



## THE MATHEMATICAL MODELING OF METALS CONTENT IN PEAT

### *METĀLU SATURA KŪDRĀ MATEMĀTISKĀ MODELĒŠANA*

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**Abstract.** *Metals deposition in peat can aid to evaluate impact of atmospheric or wastewaters pollution and thus can be a good indicator of recent and historical changes in the pollution loading. For peat using in agriculture, industrial, heat production etc. knowledge of peat metals content is important. Experimental determination of metals in peat is very long and expensive work. Using experimental data the mathematical model for calculation of concentrations of metals in different points for different layers is developed. The values of the metals (Ca, Mg, Fe, Sr, Cu, Zn, Mn, Pb, Cr, Ni, Se, Co, Cd, V, Mo) concentrations in different layers in peat taken from Knavu peat bog from four sites are determined using inductively coupled plasma optical emission spectrometer. Mathematical model for calculation of concentrations of metal has been described in the paper. As an example, mathematical models for calculation of Pb concentrations have been analyzed.*

**Keywords:** *peat bog, metals, 3-D boundary-value problem, finite-difference method.*

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### Introduction

Natural peat, because of its high content of humin, humic acid and fulvic acid, generally binds metal ions strongly. Because of its high complication capacity, high cation's exchange capacity, natural moor and peat grounds have become extended sinks for metal ions transported by aquatic migration and originating from atmospheric deposition [1, 2]. The survey of the scientific literature focused on the subject "peat and metals" reveals that very many referring articles have already dealt with this theme: the investigation of depth profiles of metals in peat as historical trends in pollutant deposition [3, 4, 5, 6, 7, 8], metals in moss [9, 10, 11], soils [12] and sediments [13], mainly as a result of atmospheric depositions, reflect the impact of human growth on the accumulation of toxic metals on the global ecosystem. Other type of peat and metals studies focuses on peat use to capture dissolved metals from aquatic solution [14, 15, 16, 17, 18, 19]. It means that knowledge about metals' concentration in peat is very important. Since experimental determination of metals in peat is very long and expensive work that one can use experimental data the mathematical model for calculation of concentration of metals in different points for different layers (peat blocks) is developed.

The mathematical model is based on averaging methods along the vertical z coordinate. This method applies to mathematical simulation of the mass transfer process in multilayered underground systems [20, 21] where it was necessary to solve the 3-D boundary-value problems for elliptic type partial differential equations of second order. The considered method allows reducing the 3-D problem to a system of 2-D problems.

### Materials and methods

**Site location.** Peat sample has been carried out in Knavu peat bog in East Latvia, Rezekne district. Total area of Knavu bog is 1240.6 ha, industrial outputs are 881.7 ha and maximum

depth of peat is 5.55 m. Peat layer forms hummock and hollow peat. The sampling sites in peat bog have been chosen in natural not drained part of bog. There are four peat sampling sites in Knavu bog.

**Sampling.** The peat samples (34 cm long monoliths) were put in polyethylene film to preserve nature moisture, brought to the laboratory. The first slice (+3 to 0 cm) is corresponded to the living plant material on the bog surface. For survey of the metal concentration in the peat in the studied bog in four peat bores were sampled using a peat sampler ( $\varnothing = 8$  cm). Excess surface vegetation was removed *in situ* to facilitate penetration of the peat surface. Samples of peat were taken to a depth of 374 cm.

**Peat sample preparation and analysis of metals.** Study has been carried out using air dry peat from peat bog. Analysis has been performed using A class vessels, calibrated measuring instruments and equipment. Analytical quality reagents have been used without further purification. All chemicals used in this study were of high purity. For preparation of solutions high purity deionized water has been used throughout. Glass and quartz vessels utilized in the study have been pre-cleaned by treating with  $K_2Cr_2O_7$  and concentrated sulfurous acid mix.

All peat samples have been analyzed in triplicate.

