Mathematical Modeling for the Accumulation of Cadmium, Zinc and Arsenic from the Soil in the Case of Bulrush Plant Type

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This paper proposes a tridimensional mathematical model of the accumulation of cadmium, arsenic and zinc from the soil in the case of bulrush plant type (the soil and plant samples was taken from two points along the Bistrița River, belonging to the Siret hydrographic basin). The variable measures taken into consideration when carrying out the experiments and realizing the mathematical model are the distance from the water-soil interface from which the plant samples were taken and the content of cadmium, arsenic and zinc in the soil. The mathematical model was elaborated and tested by means of the TableCurve 3D program used for generating linear and non-linear equations. A reduced accumulation capacity of arsenic from the soil was registered. A high accumulation of cadmium from the soil was registered, in the case of bulrush plant type (765÷875 % higher than in the soil). The correlation coefficient of the mathematic model was between 0.94-0.99.

Keywords: cadmium, arsenic, zinc, mathematical model, accumulation, Typha Latifola’s

Unlike the other components of the environment, the soil plays the role of a biological pollutant absorber, purifier and neutralizer, mineralizing organic residues [1-7].

For a long time the soil has the capacity of natural self-cleaning in the environment. [2, 5, 8-19].

The main sources of pollution of water and sediments with heavy metals are: geological (natural) sources, industrial and domestic uses of heavy metal salts (for example, copper, arsenic, zinc and mercury in pesticides or lead in gasoline), from excretions human and animals, infiltration from garbage dumps, etc. Sediments accumulate metal compounds that, under some special conditions, can be released into water. The concentrations of heavy metals in sediments are much higher than in water, they are perfect deposits for polluting sediment and represent an important source of passage to living organisms, which play an important role in maintaining the balance of any aquatic ecosystem. Metals are the components essentials of life, but they become harmful when they are present in excess [3, 5, 6, 8, 19 ÷ 29].

This paper proposes a mathematical model of the accumulation of cadmium, arsenic and nickel from the soil in the bulrush plant type (Typha Latifola’s).

Experimental part

Points taken into consideration for prelevation specimens along the Bistrita River, the Siret hydrographic basin [3] of soil and plants are presented in figure 1. Sediments were sampled from two points along the Bistrita River, belonging to the Siret hydrographic basin (downstream of Batca Doamnei lake - upstream of Piatra Neamt city and Dumbrava Rosie - downstream of Piatra Neamt city) [3, 19, 28].

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The experimental variants carried out at Siret hydrographic basin have been presented in figure 2.

**Results and discussions**

Tabel 1 presented the experimental values determined for three heavy metals (cadmium, arsenic and zinc) in the soil and bulrush plant type from unpolluted soils (witness sample).

<table>
<thead>
<tr>
<th>Point unpolluted</th>
<th>Cadmium [mg/kg dry matter]</th>
<th>Arsenic</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>0.67</td>
<td>26</td>
<td>124</td>
</tr>
<tr>
<td>Bulrush</td>
<td>0.024</td>
<td>0.03</td>
<td>14.03</td>
</tr>
<tr>
<td>Root + stem + leaf</td>
<td>0.024</td>
<td>0.03</td>
<td>14.03</td>
</tr>
</tbody>
</table>

Table 2 presented the experimental values determined for three heavy metals (cadmium, arsenic and zinc) in the soil in two sampling points: downstream of Batca Doamnei lake - upstream of Piatra Neamt city and Dumbrava Rosie - downstream of Piatra Neamt city.
The permissible limit for cadmium (0.8 mg/kg dry matter), is not exceeded in downstream of Bătca Doamnei lake - upstream of Piatra Neamt city sampling point (the maximum values determined was 0.338 mg/kg dry matter).

The permissible limit for arsenic (29 mg/kg dry matter) is not exceeded in downstream of Bătca Doamnei lake - upstream of Piatra Neamt city sampling point and the determined values ranged between 15.1 mg/kg dry matter and 17.28 mg/kg dry matter (Table 2).

