Mathematical Modeling for the Absorption Capacity of Heavy Metals from the Soil in the Case of *Phragmites Australis* Plant Species

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This paper proposes a tridimensional mathematical model of the absorption capacity of heavy metals (cadmium and nickel) from the soil in the case of Phragmites Australis plant species (the soil and plant samples was taken from six locations/areas along the Bistrifa and Cracãu Rivers, 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 concentration of the heavy metals 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 very high absorption capacity of cadmium from the soil was recorded A very high absorption capacity of cadmium from the soil was recorded A very high absorption coefficient of the mathematic model was between 0.90 and 0.98.

Keywords: nickel, cadmium, mathematic model, absorption capacity, Phragmites Australis

As an ecosystem, the soil fulfils a series of very important functions, such as [1-18]:

- it contributes to the reduction of sudden variations of the soil's characteristics, with favourable effects for plants;

- it contributes to filtering various polluting substances and preventing phreatic waters from contamination;

- it contributes to cleaning the environment due to the self-cleaning process and to neutralizing polluting organic substances and pathogenic micro-organisms reaching the soil;

- it contributes to the genetic protection of some species of micro-organisms because soils represent their habitat;

- it represents the main means of production in agriculture - food products and some agroindustrial raw materials;

- it constitutes the major method of production in silviculture.

Heavy metals constitute an important category of stable toxic pollutants. Unlike organic pollutants, metals are not biodegradable, they generally have little mobility and, for this reason, they persist in storage compartments (soil, sediments) for a long time [3, 8, 9, 19-24].

The transfer of metals from the soil to plants is influenced by a variety of soil parameters. The main parameters of the soil which influence absorption and desorption processes are [3, 8, 9, 19-28]:

*p*Ĥ values;

- fine granulometric fraction (<0.02 mm);

- oxides and hydroxides, especially Fe, Mn, Al;
- microorganisms.

This paper proposes a mathematical model of the absorption capacity of heavy metals (cadmium and nickel) from the soil in the case of *Phragmites Australis* plant species (common reed).

Experimental part

Sections taken into consideration for taking samples of soil and plants are presented in figure 1. Sediments were sampled from six locations/areas along the Bistrilta and Cracãu Rivers, belonging to the Siret hydrographic basin (Pangarati and downstream of Batca Doamnei lake, upstream of Piatra Neamþcity, Dumbrava Rosie, Roznovplatform Fibrex Savinesti, River Cracau, Pod Frunzeni, downstream of Piatra Neamt city).

For the sections targeted the sediment stratum was thick and its granulosity was lower than $63 \mu m$, consisting of clay and slime. Together with the sampling of sediment the sampling of vegetation also took place (samples of bulrush and common reed) from the banks of the tributaries under study [29].

Phragmites australis (common reed, fig. 2) is a perennial herbaceous plant from the Gramineae family (Poaceae), having a rigid stalk of about 1-4 m, green-bluish lanceolate leaves and flowers laid out in tassels and is a good accumulator of heavy metals and hydrocarbons [8, 9].

Soil and plants samples were taken at 10 cm deep in the soil, for three levels:

minimum level: soil-water interface level of 0 cm;

- medium level: soil-water interface level of 50 cm, on the river bank;

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⁻ organic matter;



Fig. 1. Sections taken into consideration for taking samples of soil and plants along the Bistrita and Cracau Rivers, the Siret hydrographic basin



Fig. 2. *Phragmites Australis* [8, 9]

- maximum level: soil-water interface level of 100 cm, on the river bank.

The nickel and cadmium content in the soil samples has been determined by using the atomic absorption spectrometer (AAS), ZEENIT AAS version (fig. 3) [30].



Fig. 3. Atomic absorption spectrometer (AAS), Zeenit 700 version [30]

Results and discussions

Tabel 1 presented the experimental values determined for two heavy metals (cadmium an nickel) in the soil, respectively for the witness sample of *Phragmites Australis* plant species from unpolluted soils.

Figure 4 represents graphically the cadmium concentration in the soil in two sampling points: Pangarati and downstream of Batca Doamnei lake, upstream of Piatra Neamt city.

