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 Bistriţa 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, mathematic 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.

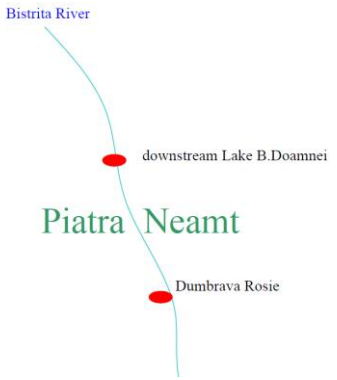

Fig. 1. The points analyzed for prelevation specimens of soil and plants along the Bistrita River, the Siret hydrographic basin [3]

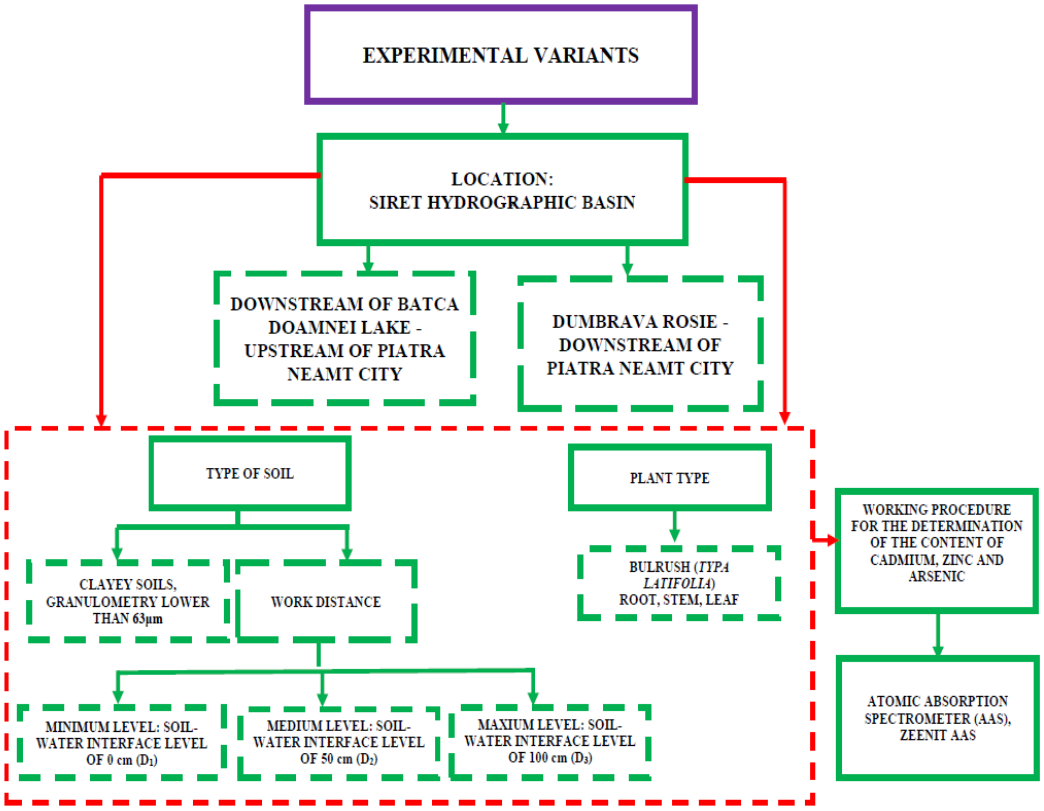

Fig. 2. Experimental variants carried out at Siret hydrographic basin

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 1
THE EXPERIMENTAL VALUES DETERMINED FOR CADMIUM IN THE SOIL AND BULRUSH PLANT TYPE FROM UNPOLLUTED SOILS (WITNESS SAMPLE)

Point unpolluted	Cadmium	Arsenic	Zinc
	[mg/kg dry matter]		
Soil	0.67	26	124
Bulrush Root + stem + leaf	0.024	0.03	14.03

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 Bâtca Doamnei lake - upstream of Piatra Neamț 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 Bâtca Doamnei lake - upstream of Piatra Neamț 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