Metals were determined after acid digestion [22]. Peat samples were digested heating 1.5 g of peat with 15 mL conc.  $HNO_3$  at  $95^\circ C$  for 2 hours. Samples were filtered through filter which previously has been washed with 0.5% conc.  $HNO_3$  solution, and then the filtrate was diluted to the volume of 65 mL with deionized water. Metal (Ca, Mg, Fe, Mn, Zn, Cu, Cd, Pb, Co, Cr, Ni, Mo, V, Se, Sr) concentrations were measured by Inductively coupled plasma optical emission spectrometer OPTIMA 2100 DV ICP/OES from PerkinElmer.

**A mathematical model.** The process of diffusion we will consider in 3-D parallelepiped

$$\Omega = \{ (x, y, z) : 0 \leq x \leq l, 0 \leq y \leq L, 0 \leq z \leq Z \}.$$

The domain  $\Omega$  consists of multilayer medium. We will consider the stationary 3-D problem of the linear diffusion theory for multilayered piece-wise homogenous materials of  $N$  layers in the form

$$\Omega = \{ (x, y, z) : x \in (0, l), y \in (0, L), z \in (z_{i-1}, z_i) \}, i = \overline{1, N}$$

where  $H_i = z_i - z_{i-1}$  is the height of layer  $\Omega_i$ ,  $z_0 = 0$ ,  $z_N = Z$ . We will find the distribution of concentrations  $c_i = c_i(x, y, z)$  in every layer  $\Omega_i$  at the point  $(x, y, z) \in \Omega_i$  by solving the following partial differential equation (PDE):

$$D_{ix} \partial^2 c_i / \partial x^2 + D_{iy} \partial^2 c_i / \partial y^2 + D_{iz} \partial^2 c_i / \partial z^2 + f_i(x, y, z) = 0, \quad (1)$$

where  $D_{ix}$ ,  $D_{iy}$ ,  $D_{iz}$  are constant diffusions coefficients,  $c_i = c_i(x, y, z)$  - the concentrations functions in every layer,  $f_i(x, y, z)$  - the fixed sours function. The values  $c_i$  and the flux functions  $D_{iz} \partial c_i / \partial z$  must be continued on the contact lines between the layers

$$z = z_i, i = \overline{1, N-1} :$$

$$c_i|_{z_i} = c_{i+1}|_{z_i}, D_{iz} \partial c_i / \partial z|_{z_i} = D_{(i+1)z} \partial c_{i+1} / \partial z|_{z_i}, i = \overline{1, N-1} \quad (2)$$

where  $i = \overline{1, N-1}$ .

We assume that the layered material is bounded above and below with the plane surfaces  $z_0 = 0, z = Z$  with fixed boundary conditions in following form:

$$D_{1z} \partial c_1(x, y, 0) / \partial z = 0, c_N(x, y, Z) = C_a(x, y), - \text{the boundary conditions of the second type} \quad (3)$$

$$c_1(x, y, 0) = C_0(x, y), c_N(x, y, Z) = C_a(x, y), - \text{the boundary conditions of the first type} \quad (4)$$

where  $C_0(x, y)$ ,  $C_a(x, y)$  are given concentration-functions.

We have two forms of fixed boundary conditions in the  $x, y$  directions:

1) the periodical conditions by  $x = 0, x = l$  in the form

$$c_i(0, y, z) = c_i(l, y, z), \partial c_i(0, y, z) / \partial x = \partial c_i(l, y, z) / \partial x, \quad (5)$$

2) the symmetrical conditions by  $y = 0, y = L$

$$\partial c_i(x, 0, z) / \partial y = \partial c_i(x, L, z) / \partial y = 0. \quad (6)$$

For solving the problem (1)-(6) we will consider conservative averaging (AV) and finite difference (FD) methods. These procedures allow to reduce the 3-D problem to some 2D boundary value problem for the system of partial differential equations with circular matrix in the  $x$ -directions.