Table 1

THE EXPERIMENTAL VALUES DETERMINED FOR TWO HEAVY METALS (CADMIUM AN NICKEL) IN THE SOIL, RESPECTIVELY FOR THE WITNESS SAMPLE OF *PHRAGMITES AUSTRALIS* PLANT SPECIES FROM UNPOLLUTED SOILS

T	Cd	Ni	
Location unpolluted	[mg/kg dry matter]		
Soil	0.67	33	
Phragmites Australis Root + stem + leaf	0.1	1.31	



Fig. 4. The cadmium concentration in the soil in two sampling points: Pangarati and downstream of Batca Doamnei lake, upstream

of Piatra Neamt city

The established maximum limit for cadmiu (0.8 mg/kg dry matter), is not exceeded in any of the two sampling points and the determined values ranged between 0.189 mg/kg dry matter and 0.766 mg/kg dry matter

The absorption capacity of cadmium from the soil at the minimum level of soil-water interface (Pangarati, sampling point), for *Phragmites Australis* plant species was the highest as compared to the other levels, the value determined in the plant being 203 % lower than in the soil (fig. 5).



Fig. 5. The cadmium concentration in the *Phragmites Australis* plant species, in two sampling points: Pangarati and downstream of Batca Doamnei lake, upstream of Piatra Neamt city

The lower soil cadmium absorption capacity of the *Phragmites Australis* plant species was recorded for the minimum and maximum water-soil interface levels (Pângãraļi, sampling section), the value determined in the plant being 194.54% and 192.32% higher than in the soil.

A higher absorption capacity of cadmium from the soil was recorded, in downstream of Batca Doamnei lake sampling point, upstream of Piatra Neamt city, in the case of *Phragmites Australis* plant species.

The lowest soil cadmium absorption capacity of the *Phragmites Australis* plant species was recorded for the medium and maximum water-soil interface levels (downstream of Batca Doamnei lake sampling point), the value determined in the plant being 202.29 and 222.75% higher than in the soil.

The higher soil cadmium absorption capacity of the *Phragmites Australis* plant species was recorded for the minimum water-soil interface levels (downstream of Batca Doamnei lake sampling point), the value determined in the plant being 228.99% higher than in the soil.

Figure 6 represents graphically the cadmium concentration in the soil in four sampling points: Dumbrava

Rosie, Roznov (platform Fibrex Savinesti), River Cracau, Pod Frunzeni, downstream of Piatra Neamt city.

In the case of Dumbrava Rosie sampling point the established maximum limit for cadmium in the soil, for a minimum level soil-water interface is exceeded with 35.25%.

For a level 50 cm soil-water interface, the established maximum limit for cadmium in the soil is exceeded with 33.37 %, and for level 100 cm soil-water interface, the established maximum limit for cadmium in the soil is exceeded with 10.37 %.

In the case of Roznov (platform Fibrex Savinesti) sampling point the established maximum limit for cadmium in the soil, for a level 50 cm soil-water interface is exceeded with 36.75%, and for level 100 cm soil-water interface, the established maximum limit for cadmium in the soil is exceeded with 33.25 %. For a level 0 cm soil-water interface, the established maximum limit for cadmium in the soil is exceeded with 12.75 %.

The established maximum limit for cadmiu, is not exceeded in the confluence of the Bistrita River with Cracau River sampling points (the determined values are between 0.189 mg/kg dry matter and 0.766 mg/kg dry matter).

In the case of Pod Roznov downstream of Piatra Neamt city sampling point the established maximum limit for cadmium in the soil, for a level 50 cm soil-water interface is exceeded with 21.87%, and for level 100 cm soil-water interface, the established maximum limit for cadmium in the soil is exceeded with 14.5 %. For a level 0 cm soilwater interface, the established maximum limit for cadmium in the soil is exceeded with 3.75 %.

A very high absorption capacity of cadmium from the soil was recorded for all the three levels of soil-water interface, in sampling point Dumbrava Rosie, downstream of Piatra Neamt city, in the case of *Phragmites Australis* plant species (fig. 7), as follows:

- for the minimum level of soil-water interface, it was 234.65 % higher than in the soil;

- for the medium level of soil-water interface, it was 232.89 % higher than in the soil;

- for the maximum level of soil-water interface, it was 201.47 % higher than in the soil.

The absorption capacity of cadmium from the soil in Roznov sampling point (Fibrex Savinesti platform) was the highest for the minimum level of soil-water interface, the value detected being 201.66 % higher than in the soil.

The lowest absorption capacity of cadmium from the soil, in the case of *Phragmites Australis* plant species, was detected for the maximum level of soil-water interface (Roznov sampling point - Fibrex Savinesti platform), the value identified being 190.8 % higher than in the soil.