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

Points polluted	**Cd**	**As**	**Zn**
Downstream of BATCA DOAMNEI LAKE	[mg/kg dry matter]		
D_1	0.338	16.4	128.3
D_2	0.269	15.1	94.73
D_3	0.189	17.28	105
DUMBRAVA ROSIE	[mg/kg dry matter]		
D_1	1.082	21.24	315.5
D_2	1.067	17.63	326.0
D_3	0.883	18.07	235.8

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 D_1, it was 796.15 % higher from the content from soil;
- for the work distance D_2, it was 875.09 % higher from the content from soil;
- for the work distance D_3, it was 870.89 % higher from the content from soil.

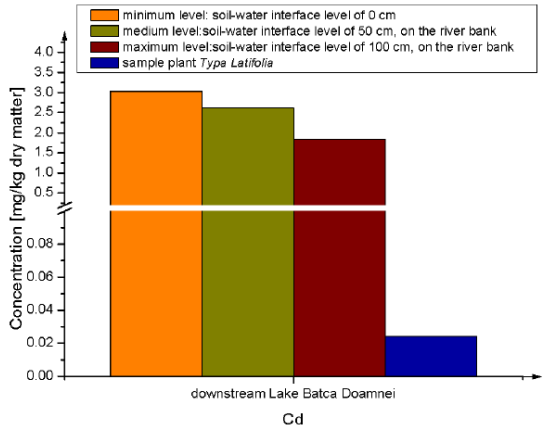

Fig. 3. The cadmium concentration in the bulrush plant type, in one location:Dumbrava Rosie, dowstream of Piatra Neamt city

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 D_1), in downstream of Batca Doamnei lake sampling point, upstream of Piatra Neamt city, in the case of bulrush plant type (Fig. 4).

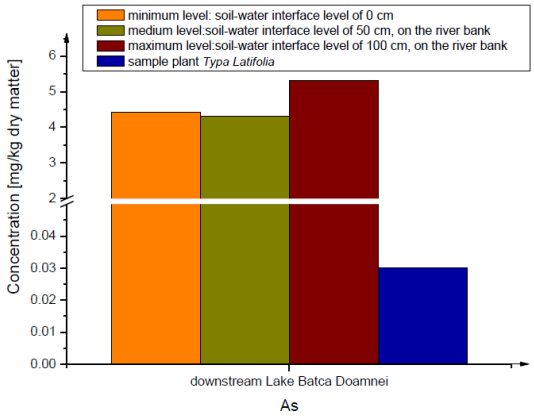

Fig. 4. The arsenic concentration in the bulrush plant type, in one location: downstream of Batca Doamnei lake, upstream of Piatra Neamt city

The accumulation of arsenic from the soil in downstream of Batca Doamnei lake sampling point, upstream of Piatra Neamt city sampling point, in the case of bulrush plant type, was the lower for the work distance D_3, 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 Neamt 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 Neamt city, in the case of bulrush plant type (Fig. 5), as follows:

- for the work distance D_1, it was 180.9% higher from the content from soil;
- for the work distance D_2, it was 192.51% higher from the content from soil;
- for the work distance D_3, it was 188 % higher from the content from soil.

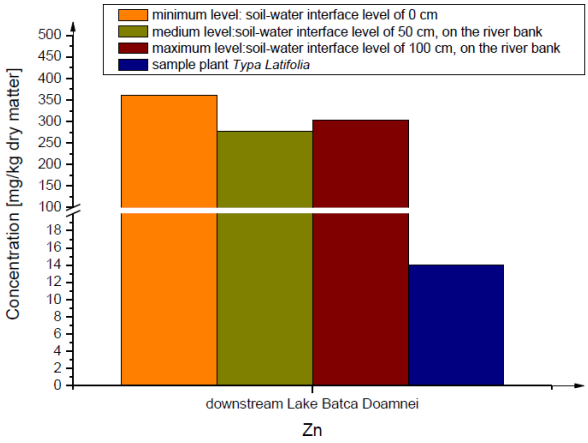

Fig. 5. The zinc concentration in the the bulrush plant type, in one location:downstream of Batca Doamnei, upstream of Piatra Neamt city

In case of Dumbrava Rosie downstream of Piatra Neamt city sampling point the permissible limit for cadmium in the soil, for work distance D_1 is exceded with 35.25 %.For work distance D_2 the permissible limit for cadmium in the soil is exceded with 33.37 % and for work distance D_3 the permissible limit for cadmium in the soil is exceded with 10.37 %.