### The AV-method with quadratic splines.

The equation of (1) are averaged along the heights  $H_i$  of layers  $\Omega_i$  and quadratic integral splines along  $z$  coordinate in following form one used [21]

$$c_i(x, y, z) = C_i(x, y) + m_i(x, y)(z - \bar{z}_i) + e_i(x, y)G_i((z - \bar{z}_i)^2 / H_i^2 - 1/12) \quad (7)$$

where  $G_i = H_i / D_{iz}$ ,  $\bar{z}_i = (z_{i-1} + z_i) / 2$ ,  $m_i, e_i, C_i$  are the unknown coefficients of the spline-function,  $C_i = H_i^{-1} \int_{z_{i-1}}^{z_i} c_i(x, y, z) dz$  are the average values of  $c_i, i = \overline{1, N}$ .

After averaging the system (1) along every layer  $\Omega_i$ , we obtain

$$D_{ix} \partial^2 C_i / \partial x^2 + D_{iy} \partial^2 C_i / \partial y^2 + 2H_i^{-1} e_i + F_i(x, y) = 0, \quad (8)$$

where  $F_i = H_i^{-1} \int_{z_{i-1}}^{z_i} f_i(x, y, z) dz$  are the average values of  $f_i, i = \overline{1, N}$ .

From (2),(7) follows

$$\begin{cases} 6C_i + 3H_i m_i + e_i G_i = 6C_{i+1} - 3H_{i+1} m_{i+1} + e_{i+1} G_{i+1}, & i = \overline{1, N-1} \\ D_{iz} m_i + e_i = D_{(i+1)z} m_{i+1} - e_{i+1} \end{cases} \quad (9)$$

Excluding  $m_{i+1}$  from (9) and then decreasing  $i$  and excluding  $m_{i-1}$  we obtain for determined  $e_i^j$  following system of  $N - 2$  algebraic equations

$$\begin{aligned} 2e_{i-1} G_{i-1} (G_i + G_{i+1}) + e_i ((G_i + 3G_{i-1})(G_i + G_{i+1}) + (G_i + 3G_{i+1})(G_i + G_{i-1})) + \\ + 2e_{i+1} G_{i+1} (G_i + G_{i-1}) = 6(C_{i+1} - C_i)(G_i + G_{i-1}) - 6(C_i - C_{i-1})(G_i + G_{i+1}) \end{aligned} \quad (10)$$

where  $i = \overline{2, N-1}$ .

From boundary conditions (3), (4) we can obtain 2 algebraic equations for  $i = 1, i = N$ : at first from (3) and (7) we have

$$D_{1z} m_1 - e_1 = 0 \quad C_N + m_N H_N / 2 + e_N G_N / 6 = C_a, \text{ or from (4)}$$

$$C_1 - m_1 H_1 / 2 + e_1 G_1 / 6 = C_0 \text{ and then from (2.4) for } i = 1 \text{ and } i = N \text{ from (9) we obtain}$$

$$3m_1 D_{1z} (G_1 + G_2) + e_1 (G_1 + 3G_2) + 2e_2 G_2 = 6(C_2 - C_1)$$

$$3m_N D_{Nz} (G_N + G_{N-1}) - e_N (G_N + 3G_{N-1}) - 2e_{N-1} G_{N-1} = 6(C_N - C_{N-1}).$$

Therefore, excluding  $m_1, m_N$  we obtain

$$\begin{aligned} e_1 (4G_1 + 6G_2) + 2e_2 G_2 = 6(C_2 - C_1) \\ (2G_N + 4G_{N-1})e_N + 2e_{N-1} G_{N-1} = -6(C_N - C_{N-1}) + 6(C_a - C_N)(1 + G_{N-1} / G_N), \end{aligned} \quad (11)$$

from (4) we obtain

$$(2G_N + 4G_2)e_1 + 2e_2 G_2 = 6(C_2 - C_1) - 6(C_1 - C_0)(1 + G_2 / G_1).$$

We can rewrite the system of algebraic equations (10),(11) in the form  $i = \overline{1, N}$

$$A_i e_{i-1} (A_i + B_i + 1) e_i + B_i e_{i+1} = a_i (C_{i+1} - C_i) - b_i (C_i - C_{i-1}) \quad (12)$$

where  $A_i = G_{i-1} / (G_i + G_{i-1}), B_i = G_{i+1} / (G_i + G_{i+1}), a_i = 3 / (G_i + G_{i+1}), b_i = 3 / (G_{i-1} + G_i), e_0 = b_1 = 0, A_1 = 1, G_{N+1} = 0, C_{N+1} = C_a, G_0 = 0$ .