Fig. 6. The cadmium concentration in the soil in four sampling points: Dumbrava Rosie, Roznov (platform Fibrex Savinesti), River Cracau, Pod Frunzeni, downstream of Piatra Neamt city In the Cracau River sampling point, the highest absorption capacity of cadmium from the soil, in the case of *Phragmites Australis* plant species, was detected for the medium level of soil-water interface, the value obtained being 204.18 % higher than that in the soil.

In the Cracau River sampling point, the lower absorption capacity of cadmium from the soil, in the case of *Phragmites Australis* plant species, was detected for the maximum level of soil-water interface, the value obtained being 196.19 % higher than that in the soil.

A very high absorption capacity of cadmium from the soil was recorded for all the three levels of soil-water interface, in sampling point Pod Frunzeni, downstream of Piatra Neamt city, in the case of *Phragmites Australis* plant species (fig. 7), as follows:

- for the minimum level of soil-water interface, it was 214.07% % higher than in the soil;

- for the medium level of soil-water interface, it was 199.48% higher than in the soil;

- for the maximum level of soil-water interface, it was 192.57% higher than in the soil.



Fig. 7. The cadmium concentration in the *Phragmites Australis* plant species, in four sampling points: Dumbrava Rosie, Roznov (platform Fibrex Savinesti), River Cracau and Pod Frunzeni, dowstream of Piatra Neamt city

Figure 8 represents graphically the nickel concentration in the soil in two sampling points: Pangarati and downstream of Batca Doamnei lake, upstream of Piatra Neamt city.

The established maximum limit for nickel (35 mg/kg dry matter) is exceeded in any of the two sampling points, and the determined values ranged, as follows:

- for Pangarati sampling points:

-for the minimum level of soil-water interface, it was 34.2 % higher;

-for the medium level of soil-water interface, it was 38.2 % higher;

-for the maximum level of soil-water interface, it was 28.97 % higher.

- for downstream of Batca Doamnei lake sampling points:

-for the minimum level of soil-water interface, it was 22.94 % higher;

-for the medium level of soil-water interface, it was 6.42 % higher;

-for the maximum level of soil-water interface, it was 21.71 % higher.

The absorption capacity of nickel from the soil at the maximum level of soil-water interface (Pangarati sampling point, fig. 9), for *Phragmites Australis* plant species was the highest as compared to the other levels, the value determined in the plant being 52.11 % lower than in the soil.



Fig. 8. The nickel concentration in the soil in two sampling points: Pangarati and downstream of Batca Doamnei lake, upstream of Piatra Neamt city

The lowest absorption capacity of nickel from the soil, in the case of *Phragmites Australis* plant species, was detected for the minimum level of soil-water interface (Pangarati sampling point), the value identified being 55.3 % lower than in the soil.

In the case of downstream of Batca Doamnei lake sampling point the absorption capacity of cadmium from the soil, in the case of *Phragmites Australis* plant species was:

- for the minimum level of soil-water interface, it was 55.69% % lower than in the soil;

- for the medium level of soil-water interface, it was 52.74% lower than in the soil;

- for the maximum level of soil-water interface, it was 56.45% lower than in the soil.



Fig. 9. The nickel concentration in the *Phragmites Australis* plant species, in two sampling points: Pangarati and downstream of Batca Doamnei lake, upstream of Piatra Neamt city

Figure 10 represents graphically the nickel concentration in the soil in four sampling points: Dumbrava Rosie, Roznov (platform Fibrex Savinesti), River Cracau and Pod Frunzeni, downstream of Piatra Neamt city.



Fig. 10. The nickel concentration in the soil in four sampling points: Dumbrava Rosie, Roznov (platform Fibrex Savinesti), River Cracau and Pod Frunzeni, downstream of Piatra Neamt city The established maximum limit for nickel in the soil is exceeded as follows:

- for Dumbrava Rosie sampling points:

-for the minimum level of soil-water interface, it was 2.45 % higher;

-for the medium level of soil-water interface, it was 8.25 % higher;

- for Roznov (platform Fibrex Savinesti)lake sampling points:

-for the medium level of soil-water interface, it was 8.34 % higher;

- for River Cracau lake sampling points:

-for the medium level of soil-water interface, it was 2.2 % higher;

The absorption capacity of nickel from the soil at the minimum level of soil-water interface (Dumbrava Rosie sampling point), for *Phragmites Australis* plant species was the highest as compared to the other levels, the value determined in the plant being 51.67 % lower than in the soil (fig. 11).

