>
<td>0.12</td>
<td>727±218</td>
<td>0.22</td>
<td>168±101</td>
<td>12.33</td>
<td>392000±19600</td>
<td>0.04</td>
<td>108.0±8.6</td>
<td>0.01</td>
<td>24.9±2.5</td>
<td>4.29</td>
<td>108000±32400</td>
</tr>
<tr>
<td>3</td>
<td>8.3</td>
<td>1.36</td>
<td>3590±1185</td>
<td>54.2</td>
<td>2350±1410</td>
<td>18.69</td>
<td>70840±3542</td>
<td>0.68</td>
<td>85.8±6.9</td>
<td>0.13</td>
<td>23.0±2.3</td>
<td>14.85</td>
<td>4813±1444</td>
</tr>
<tr>
<td>4</td>
<td>8.3</td>
<td>0.22</td>
<td>9450±2835</td>
<td>0.42</td>
<td>5000±3000</td>
<td>8.32</td>
<td>103000±5150</td>
<td>0.02</td>
<td>103.5±8.3</td>
<td>0.02</td>
<td>56.1±5.6</td>
<td>3.71</td>
<td>3601±10800</td>
</tr>
<tr>
<td>5</td>
<td>8.2</td>
<td>0.50</td>
<td>17800±5340</td>
<td>0.18</td>
<td>8995±5397</td>
<td>0.09</td>
<td>7541±377</td>
<td>&lt;LOD</td>
<td>99.0±7.9</td>
<td>0.02</td>
<td>246.0±24.6</td>
<td>0.06</td>
<td>188±56</td>
</tr>
<tr>
<td>6</td>
<td>8.1</td>
<td>0.50</td>
<td>9060±2718</td>
<td>0.74</td>
<td>7510±4506</td>
<td>0.28</td>
<td>1175±59</td>
<td>0.02</td>
<td>173.0±13.8</td>
<td>0.02</td>
<td>99.5±9.9</td>
<td>0.07</td>
<td>464±139</td>
</tr>
<tr>
<td>7</td>
<td>8.1</td>
<td>0.18</td>
<td>5720±1716</td>
<td>1.04</td>
<td>5855±3513</td>
<td>0.09</td>
<td>882±44</td>
<td>0.06</td>
<td>56.0±4.5</td>
<td>0.02</td>
<td>55.0±5.5</td>
<td>0.03</td>
<td>225±68</td>
</tr>
<tr>
<td>8</td>
<td>8.0</td>
<td>0.07</td>
<td>8960±2688</td>
<td>0.16</td>
<td>6955±4173</td>
<td>0.29</td>
<td>632±32</td>
<td>&lt;LOD</td>
<td>78.7±6.3</td>
<td>0.01</td>
<td>83.0±8.3</td>
<td>0.01</td>
<td>281±84</td>
</tr>
</tbody>
</table>
Laser diffraction is gaining increasing popularity as a method of particle size analysis for wastewater and sediment samples [17-20]. Each sediment and water sample was analyzed in six replicates. These results were then averaged to get the PSD. Water samples required 100-fold preconcentration by evaporation before the analysis. The results were recorded as the particle volume percent in 100 discrete size ranges between 0.02 and 2000 μm. After measurement the results were recalculated as the particle number percent. The number-based PSD (averaged results) of the analyzed samples is illustrated in Figure 4. A good reproducibility was obtained between 6 measurements for each sample, standard deviations for PSD parameters are given in Tables 2 and 3. Figure 5 shows the percentage of particles by volume.

Different patterns of PSD were obtained for the sediment and water samples. The number-based PSD shows that the fraction of particles smaller than 300 nm is neglected for all samples. Water samples have
Table 2. Particle size distribution parameters for water samples (v.b. - volume-based; n.b. - number-based)