We can seek the solution of system (12) in the form [22]:  $e_i = \sum_{k=1}^N (-1)^{k+i} \beta_{i,k} (C_{k+1} - C_k)$ , (13)

where the unknown variables  $\beta_{i,k}$  do not depend on  $C_k$  and these we can determine from monotonous finite-difference scheme by factorization method (Thomas algorithm) for tri-diagonal matrix [23]. Therefore, from (7) we obtain the systems of  $N$  partial differential equations (PDE), where the boundary conditions for  $C_i$  are determined from (5)-(6) in the  $x, y$  -directions for averaged values

$$C_i(0, y) = C_i(l, y), \partial C_i(0, y) / \partial x = \partial C_i(l, y) / \partial x, \quad (14)$$

$$\partial C_i(x, 0) / \partial y = \partial C_i(x, L) / \partial y = 0. \quad (15)$$

In the case  $N = 2$  (two layers) we have from (2.2) the following system of two PDE

$$\begin{cases} D_{1x} \partial^2 C_1(x, y) / \partial x^2 + D_{1y} \partial^2 C_1(x, y) / \partial y^2 + 2H_1^{-1} e_1(x, y) + F_1 = 0 \\ D_{2x} \partial^2 C_2(x, y) / \partial x^2 + D_{2y} \partial^2 C_2(x, y) / \partial y^2 + 2H_2^{-1} e_2(x, y) + F_2 = 0 \end{cases}, \quad (16)$$

where concentration of metals of the first layer  $c_1(x, y, z)$  and the second layer  $c_2(x, y, z)$  under the formula (7) according to system (16) is calculated:

$$c_1(x, y, z) = C_1(x, y) + m_1(x, y)(z - H_1 / 2) + e_1(x, y) G_1 \left( (z - H_1 / 2)^2 / H_1^2 - 1 / 12 \right), z \in [0, H_1]$$

$$c_2(x, y, z) = C_2(x, y) + m_2(x, y)(z - (2H_1 + H_2) / 2) +$$

$$e_2(x, y) G_2 \left( (z - (2H_1 + H_2) / 2)^2 / H_2^2 - 1 / 12 \right), z \in [H_1, Z]$$

$$m_1(x, y) = e_1(x, y) / D_{1z}, \quad m_2(x, y) = (2e_1(x, y) + e_2(x, y)) / D_{2z},$$

or for the boundary condition (4) we have

$$m_1(x, y) = e_1(x, y) / (3D_{1z}) + 2(C_1(x, y) - C_0(x, y)) / H_1,$$

$$m_2(x, y) = -e_2(x, y) / (3D_{2z}) + 2(C_a(x, y) - C_2(x, y)) / H_2.$$

If  $N = 1$  (one layer), then from boundary conditions (3) follows  $e_1 = 1.5(C_a - C_1) / G_1$ , but from (4) follows  $e_1 = 3(C_a - C_1 + C_0 - C_1) / G_1$ .

### The FD – method for two layers.

We consider an uniform grid  $(N_x \times (N_y + 1))$ :

$$\omega_h = \{(x_i, y_j), x_i = ih_x, y_j = (j-1)h_y, i = \overline{1, N_x}, j = \overline{1, N_y + 1}, N_x h_x = l, N_y h_y = L\}.$$

Subscripts  $(i, j)$  refer to  $x, y$  indices, the mesh spacing in the  $x_i, y_j$  directions are  $h_x$  and  $h_y$ .

For two layers we can the PDEs (2.10) rewritten in following vector form:

$$D_x \partial^2 C / \partial x^2 + D_y \partial^2 C / \partial y^2 - AC + F = 0 \quad (17)$$

where  $D_x, D_y$  are the 2-nd order diagonal matrices with elements  $D_{1x}, D_{2x}$  and  $D_{1y}, D_{2y}$ .