### Table 2

<table>
<thead>
<tr>
<th>Points polluted</th>
<th>Cadmium (Cd) [mg/kg dry matter]</th>
<th>Arsenic (As) [mg/kg dry matter]</th>
<th>Zinc (Zn) [mg/kg dry matter]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Downstream of BATCA DOAMNEI LAKE</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₁</td>
<td>0.338</td>
<td>16.4</td>
<td>128.3</td>
</tr>
<tr>
<td>D₂</td>
<td>0.269</td>
<td>15.1</td>
<td>94.73</td>
</tr>
<tr>
<td>D₃</td>
<td>0.189</td>
<td>17.28</td>
<td>105</td>
</tr>
<tr>
<td><strong>DUMBRAVA ROSIE</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₁</td>
<td>1.082</td>
<td>21.24</td>
<td>315.5</td>
</tr>
<tr>
<td>D₂</td>
<td>1.067</td>
<td>17.63</td>
<td>326.0</td>
</tr>
<tr>
<td>D₃</td>
<td>0.883</td>
<td>18.07</td>
<td>235.8</td>
</tr>
</tbody>
</table>

A high accumulation of cadmium from the soil was registered for all the three work distances of soil-water interface, in sampling point downstream of Batca Doamnei, upstream of Piatra Neamt city, in the case of bulrush plant type (Fig. 3), as follows:

- for the work distance D₁, it was 796.15 % higher from the content from soil;
- for the work distance D₂, it was 875.09 % higher from the content from soil;
- for the work distance D₃, it was 870.89 % higher from the content from soil.

A higher accumulation of arsenic from the soil was registered (the value registered in the bulrush plant was 69.20 % lower from the content from soil, for the work distance D₁), in downstream of Batca Doamnei lake sampling point, upstream of Piatra Neamt city, in the case of bulrush plant type (Fig. 4).
The accumulation of arsenic from the soil in downstream of Batca Doamnei lake sampling point, upstream of Piatra Neamț city sampling point, in the case of bulrush plant type, was the lower for the work distance D₃, the value detected being 73.04 % lower than in the soil.

The permissible limit for zinc (150 mg/kg dry matter) is not exceeded in downstream of Batca Doamnei lake - upstream of Piatra Neamț city sampling point and the determined values ranged between 235.8 mg/kg dry matter and 326 mg/kg dry matter.

A high accumulation of zinc from the soil was registered for all the three work distances of soil-water interface, in sampling point downstream of Batca Doamnei, upstream of Piatra Neamț city, in the case of bulrush plant type (Fig. 5), as follows:
- for the work distance D₁, it was 180.9% higher from the content from soil;
- for the work distance D₂, it was 192.51% higher from the content from soil;
- for the work distance D₃, it was 188% higher from the content from soil.

In case of Dumbrava Rosie downstream of Piatra Neamț city sampling point the permissible limit for cadmium in the soil, for work distance D₁ is exceeded with 35.25 %. For work distance D₂ the permissible limit for cadmium in the soil is exceeded with 33.37 % and for work distance D₃ the permissible limit for cadmium in the soil is exceeded with 10.37 %.

The accumulation of cadmium from the soil for the three work distance D₁, D₂ and D₃ of soil-water interface (in Dumbrava Rosie sampling area), in the case of bulrush plant type (Fig. 6) was very high, the value detected in the plant being 858.41 % / 840.95 % / 765.23 % higher than in the soil.
The established maximum limit for arsenic is not exceeded in Dumbrava Rosie downstream of Piatra Neamț city sampling point and the determined values ranged between 17.63 mg/kg dry matter and 21.24 mg/kg dry matter.

A higher accumulation of arsenic from the soil was registered (the value registered in bulrush plant type being 60.81% lower from the content from soil, for the work distance D₁), in Dumbrava Rosie downstream of Piatra Neamț city sampling point, in the case of bulrush plant type (Fig. 7).

Accumulation of arsenic determined in the soil in Dumbrava Rosie downstream of Piatra Neamț city sampling point, in the case of bulrush plant type, was the lower for the work distance D₁, the value detected being 69.13% lower than in the soil.

The permissible limit for zinc for Dumbrava Rosie downstream of Piatra Neamț city sampling point is exceeded in any of the three levels (Table 2):
- for the work distance D₁, it was with 110.33% over the epermissible limit;
- for the work distance D₂, it was with 117.33% over the epermissible maximum limit;
- for the work distance D₃, it was with 57.2% over the epermissible maximum limit.