The absorption capacity of nickel from the soil at the maximum level of soil-water interface (Dumbrava Rosie sampling point), for *Phragmites Australis* plant species was the lower as compared to the other levels, the value determined in the plant being 65.77 % lower than in the soil.

In the Roznov (platform Fibrex Savinesti) sampling point, the highest absorption capacity of nickel from the soil, in the case of *Phragmites Australis* plant species, was detected for the minimum level of soil-water interface, the value obtained being 58.87 % lower than that in the soil.



Fig. 11. The nickel concentration in the *Phragmites Australis* plant species, in four sampling points: Dumbrava Rosie, Roznov (platform Fibrex Savinesti), River Cracau and Pod Frunzeni, dowstream of Piatra Neamt city

The lowest absorption capacity of nickel from the soil, in the case of *Phragmites Australis* plant species, was detected for the maximum level of soil-water interface (Roznov-platform Fibrex Savinesti sampling point), the value identified being 64.38 % lower than in the soil.

In the Cracau River sampling point, the highest absorption capacity of nickel from the soil, in the case of *Phragmites Australis* plant species, was detected for the maximum level of soil-water interface, the value obtained being 62.86 % lower than that in the soil.

The lowest absorption capacity of nickel from the soil, in the case of *Phragmites Australis* plant species, was detected for the medium level of soil-water interface (Cracau River sampling point), the value identified being 65.03 % lower than in the soil.

The absorption capacity of nickel from the soil at the maximum level of soil-water interface (Pod Frunzeni

sampling point), for *Phragmites Australis* plant species was the highest as compared to the other levels, the value determined in the plant being 62.37 % lower than in the soil.

The lowest absorption capacity of nickel from the soil, in the case of *Phragmites Australis* plant species, was detected for the medium level of soil-water interface (Pod Frunzeni sampling point), the value identified being 65.37 % lower than in the soil.

Experimental results show that the absorption capacity of heavy metals from the soil in the case of plant species, *Phragmites Australis* depends on the distance from the water-soil interface where the plant samples were collected and on the concentration of heavy metals in the soil.

By employing the TableCurve 3D program for generating linear and non-linear equations the mathematical models for the absorption capacity of heavy metals from the soil in the case of plant species, *Phragmites Australis*, 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 12 and 13 present the variations of the absorption capacity of cadmium and nickel from the soil in the case of *Phragmites Australis* plant species.

The surface obtained is characterized by the following of equation (1):







Fig. 13. The variations of the absorption capacity of nickel from the soil in the case of *Phragmites Australis* plant species

In wich: x is concentration of cadmium/nickel from soil [mg/kg dry matter], y is the distance [cm].

The correlation coefficient which corresponds to this equation is $r^2=0.90\div0.98$.

In tables 2 and 3 are presented the values of the constants from relation (1) for cadmium and nickel, corresponding to the city of Piatra Neamt.

Table 2THE EQUATION CONSTANTS VALUES THAT DESCRIBE THEMATHEMATICAL MODEL FOR CADMIUM, CORRESPONDING TOTHE CITY OF PIATRA NEAMT

Equation constants	Piatra Neamț	Correlation coefficient
a	0.35537351	
ь	1.8725309	
с	-0.000834342	0.98
d	-0.29765724	
e	0.000105639	

Table 3

THE EQUATION CONSTANTS VALUES THAT DESCRIBE THE MATHEMATICAL MODEL FOR NICKEL, CORRESPONDING TO THE CITY OF PIATRA NEAMT

Equation constants	Piatra Neamț	Correlation coefficient
а	4.3914212	
b	0.079989847	
с	-0.005855947	0.90
d	-0.013883608	
е	-0.00011195	