$A$  is matrix of second order with elements  $H_1, H_2, G_1, G_2$  and  $C, F$  are the 2-nd order vectors-columns with elements  $C_1, C_2$  [23].

The equation (17) for vector function  $C$  in the uniform grid  $(x_i, y_j)$  is replaced by vector difference equations of second order approximation in 3 - point stencil

$$AA_j W_{j-1} - CC_j W_j + BB_j W_{j+1} + F_j = 0 \quad (18)$$

where  $W_j$  are vectors -column  $W_j \approx (C_{1,j}, C_{2,j}, \dots, C_{N_x,j})^T$ ,  $F_j$  are vectors-column with elements  $(F_{1,j}, F_{2,j}, \dots, F_{N_x,j})^T$ ,  $j = \overline{2, N_y}$ ,  $AA_j, CC_j, BB_j = AA_j$  are the block- matrices of second order with the elements of the circular symmetric matrix with

$N_x = M$  in the following form (the circular matrix  $A$  can be written down with the first rows in the form  $A = [a_{1,1}, a_{1,2}, \dots, a_{1,M}]$ ):

$$AA_j = \begin{bmatrix} [D_{1y} / h_y^2, 0, \dots, 0] & 0 \\ 0 & [D_{2y} / h_y^2, 0, \dots, 0] \end{bmatrix}, \quad CC_j = \begin{bmatrix} cc_1 & cc_2 \\ cc_3 & cc_4 \end{bmatrix},$$

where the circular matrices  $cc_1, cc_2, cc_3, cc_4$  are

1) for boundary condition (3)

$$cc_1 = [2(D_{1x} / h_x^2 + D_{1y} / h_y^2) + 12 / (H_1 d_1), -D_{1x} / h_x^2, 0, \dots, 0, -D_{1x} / h_x^2],$$

$$cc_2 = [-18 / (H_1 d_1), 0, \dots, 0], \quad cc_3 = [-18 / (H_2 d_1), 0, \dots, 0],$$

$$cc_4 = [2(D_{2x} / h_x^2 + D_{2y} / h_y^2) + 12(3 + k) / (H_2 d_1), -D_{2x} / h_x^2, 0, \dots, 0, -D_{2x} / h_x^2],$$

2) for boundary condition (4)

$$cc_1 = [2(D_{1x} / h_x^2 + D_{1y} / h_y^2) + (12 + 3k^{-1}) / (H_1 d_1), -D_{1x} / h_x^2, 0, \dots, 0, -D_{1x} / h_x^2],$$

$$cc_2 = [-9 / (H_1 d_1), 0, \dots, 0], \quad cc_3 = [-9 / (H_2 d_1), 0, \dots, 0],$$

$$cc_4 = [2(D_{2x} / h_x^2 + D_{2y} / h_y^2) + 12(3 + k) / (H_2 d_1), -D_{2x} / h_x^2, 0, \dots, 0, -D_{2x} / h_x^2].$$

The vectors –column  $w_j$  from (18) is calculated on Thomas algorithm [23] in the matrix form using program MATLAB.

### Results and Discussion

Average concentrations of the elements in the peat sections of the studied Knavu bog are shown in Fig. 1-3. The profile of concentration changes elements at first can influence their biogenic recycling and low mobility of these elements considering also the changes of the water table [24]. Changes of concentrations of studied elements in all studied points in Knavu bog have similar character: higher concentrations at upper layer are decreasing of the element concentration starting from a depth 50 cm – 100 cm.