The accumulation of cadmium from the soil for the three work distance D_1, D_2 and D_3 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.

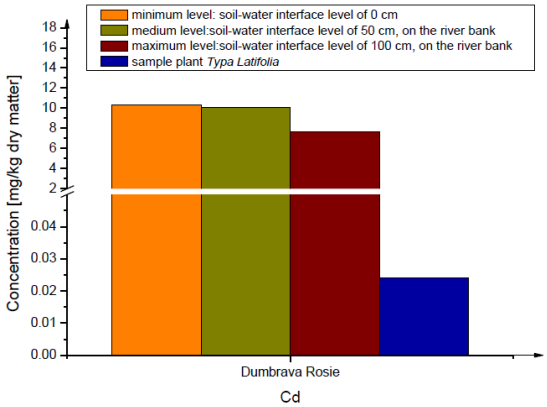

Fig. 6. The cadmium concentration in the bulrush plant type, in one location: Dumbrava Rosie, dowstream of Piatra Neamt city

The established maximum limit for arsenic is not exceeded in Dumbrava Roşie downstream of Piatra Neamt 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 D_1), in Dumbrava Rosie downstream of Piatra Neamt city sampling point, in the case of bulrush plant type (Fig. 7).

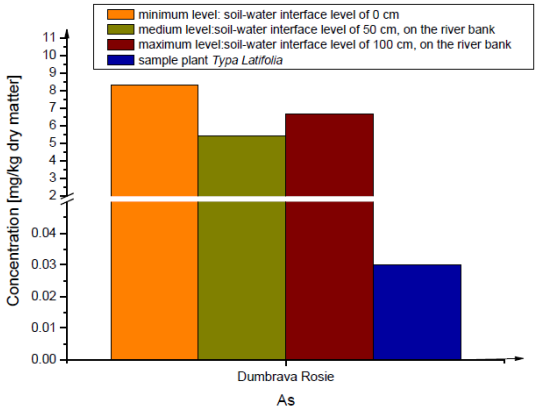

Fig. 7. The arsenic concentration in the bulrush plant type, in one location: Dumbrava Rosie, dowstream of Piatra Neamt city

Accumulation of arsenic determined in the soil in Dumbrava Rosie downstream of Piatra Neamt city sampling point, in the case of bulrush plant type, was the lower for the work distance D_1, the value detected being 69.13 % lower than in the soil.

The permissible limit for zinc for Dumbrava Rosie downstream of Piatra Neamt city sampling point is exceeded in any of the three levels (Table 2):

- for the work distance D_1, it was with 110.33% over the epermissible limit;
- for the work distance D_2, it was with 117.33% over the epermissible maximum limit;
- for the work distance D_3, 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 Neamt city, in the case of bulrush plant type (Fig. 8), as follows:

- for the work distance D_1, it was 179.74 % higher from the content from soil;
- for the work distance D_2, it was 185 % higher from the content from soil;
- for the work distance D_3, it was 179.68 % higher from the content from soil.

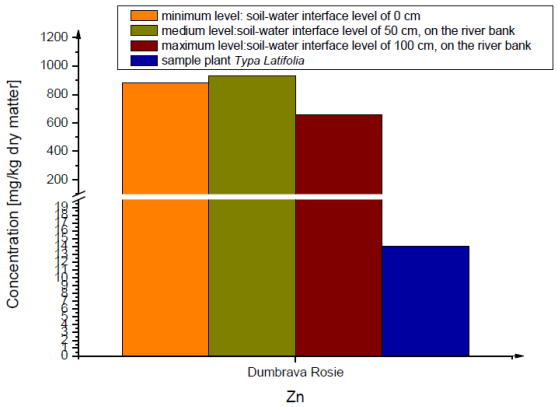

Fig. 8. The zinc concentration in the bulrush plant type, in one location: Dumbrava Rosie, dowstream of Piatra Neamt city

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 burlush 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):

$$z = a + b \cdot x + c \cdot y \qquad (1)$$

In wich: 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 $r^2 = 0.94 \div 0.99$.