A high accumulation of zinc from the soil was registered for all the three work distance of soil-water interface, in sampling point Dumbrava Rosie, downstream of Piatra Neamț city, in the case of bulrush plant type (Fig. 8), as follows:
- for the work distance D₁, it was 179.74% higher from the content from soil;
- for the work distance D₂, it was 185% higher from the content from soil;
- for the work distance D₃, it was 179.68% higher from the content from soil.

By employing the TableCurve 3D program for generating linear and non-linear equations the mathematical models for the accumulation of cadmium, arsenic and zinc from the soil in the case of bulrush plant type, were obtained for each heavy metal in turn, depending on the distance from the water-soil interface where the plant samples were collected and on the concentration of heavy metals in the soil.

Figures 9 present the variations of the accumulation of cadmium from the soil in bulrush plant type. It was obtained the same mathematical model for all the three heavy metals (cadmium, arsenic and zinc). The surface obtained is characterized by the following of equation (1):

\[ z = a + b \cdot x + c \cdot y \]  

In which: \( x \) is concentration of cadmium/arsenic/zinc from soil [mg/kg dry matter], \( y \) is the distance [cm].

The correlation coefficient which corresponds to this equation is \( r^2 = 0.94\div0.99 \).
Fig. 9. The variations of the accumulation of cadmium from the soil in the bulrush plant type

In Table 3 are presented the values of the constants from relation (1) for cadmium, arsenic and zinc, corresponding to the city of Piatra Neamt.

<table>
<thead>
<tr>
<th>Equation constants</th>
<th>Piatra Neamt</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cd</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>0.21185878</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>9.2303097</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>-0.003559261</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>As</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>-7.4276143</td>
<td>0.94</td>
</tr>
<tr>
<td>b</td>
<td>0.7343394</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>0.004636582</td>
<td></td>
</tr>
<tr>
<td><strong>Zn</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>4.3687198</td>
<td>0.99</td>
</tr>
<tr>
<td>b</td>
<td>2.7992747</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>0.036126428</td>
<td></td>
</tr>
</tbody>
</table>

For the verification of the model, one equation was chosen from each investigated method, respectively:
- variations in the accumulation of cadmium, arsenic and zinc from the soil in the bulrush plant type, for the city of Piatra Neamt (equation (2) - (4)):

\[
Z_{Typha \ Latifolia} = 0.21185878 + 9.2303097 \cdot X_{Cd} + (-0.003559261) \cdot Y
\]  

(2)

\[
Z_{Typha \ Latifolia} = (-7.4276143) + 0.7343394 \cdot X_{As} + 0.004636582 \cdot Y
\]  

(3)

\[
Z_{Typha \ Latifolia} = 4.3687198 + 2.7992747 \cdot X_{Zn} + 0.036126458 \cdot Y
\]  

(4)

In Tables 4 are comparatively presented the values obtained using the mathematical model and the values obtained from the experimental determinations.

<table>
<thead>
<tr>
<th>City</th>
<th>Distance [cm]</th>
<th>Concentration of heavy metals from soil [mg/kg dry matter]</th>
<th>Capacity of absorption [mg/kg dry matter]</th>
<th>Relative deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mathematical model</td>
<td>Experimental</td>
</tr>
<tr>
<td>Piatra Neamt</td>
<td>0</td>
<td>0.338</td>
<td>3.331703459</td>
<td>3.029</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.269</td>
<td>2.516849034</td>
<td>2.623</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.189</td>
<td>1.600461203</td>
<td>1.835</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.082</td>
<td>10.19905388</td>
<td>10.37</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.067</td>
<td>9.882636175</td>
<td>10.04</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.883</td>
<td>8.06296135</td>
<td>7.64</td>
</tr>
</tbody>
</table>

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The experiments were conducted in areas with high risks of stream pollution with heavy metals, as follows:
- the Bistrita River – upstream and downstream of the urban residential area of Piatra Neamț.

The bulrush plant type, has accumulated a very high cantitaty of cadmium and zinc, and for this reasons can be used in the process of cleaning soil.

Regarding the arsenic content, the bulrush plant type, it turned out to be a very poor accumulator.

The difference between the experimental values and the values obtained with the mathematical models is insignificant, the correlation coefficient being between 0.94 and 0.99.

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