<table>
<thead>
<tr>
<th>Sample</th>
<th>d(0.1) / μm</th>
<th>d(0.5) / μm</th>
<th>d(0.9) / μm</th>
<th>D[4,3] / μm</th>
<th>D[1,0] / μm</th>
<th>Span</th>
</tr>
</thead>
<tbody>
<tr>
<td>v.b.</td>
<td>n.b.</td>
<td>v.b.</td>
<td>n.b.</td>
<td>v.b.</td>
<td>n.b.</td>
<td></td>
</tr>
<tr>
<td>1W</td>
<td>10±1</td>
<td>0.40±0.02</td>
<td>50±2</td>
<td>0.51±0.01</td>
<td>161±6</td>
<td>0.84±0.03</td>
</tr>
<tr>
<td>2W</td>
<td>9±1</td>
<td>0.45±0.02</td>
<td>35±2</td>
<td>0.56±0.01</td>
<td>108±5</td>
<td>0.92±0.03</td>
</tr>
<tr>
<td>3W</td>
<td>10±1</td>
<td>0.45±0.02</td>
<td>59±2</td>
<td>0.57±0.01</td>
<td>410±5</td>
<td>0.96±0.03</td>
</tr>
<tr>
<td>4W</td>
<td>10±1</td>
<td>0.42±0.02</td>
<td>37±2</td>
<td>0.54±0.01</td>
<td>98±5</td>
<td>0.90±0.03</td>
</tr>
<tr>
<td>5W</td>
<td>3±1</td>
<td>0.39±0.02</td>
<td>48±2</td>
<td>0.51±0.01</td>
<td>141±5</td>
<td>0.83±0.03</td>
</tr>
<tr>
<td>6W</td>
<td>12±1</td>
<td>0.40±0.02</td>
<td>48±2</td>
<td>0.52±0.01</td>
<td>141±5</td>
<td>0.83±0.03</td>
</tr>
<tr>
<td>7W</td>
<td>16±1</td>
<td>0.39±0.02</td>
<td>70±2</td>
<td>0.51±0.01</td>
<td>198±7</td>
<td>0.81±0.03</td>
</tr>
<tr>
<td>8W</td>
<td>11±1</td>
<td>0.45±0.02</td>
<td>40±2</td>
<td>0.57±0.01</td>
<td>100±5</td>
<td>0.93±0.03</td>
</tr>
</tbody>
</table>

Figure 4. Number-based particle size distribution of W (a) and S (b) samples.
Table 3. Particle size distribution parameters for sediment samples (v.b. - volume-based; n.b. - number-based)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d(0.1) ) / ( \mu m )</th>
<th>( d(0.5) ) / ( \mu m )</th>
<th>( d(0.9) ) / ( \mu m )</th>
<th>( D[4,3] ) / ( \mu m )</th>
<th>( D[1,0] ) / ( \mu m )</th>
<th>Span</th>
</tr>
</thead>
<tbody>
<tr>
<td>v.b.</td>
<td>n.b.</td>
<td>v.b.</td>
<td>n.b.</td>
<td>v.b.</td>
<td>n.b.</td>
<td>v.b.</td>
</tr>
<tr>
<td>1S</td>
<td>24 ± 4</td>
<td>0.95 ± 0.08</td>
<td>107 ± 7</td>
<td>1.2 ± 0.1</td>
<td>396 ± 16</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>2S</td>
<td>5 ± 2</td>
<td>0.35 ± 0.07</td>
<td>38 ± 6</td>
<td>0.5 ± 0.1</td>
<td>533 ± 20</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>3S</td>
<td>19 ± 3</td>
<td>0.84 ± 0.08</td>
<td>139 ± 7</td>
<td>1.1 ± 0.1</td>
<td>458 ± 20</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>4S</td>
<td>6 ± 3</td>
<td>0.45 ± 0.07</td>
<td>32 ± 6</td>
<td>0.6 ± 0.1</td>
<td>168 ± 15</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>5S</td>
<td>6 ± 3</td>
<td>0.48 ± 0.07</td>
<td>47 ± 5</td>
<td>0.7 ± 0.1</td>
<td>346 ± 20</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>6S</td>
<td>9 ± 3</td>
<td>0.83 ± 0.08</td>
<td>70 ± 6</td>
<td>1.0 ± 0.1</td>
<td>312 ± 18</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>7S</td>
<td>12 ± 3</td>
<td>0.83 ± 0.08</td>
<td>72 ± 6</td>
<td>1.0 ± 0.1</td>
<td>334 ± 20</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>8S</td>
<td>18 ± 4</td>
<td>0.83 ± 0.08</td>
<td>72 ± 6</td>
<td>1.0 ± 0.1</td>
<td>213 ± 18</td>
<td>1.9 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 5. Volume-based particle size distribution of W (a) and S (b) samples.

approximately the same number-based size distribution curves, regardless of the distance from the wastewater inflow. This is due to high water velocity in spring and the fact that the dispersed materials are incorporated into wastewater. Than the wastewater suspension system has the ability to stay in waste suspension longer and therefore transported to a greater distance. The most common values of the fre-
quency distribution curve (mode) for water samples are in the size range of 400-500 nm. The maxima on the number-based PSD curves for water samples are shifted towards smaller particles compared to sediment samples, except for the samples collected at sites 2 and 4.

