Multielement sorption of cadmium, zinc, copper and lead onto a Fluvisol profile at the Stara Loza site, Croatia

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Abstract: The subject of this study is the Fluvisol profile, developed in the Stara Loza water wellfield area of the Zagreb aquifer. The main objectives of the investigation were: 1) to determine the sorption characteristics of lead, zinc, copper and cadmium using a batch experiment and 2) to build isotherms of potentially toxic metals (PTMs) in soil horizons of Fluvisol. The soil texture is silt loam of a light yellow colour, and granular structure. The pH values of the soil vary from 7.97 to 8.38. Cation exchange capacity (CEC) has higher values in the first three horizons. Based on the results of the experiment, linear sorption isotherms were created for all the soil horizons. Freundlich distribution coefficients are determined from sorption isotherms, and the sequence is Pb > Cu > Cd > Zn. The comparison of sorption isotherms has determined that lead has the best sorption in the soil. Sorption of potentially toxic metals decreases with depth.

Keywords: sorption; Fluvisol; potentially toxic metals; Croatia.

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Teo Jašaragić Rako has studied Petrology and Mineral Resources in the Faculty of Mining, Geology and Petroleum Engineering at the University of Zagreb, Croatia. He has experience in mineralogical and chemical investigation of sediments and soils using atomic absorption spectrometry (AAS).
1 Introduction

Soil plays an important role in a substance’s circulation in nature, including metal cations. The accumulation of metal cations in the soil, and their transport through the soil to the aquifer, is a serious problem in the preservation of the soil and underground water which is used for human consumption. In this study, a soil profile located in the Zagreb aquifer is sampled and analysed. The Zagreb aquifer is an open and shallow type, which presents a high risk of contamination. Potential sources of contamination near the soil sampling area are industrial plants, traffic and intensive agriculture. The study of sorption properties of the soil is important because it can help solve the problem of contamination. Soil can immobilise and thereby reduce the migration of potentially toxic metals (PTMs) in its deeper parts, depending on the soil and the contaminants’ characteristics.

Adsorption processes are often influenced by various soil factors, which are difficult to measure. Often, empirical models, which represent a description of adsorption data, are applied. The two empirical models most frequently used to describe PTMs adsorption in/on soil components are Freundlich (1909) and Langmuir (1917) isotherms. These simple models are often used to express laboratory sorption data if specific models are lacking. Amongst others, Sipos (2009) and Liang et al. (2010) modelled the adsorption of Cu, Pb, and Zn onto various soils and sediments using Freundlich and Langmuir isotherms. Sipos (2009) studied the sorption of copper, lead and zinc on a silty loam type of soil. Liang et al. (2010) studied the sorption of copper and lead on a silty loam type of soil as well.

Numerous studies of the contamination of soils and sediments with PTMs were carried out in the area of the Zagreb aquifer (Namjesnik et al., 1992; Durn et al., 1999; Romić and Romić, 2003; Sollitto et al., 2010) as parts of various professional and scientific projects. In all the aforementioned studies, the top soil distribution of metals were analysed. Ružičić (2013), in his doctoral thesis, studied the sorption of lead, zinc and cadmium in soil developed on the field of water wells of Kosnica that is a part of the Zagreb aquifer. In this study, isotherms were created from the sorption experiment. The best sorption properties were determined in surface horizons (which have a higher CEC), while the difference in sorption between individual metals was small. Romić (2002), in her doctoral thesis studied sorption and the distribution of lead, zinc, copper and cadmium in soils which were located in the Zagreb county and the city of Zagreb. In this study, the author concluded that various PTMs are bounded and distributed for different fractions of soil. Marić (2014), in his diploma thesis created sorption isotherms of copper in Fluvisol developed on the field of water wells of Kosnica. The best sorption properties were determined in surface horizons, while sorption values decrease with an increase in depth.

Vega et al. (2008), made a sorption experiment of Cu, Pb and Cd on 20 soil samples from Spain. They studied the sorption of metals prepared from single and multi-element solutions.