City	Distance	Concentration of cadmium from soil	Capacity of absorbtion [mg/kgdry matter]		Relative	
	[cm]	[mg/kg dry matter]	Mathematical model	Experimental	deviation	
	0	0.7	2.104675462	2.062	-2.02765	
	50	0.766	2.248897376	2.321	3.206132	
	100	0.765	2.177188686	2.239	2.839043	
	0	0.338	1.098841346	1.112	1.197503	Table 4
	50	0.269	0.883437614	0.832	-5.82244	THE VALUES OF CADMIUM
	100	0.189	0.655813949	0.61	-6.98581	ABSORPTION CAPACITY
	0	1.082	3.51280346	3.621	3.080062	FROM SOIL IN THE
	50	1.067	3.361507204	3.552	5.666886	PHRAGMITES AUSTRALIS
Piatra	100	0.883	2.57496361	2.662	3.380102	PI ANT SPECIES
Neamț	0	0.902	2.794749933	2.721	-2.63887	COPPESPONDING TO THE
	50	1.094	3.475646088	3.2	-7.93079	CITY OF DIATDA NEAMT
	100	1.066	3.271576467	3.1	-5.24446	
	0	0.76	2.298451563	2.26	-1.67293	
	50	0.789	2.324782785	2.4	3.235451	
	100	0.709	2.000642757	2.1	4.966266	
	0	0.831	2.539632936	2.61	2.770757	7
	50	0.975	2.991854788	2.92	-2.40168	7
	100	0.916	2.692981532	2.68	-0.48205	

CORRESPONDING TO THE CITY OF PIATRA NEAMT					
City	Distance	Concentration of nickel from soil	Capacity o [mg/kgd	Relative	
	[cm]	[mg/kg dry matter]	Mathematical model	Experimental	deviation
	0	46.97	23.42296752	20.995	-10.3658
	50	48.37	24.67918116	22.665	-8.16146
	100	49.28	25.43400024	23.6	-7.21082
	0	43.03	19.4575535	19.066	-2.01235
	50	37.25	14.8316855	17.601	18.67161
	100	42.6	18.15314468	18.551	2.191661
	0	35.86	14.45801272	17.33	19.86433
	50	37.89	15.22237528	17.31	13.71419
Distra Manut	100	29.95	10.82307181	10.25	-5.29491
Flatra Neami,	0	32.39	12.68792707	13.32	4.981688
	50	37.92	15.24105292	16.66	9.310033
	100	25.44	9.189289929	9.06	-1.40696
	0	20.24	8.359459012	7.32	-12.4345
	50	35.78	13.98714408	12.51	-10.5607
	100	20.44	7.717210094	7.59	-1.64839
	0	28.85	11.17531053	9.99	-10.6065
	50	30.19	11.32280745	10.91	-3.6458
	100	30.91	11 21802936	11.63	3 672398

 Table 5

 THE VALUES OF NICKEL ABSORPTION CAPACITY FROM SOIL IN THE PHRAGMITES AUSTRALIS PLANT SPECIES CORRESPONDING TO THE CITY OF PIATRA NEAMT

For the verification of the model, one equation was chosen from each investigated method, respectively:

- variations in the absorption capacity of cadmium and nickel from the soil in the *Phragmites Australis* plant species, for the city of Piatra Neamt (equation (2) and (3)):

$$Z_{Phragmites Australis} = \frac{0.35537351 + 1.8725309 \cdot X_{Cd} + (-0.000834342) \cdot Y}{1 + (-0.29765724) \cdot X_{Cd} + 0.000105639 \cdot Y}$$
(2)

$$Z_{Phragmites Australis} = \frac{4.3914212+0.079989847 \cdot X_{Ni} + (-0.005855947) \cdot Y}{1 + (-0.013883608) \cdot X_{Ni} + (-0.00011195) \cdot Y}$$
(3)

In tables 4 and 5 are comparatively presented the values obtained using the mathematical model and the values obtained from the experimental determinations.

Conclusions

Characteristic sections of the six areas were explored so that they can allow the evaluation of the ecological impact of residual soil pollution by heavy metals from the banks of the two rivers, both by the residual waters from the industrial platforms and the domestic wastewater produced by the urban residential areas in city such as Piatra Neamt.

Phragmites Australis plant species is proved to be very good accumulators of heavy metals, a fact which shows that they can be used in soil phyto-remediation processes, particularly in phyto-extraction processes for the removal of heavy metals from contaminated soils.

Comparing the absorption capacity of heavy metals from the soil (cadmium and nickel) in the case of *Phragmites Australis* plant species it was observed that:

-.a very poor accumulator of heavy metal like nickel;

- a very good accumulator of cadmium.

The difference between the experimental values and the values obtained with the mathematical models is insignificant, the correlation coefficient being between 0.90 and 0.98.

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