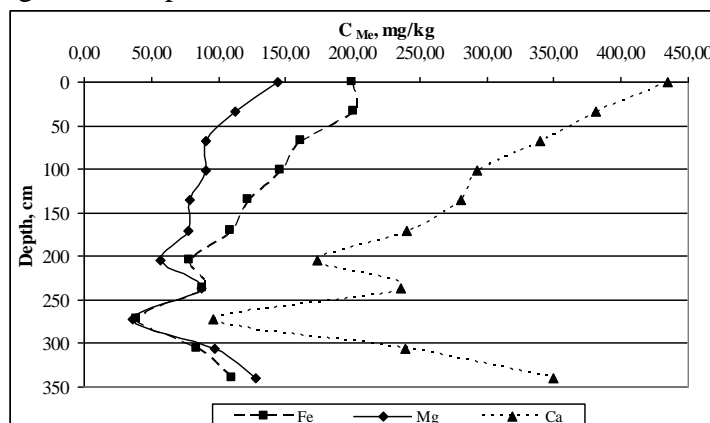


Fig. 1. Fe, Mg, Ca concentrations (mg/kg) in peat core from Knavu bog

For several elements (Fe, Sr, Zn, Mn, Ca, Mg) their concentrations again are increasing from a depth starting from 2 – 3 m most probably due to supply with ground waters. Trends of changes of concentrations of evidently anthropogenic elements (Pb, Cr, Cd and others) follow a similar trend at both sites: concentrations within the bulk of the peat section are stable, but then steeply are increasing towards the surface of the bog, again slightly decreasing at approximately 10 – 20 cm below the surface.

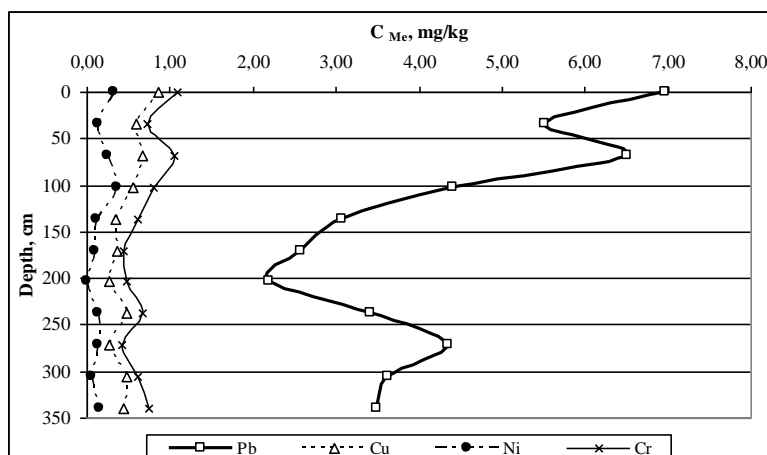


Fig. 2. Pb, Cu, Ni, Cr concentrations (mg/kg) in peat core from Knavu bog

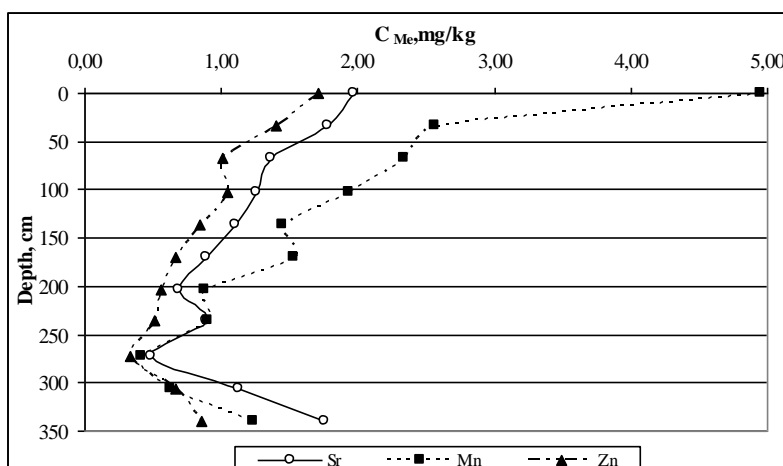


Fig. 3. Sr, Mn, Zn concentrations (mg/kg) in peat core from Knavu bog

For mathematical model experimental data has been used – concentrations of Pb in four sites in Knavu peat bog in depth from 0 cm till 340 cm.