The authors found that lead absorbs in the soil equally well in both solutions. The sorption of lead is greater than that of copper, while the sorption of copper is higher than cadmium sorption. Lofti et al. (2009) made the sorption experiment of lead and zinc in the soil samples taken near the town of Amizour (Algeria) as a function of reaction time, pH, ionic strength and the concentration of metal in solution. The isotherm results show that lead has a higher affinity in comparison to zinc for binding on soil particles.
The subject of this study is the Fluvisol profile developed in the area of the water wellfield Stara Loza of the Zagreb aquifer. The main objectives of the investigation were:

1. to determine the sorption characteristics of lead, zinc, copper and cadmium using a batch experiment
2. to build PTMs isotherms in soil horizons of Fluvisol.

2 Materials and methods

2.1 Study area

The studied soil profile is Fluvisol (FAO, 2006), which was formed on former flood fields or on their elevated parts that were frequently flooded during the earlier period where the frequent deposition of particles prevented the development of the soil. The investigated Fluvisol profile is located in the eastern part of the city of Zagreb, about six hundred and fifty metres from the left bank of the Sava river (X:5568734; Y:5072217) (Figure 1). Location sampling is located in the third zone of sanitary protection of the Stara Loza water well field. The studied soil is inside the Fluvisols that cover about 41% of the Zagreb aquifer (Ružičić, 2013). The soil profile is mainly silt loam in texture; in some parts sandy loam prevails. The following soil horizons were recognised: A-C-2C-3C-4C-5Cl. The structure of the soil profile is mainly granular. Chemical, physical and mineralogical properties of the studied profile are summarised in Table 1. This soil was created in terms of specific pedogenetic processes, where the dominant factors are relief, parent material and vegetation cover.

Table 1  Physical and chemical characteristics of the studied soil. Legend: Dol-dolomite, Cal-calcite, Chl-chlorite, Kl-kaolinite

<table>
<thead>
<tr>
<th>Soil horizon</th>
<th>Depth (cm)</th>
<th>Colour</th>
<th>Clay (%)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>pH (H2O)</th>
<th>CEC (cmol/kg)</th>
<th>Carbonate (%)</th>
<th>Clay mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0–20</td>
<td>2.5 Y 6/4</td>
<td>8</td>
<td>8</td>
<td>84</td>
<td>8</td>
<td>23.21</td>
<td>~ 30% (Dol &gt;&gt; Cal)</td>
<td>Chl; Kl</td>
</tr>
<tr>
<td>C</td>
<td>20–50</td>
<td>2.5 Y 6/4</td>
<td>12</td>
<td>6</td>
<td>82</td>
<td>7.97</td>
<td>24.1</td>
<td>~ 35% (Dol &gt;&gt; Cal)</td>
<td>Chl; Kl</td>
</tr>
<tr>
<td>2C</td>
<td>50–80</td>
<td>2.5 Y 6/4</td>
<td>40</td>
<td>4</td>
<td>46</td>
<td>8.14</td>
<td>22.9</td>
<td>~ 30–35% (Dol &gt;&gt; Cal)</td>
<td>Chl; Kl</td>
</tr>
<tr>
<td>3C</td>
<td>80–100</td>
<td>2.5 Y 6/3</td>
<td>21</td>
<td>18</td>
<td>61</td>
<td>8.1</td>
<td>15.97</td>
<td>~ 40% (Dol &gt;&gt; Cal)</td>
<td>Chl; Kl</td>
</tr>
<tr>
<td>4C</td>
<td>100–140</td>
<td>2.5 Y 6/3</td>
<td>18</td>
<td>30</td>
<td>52</td>
<td>8.29</td>
<td>14.86</td>
<td>~ 50% (Dol &gt;&gt; Cal)</td>
<td>Chl; Kl</td>
</tr>
<tr>
<td>5C1</td>
<td>140–170</td>
<td>2.5 Y 6/3</td>
<td>16</td>
<td>53</td>
<td>31</td>
<td>8.38</td>
<td>15.35</td>
<td>~ 50% (Dol &gt;&gt; Cal)</td>
<td>Chl; Kl</td>
</tr>
</tbody>
</table>
2.2 Analytical techniques