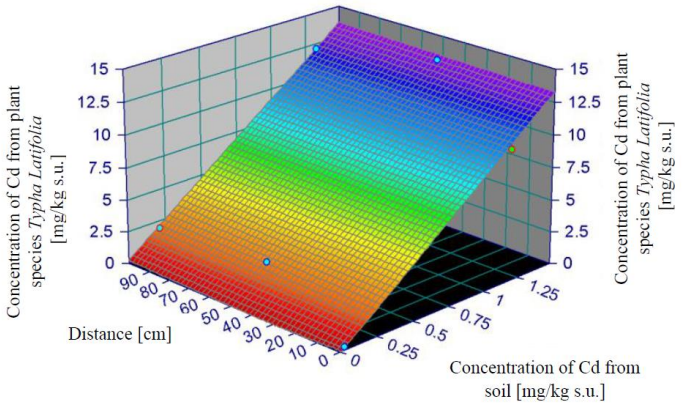

Fig. 9. The variations of the accumulation of cadmium from the soil in the bulrush plant type

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

Table 3
THE EQUATION CONSTANTS VALUES THAT DESCRIBE THE MATHEMATICAL MODEL FOR CADMIUM, ARSENIC AND ZINC CORRESPONDING TO THE CITY OF PIATRA NEAMT

Equation constants	Piatra Neamt	Correlation coefficient
Cd		
a	0.21185878	0.99
b	9.2303097	
c	-0.003559261	
As		
a	-7.4276143	0.94
b	0.73463594	
c	0.004636582	
Zn		
a	4.3687198	0.99
b	2.7992747	
c	0.036126458	

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 burlush plant type, for the city of Piatra Neamt (equation (2) - (4)):

$$Z_{Typha\ Latifolia} = 0{,}21185878 + 9{,}2303097 \cdot X_{Cd} + (-0{,}003559261) \cdot Y \quad (2)$$

$$Z_{Typha\ Latifolia} = (-7{,}4276143) + 0{,}73463594 \cdot X_{As} + 0{,}004636582 \cdot Y \quad (3)$$

$$Z_{Typha\ Latifolia} = 4{,}3687198 + 2{,}7992747 \cdot X_{Zn} + 0{,}036126458 \cdot Y \quad (4)$$

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

Table 4
THE VALUES OF CADMIUM, ARSENIC AND ZINC ACCUMULATION FROM SOIL IN THE BURLUSH PLANT TYPE CORRESPONDING TO THE CITY OF PIATRA NEAMT

City	Distance [cm]	Concentration of heavy metals from soil [mg/kg dry matter]	Capacity of absorbtion [mg/kg dry matter]		Relative deviation
			Mathematical model	Experimental	
Piatra Neamt	**Cd**				
	0	0.338	3.331703459	3.029	-9.08555
	50	0.269	2.516849034	2.623	4.217614
	100	0.189	1.600461203	1.835	14.65445
	0	1.082	10.19905388	10.37	1.676098
	50	1.067	9.882636175	10.04	1.592326
	100	0.883	8.006296135	7.64	-4.5751

	As				
	0	16.4	4.620415116	4.42	-4.3376
	50	15.1	3.897217469	4.321	10.87398
	100	17.28	5.730552893	5.322	-7.12938
	0	21.24	8.176053066	8.322	1.785054
	50	17.63	5.755846397	5.441	-5.47003
	100	18.07	6.310915286	6.665	5.610671
	Zc				
	0	128.3	363.5156638	360.4	-0.85709
	50	94.73	271.350335	277.1	2.118908
	100	105	301.9052091	302.4	0.163889
	0	315.5	887.5398877	882.6	-0.55658
	50	326	918.7385949	929.1	1.127786
	100	235.8	668.0503399	659.5	-1.27989

Conclusions

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 Neamt.

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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