Volume-based results indicate the location of most of the mass of suspended material in terms of particle size. All mode values are below 8% in mass of suspended solids. The volume-based PSD curves are rather wide. The measure of the curve width is the span. The spans for the volume-based PSD curves are larger for sediment samples than for the water samples. Characteristic parameters for PSD are given in Tables 2 and 3. The \(d(0.1), d(0.5)\) and \(d(0.9)\) values indicate that 10, 50 and 90% of the particles measured were smaller than or equal to the size stated. \(D[4,3]\) and \(D[1,0]\) are the volume-weighted and number-weighed means calculated from the volume- and number-based results, respectively. The mean values are calculated according to formula:

\[
D[m,n] = \frac{\sum f_i d_i^m}{\sum f_i d_i^n}
\]

where \(f_i\) is a fraction of particles with diameter \(d_i\).

Particle size distribution in sediment samples is also determined according to the Wentworth scale using volume based PSD results (Figure 6). The Wentworth scale, called the “Phi” scale, classifies particles by size from “colloid” to “boulder”. Particles are sized by the negative logarithm to the base 2 of the particle’s diameter in millimetres. This analysis shows that all samples, except 1S, are mainly composed of the silt (3.9-62.5 μm). The silt percentage ratio is higher for Djetinja river sediment samples than for Drageća spring samples, except for sample 4S.

One of the aims of this work was to investigate the correlation between metal content and PSD parameters. We considered both the number- and volume-based PSD parameters for both water and sediment samples, and no correlation could be ascertained between the number-based PSD parameters and concentration of the metals. A positive correlation could be determined between the volume-weighted mean \((D[4,3])\) or \(d(0.9)\) and the concentrations of Al, Cr, Ni and Fe in water samples. The increase in the volume-based PSD parameter, Figure 7, is followed by an increase in metal content. Pearson’s correlation coefficient between metal concentration and volume-weighted mean are: 0.85; 0.91; 0.89 and 0.89 for Al, Cr, Ni and Fe respectively. All values are close to 0.9, indicating high positive correlation between these two parameters.

**CONCLUSIONS**

Accordingly to the results, the studied area can be classified into two separate zones: the Drageća spring as a first zone, between the sampling sites 1 and 4, and the second zone, the Djetinja river, between the sampling site 5 and 8. The metal distribution obtained for the samples confirms the above spatial differentiation. The high concentration levels of metals were observed in zone I, while in zone II these concentrations were ten times higher in sediments.

Spring water samples have approximately the same number based size distribution curves, regardless the distance from the source of pollution. Factors that affect the velocity of a river include the slope gradient, the roughness of the channel, and water-level.

The particle size analysis was in correlation between metal content and PSD parameters. One of the results obtained had a positive correlation between the volume-weighted mean \((D[4,3])\) or \(d(0.9)\) and the
concentrations of Al, Cr, Ni and Fe in water samples. The fact that no correlation could be ascertained between the number-based PSD parameters and concentration of the metals indicated that metal concentration is not connected with the total number of suspended particles but with their mass.

The study of particle size and metals distribution through the river basin of the Djetinja has demonstrated to be an useful tool for getting information about not only the distribution degree of the polluting agents but also about their possible evolution growth and pollution sources.

The research of metals distribution and particle size analysis in water and sediment of the Djetinja river and Dragiće spring (Serbia) was conducted for the first time.

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ANALIZA RASPODELE METALA I VELIČINE ĆESTICA U VODI I SEDIMENTU REKE ĐETINJE I DRAGIĆA POTOKA (SRBIJA)

U radu su prikazani rezultati ukupne koncentracije metala (Al, Fe, Cr, Cu, Ni i Zn) u vodi i sedimentu basena reke Đetinje u zapadnoj Srbiji. Uzorci su sakupljeni u proljećnom periodu. Na osnovu poređenja koncentracijskih nivoa svih analiziranih metala ispitivana oblast je podeljena u dve različite zone: zona I (lokaliteti 1–4), okarakterisana kao direktni prijemnik otpadnih voda valjaonica bakra “Sevojno” u Dragića potoku i zona II (lokaliteti 5–8), koja obuhvata mesto ulivanja Dragića potoka u reku Đetinju i njen dalji tok. Analiza raspodele veličina suspendovanih čestica u uzorcima vode i sedimenata urađena je u opsegu 0.02–2000 μm. Ustanovljena je pozitivna korelacija parametara distribucije veličine čestica sa koncentracijama aluminijuma, cinka gvožđa i nikla u uzorcima voda. Ispitivanje raspodele veličine čestica i metala duž basena reke Đetinje predstavlja koristan metod za utvrđivanje intenziteta raspodele zagađujućih agenasa i njihovog mogućeg rasta u prisustvu izvora zagađenja. Prema našim saznanjima ispitivanja raspodele metala i veličine čestica u vodi i sedimentu reke Đetinje i Dragića potoka izvršena su po prvi put.

Ključne reči: raspodela metala; veličina čestica; sediment; zagađenje voda; reka Đetinja, Dragića potok.