One disturbed soil sample from each of the six soil horizons for laboratory analysis and experiments were collected. The soil samples were air-dried and passed through a 2 mm sieve for laboratory experiments. Soil pH was measured in water with a 1:5 soil to water ratio (ISO 10390, 2005) using a Multi 340i WTW pH meter. Particle size distribution was determined by sieving and pipette methods. The studied soil samples were characterised for mineralogical composition using a Philips diffractometer 1710 (graphite monochromator, CuKa radiation, proportional counter). The identification of clay minerals was generally based on the methods outlined by Brown (1961), Brindley and Brown (1980), and Moore and Reynolds (1989). Metal concentrations in the solutions were analysed by a Perkin Elmer AAnalyst 700 atomic absorption spectrometer (AAS). Cation exchange capacity (CEC) was determined using a barium chloride solution (ISO, 13536, 1995).

2.3 Sorption experiment

A batch sorption experiment was carried out in polypropylene centrifuge tubes of 50 ml by mixing 2 g of the sample with 30 ml of solution containing various concentrations of the studied metals ($\text{Cu}^{2+}$, $\text{Pb}^{2+}$, $\text{Cd}^{2+}$, $\text{Zn}^{2+}$) with initial concentrations of 0.01, 0.05, 0.1, 0.5 and 1 mmol/l. Metals were added to the solutions in the form of nitrates. Nitrates are often used in these types of experiments (Lofti at al., 2009; Vega et al., 2008; Kookama and Naidu, 1998; Harter and Naidu, 2001). Sorption isotherms for the analysed metals...
Multielement sorption of cadmium, zinc, copper and lead onto a Fluvisol were established for the six soil samples. The experiment was conducted with three replicates. Soils were equilibrated for 24 h by shaking at room temperature. The suspensions were then centrifuged at 3,800 rpm for 10 minutes, and the metals’ concentration in the equilibration solution was measured by atomic absorption spectrometry (AAS) (Perkin Elmer AAAnalyt 700 instrument).

2.4 Sorption data equations

The amount of metals adsorbed by the studied soil samples were calculated using the equation:

\[ S_i = \frac{(c_i - c_{eq}) \times V_i}{W} \]  

(1)

where \( S_i \) is the amount of metal removed from solution of the \( i^{th} \) sample (mg/g), \( c_i \) the concentration of metal in the solution of the \( i^{th} \) sample before mixing with soil (mg/l), \( c_{eqi} \) the equilibrium concentration of contaminant left in the solution of the \( i^{th} \) sample after the experiment (mg/l), \( V_i \) the solution volume of the \( i^{th} \) sample (l) and \( W \) the weight of air-dried soil of the \( i^{th} \) sample (g).

The linear form of the Freundlich isotherm equation was used to describe the sorption of the metals from the solution onto the studied soil samples. The simple linear relationship between sorbed and solution phases is expressed as:

\[ S = K_d c \]  

(2)

where \( S \) is the concentration of solute adsorbed onto the solid phase (mg/g), \( K_d \) the slope of the isotherm, often referred to as the distribution coefficient (l/kg), and \( c \) the metal concentration in the solution (mg/l).

Relative sorption capacity (RSC) was also used to compare the metal sorption capacity of the samples (Xiong et al., 2005). The RSC can be calculated by taking the difference between the initial and equilibrium metal concentrations, then dividing this difference by the initial metal concentration, and then expressing this as a percentage. Similarly, as is the case with the distribution coefficient, this parameter is also calculated by summarising the individual RSC values as follows:

\[ RSC_i = \frac{\sum (c_i - c_{eqi})}{\sum c_i} \times 100 \]  

(3)