### Numerical results

We consider the metal concentration in the 2 layered peat block - with following measure:

$$L = l = 1 \text{ m}, Z = H_1 + H_2 = 2.5 \text{ m}, H_1 = 1 \text{ m}, H_2 = 1.5 \text{ m}.$$

At the top of the earth ( $z = Z$ ) the concentration  $c \text{ mg / kg}$  of metals are given in following  $(x, y)$  points:  $c(0.1, 0.2) = 0.6$ ,  $c(0.1, 0.8) = 0.5$ ,  $c(0.9, 0.2) = 0.4$ ,  $c(0.9, 0.8) = 0.7$ .

This data are smoothing by 2D interpolation with MATLAB operator, using the spline function. We use following diffusion coefficients in the layers:

$$D_{1z} = 10^{-3}, D_{2z} = 5 \cdot 10^{-4}, D_{1x} = 10^{-4}, D_{2x} = 10^{-4}, D_{1y} = 10^{-5}, D_{2y} = 10^{-5}.$$

In the Fig.4 is the graphics of metal concentration  $c$  depending of vertical coordinate  $z$  by  $x = l/2$ ,  $y = L/2$  and in other points. In the Fig. 5-8 we can see the distribution of concentration  $c$  in the  $(x, y)$  plane by  $z = H_1$ ,  $z = Z$  and the averaged values  $C_1, C_2$ .