3. Results and discussion

3.1 Soil physical and chemical characteristics

The physical and chemical characteristics of the soils are summarised in Table 1. The particle size distribution of the soils exhibits a substantial variation in sand, silt, and clay contents, ranging from 4% to 53% for sand, 31% to 84% for silt, and 8% to 40% for clay. The soil pH increases with depth, ranging from 7.97 to 8.38 in a water solution. The soil is slightly alkaline, whose alkalinity can be caused by the presence of calcium and
magnesium carbonates. Romić and Romić (2003) and Ružičić (2013) determined the pH of Fluvisol on the Črnkovec and Kosnica sites which ranges from 7.3 to 8.8. The aforementioned studies of Fluvisol can be compared with the Stara Loza site soil, since their physical and chemical characteristics are similar. Inert minerals, such as quartz and feldspars, dominate in the mineralogical composition of the studied profile. Besides these minerals, carbonate minerals, such as dolomite and calcite, are also present (from 30% to 50%) in the soil profile. The carbonate component increases with depth. Dolomite is more prevalent in comparison to calcite. The increase of carbonates with depth can be connected with the increase of the pH of the soil. The clay mineralogy of the studied profile is characterised by chlorite and kaolinite. The CEC values are the highest in the first three horizons, ranging from 22.9 cmol/kg to 24.1 cmol/kg (Table 1). The sample from the 2C horizon is characterised by clay mineral accumulation and the 2C horizon is among the horizons with the highest CEC values. The soil samples from the 3C, 4C and 5C1 horizons of the profile are characterised by carbonates (approx. 50% content), as well as with the lowest CEC values in the profile.

3.2 Sorption experiment

The sorption experiment results are summarised in Table 2. The Freundlich linear adsorption isotherm showed the best fit for each of the samples and metals studied. The \( R^2 \) values were above 0.98. Copper and lead showed the highest affinity towards the studied samples, followed by cadmium and zinc (Figure 2).

Figure 2  The linear form of the Freundlich isotherms for Cd, Zn, Cu and Pb
<table>
<thead>
<tr>
<th>Metal</th>
<th>Soil horizon</th>
<th>RSC (%)</th>
<th>Isotherm</th>
<th>Kd (l/kg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>A</td>
<td>99.63</td>
<td></td>
<td>26.6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>99.21</td>
<td></td>
<td>28.4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2C</td>
<td>99.88</td>
<td></td>
<td>28.1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3C</td>
<td>99.23</td>
<td></td>
<td>27.1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4C</td>
<td>99.26</td>
<td></td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>5C1</td>
<td>99.40</td>
<td></td>
<td>26.6</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>A</td>
<td>95.11</td>
<td></td>
<td>25.1</td>
<td>0.9968</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>92.19</td>
<td></td>
<td>26.2</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>2C</td>
<td>91.72</td>
<td></td>
<td>25.3</td>
<td>0.9985</td>
</tr>
<tr>
<td></td>
<td>3C</td>
<td>87.41</td>
<td></td>
<td>23.1</td>
<td>0.9911</td>
</tr>
<tr>
<td></td>
<td>4C</td>
<td>84.63</td>
<td></td>
<td>22.5</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>5C1</td>
<td>83.83</td>
<td></td>
<td>21.8</td>
<td>0.9897</td>
</tr>
<tr>
<td>Cd</td>
<td>A</td>
<td>93.48</td>
<td></td>
<td>24.4</td>
<td>0.9976</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>91.76</td>
<td></td>
<td>25.6</td>
<td>0.9977</td>
</tr>
<tr>
<td></td>
<td>2C</td>
<td>90.94</td>
<td></td>
<td>24.8</td>
<td>0.9974</td>
</tr>
<tr>
<td></td>
<td>3C</td>
<td>90.67</td>
<td></td>
<td>24.3</td>
<td>0.9997</td>
</tr>
<tr>
<td></td>
<td>4C</td>
<td>89.03</td>
<td></td>
<td>24</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>5C1</td>
<td>87.62</td>
<td></td>
<td>23.4</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>A</td>
<td>99.86</td>
<td></td>
<td>26.7</td>
<td>1</td>
</tr>
<tr>
<td></td>
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<td>27.2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>5C1</td>
<td>99.61</td>
<td></td>
<td>26.7</td>
<td>1</td>
</tr>
</tbody>
</table>

Lead has the highest sorption coefficient in the soil (Figure 2) which is congruent with similar research by Vega et al. (2008). In their study, the authors confirmed that lead sorption in soils correlates well with the CEC values, the proportion of Mn-oxides, and the clay minerals. In their research, Vega et al. (2008) concluded that soil horizons with high sorption coefficients of lead, also have a high value of copper coefficients (Table 2). Cadmium has a lower sorption capacity in comparison to lead and copper (Figure 2). According to Dere et al. (2006), cadmium shows a tendency to migrate in the lower soil horizons which have lower contents of organic matter. In their study, Vega et al. (2006) concluded that in the presence of other metals, cadmium has less competency properties for sorption. The least competitive in this experiment is zinc. In their work, Lofti et al. (2009) explored the sorption properties of lead and zinc as a function of pH. The authors concluded that with an increase in pH, the sorption effect of the studied metals in the soil would be increased.

According to Xiong et al. (2005), relative sorption capacity is a useful measure to compare and contrast sorption between different metal ions present in varying initial
concentrations. The joint relative sorption capacity of the studied PTMs of the samples was between 99.35% and 99.92% for Pb, between 99.21 and 99.88% for Cu, between 83.83% and 95.11% for Zn and between 87.62% and 93.48% for Cd. The first horizon (A) has the maximum sorption capacity of all PTMs at 97%, while the deepest soil horizon (5C1) is 92%.

The effect of PTMs sorption is influenced by the cation exchange capacity (CEC), soil pH, redox potential, the content of clay components, the type of clay minerals, the content of organic matter, iron and manganese oxides and carbonates (McLean and Bledsoe, 1992; Bradl, 2004). The first two soil horizons (A and C), which are silts in texture, can be correlated with sorption results of lead in the same soil horizons.

**Figure 3** The correlation between the sorption experiment and cation exchange capacity results

Based on the sorption experiment and cation exchange capacity results, a correlation was made, which amounts to 0.8311 (Figure 3). It can be argued that the greatest value of CEC and sorption is just related to the first, shallowest horizon A, which also has a large content of clay and silt. During their research, Hooda and Alloway (1998) found that the soils with higher values of cation exchange capacity are better able to hold cadmium and lead.

From carbonate proportion and the sorption experiment results, a correlation was made, which amounts to 0.9559 (Figure 4). The presence of carbonates in the soil created new sorption sites and favoured the precipitation of Cu, Pb and Zn (Fontes et al., 2003). In the 5C1 soil horizon the presence of carbonates led to an elevated pH level (soil pH = 8.38) which may have encouraged copper and lead precipitation on carbonates.
4 Conclusions

The soil at the study location is Fluvisol. The texture of this soil is silt loam and the structure is granular. The soil is slightly alkaline whose alkalinity can be caused by the presence of calcium and magnesium carbonates. The XRD analyses show that quartz and feldspars dominate in the mineralogical composition of the studied profile. Besides these minerals, carbonate minerals, such as dolomite and calcite are also present (from 30 to 50%) in the soil profile. Carbonate components increase with depth. Dolomite is more prevalent in comparison to calcite. The increase of carbonates with depth can be connected with the increase of the pH of the soil. The clay mineralogy of the studied profile is characterised by chlorite and kaolinite. The CEC values are the highest in the first three horizons.

Based on the results of the sorption experiment, linear sorption isotherms were created for all the soil horizons. Freundlich distribution coefficients were determined from sorption isotherms and their sequence is Pb > Cu > Cd > Zn. The comparison of sorption isotherms of potentially toxic metals through the soil profile has determined that lead has the best sorption in the soil. The sorption of metals decreases with depth, e.g., decreases with the increase of the proportion of sand. The sorption results strongly correlate with the CEC (83%) and carbonates proportion (96%).

In the case of potential accidents and contamination with potentially toxic metals, it is evident that lead and copper will be more bonded to soil particles in comparison to cadmium and zinc. Sorption results within this study may serve as a basis and a source of
information for future work that would be interesting, such as desorption and a transport model of PTMs in the soil.

References


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