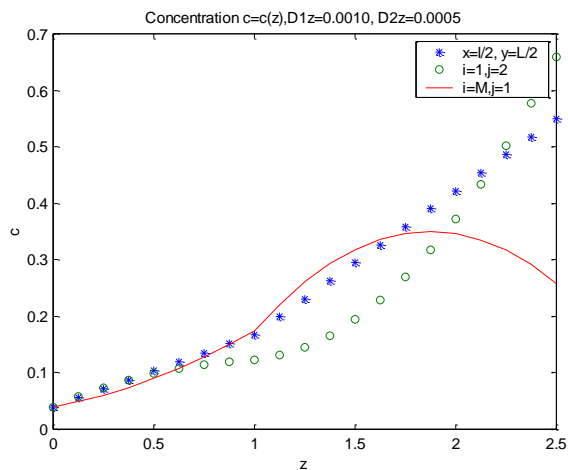


Fig. 4. The graphics of  $z = z(x)$

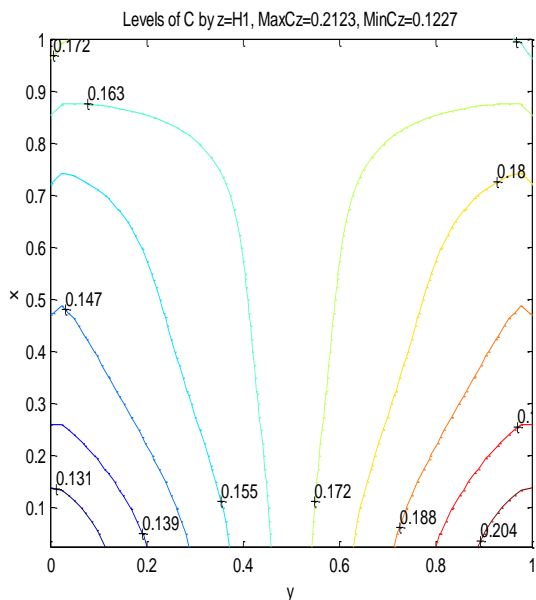


Fig. 5. Levels of  $c$  by  $z = H_1$

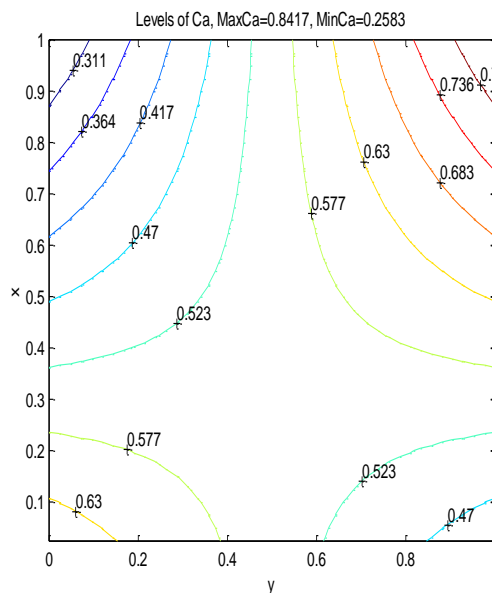


Fig. 6. Levels of  $C_a$

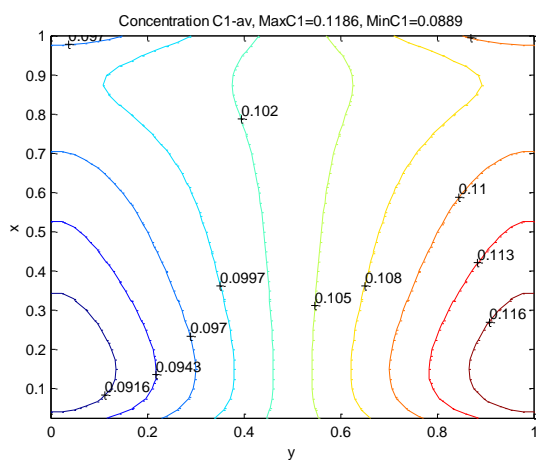


Fig. 7. Levels of  $C_1$

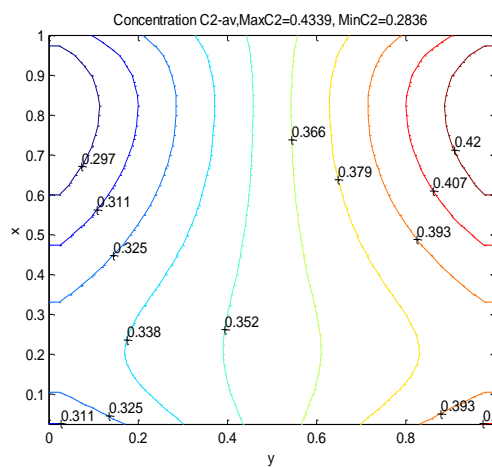


Fig. 8. Levels of  $C_2$

In the Fig. 9 and 10 are the distribution of  $c$  in the  $(z, y)$  and  $(z, x)$  plane by  $x = l/2$  and  $y = L/2$ .

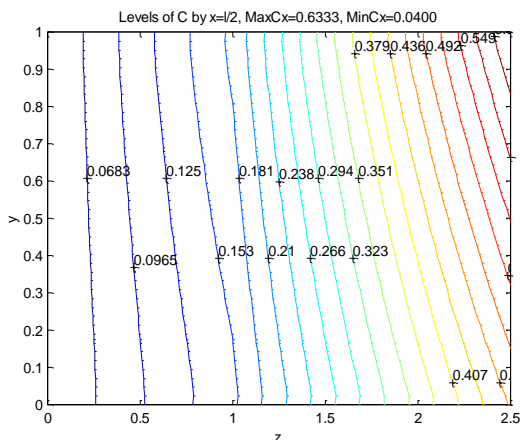


Fig. 9. Levels of  $c$  by  $x = l/2$

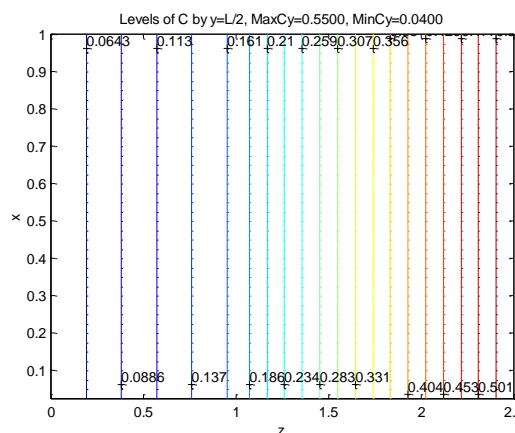


Fig. 10. Levels of  $c$  by  $y = L/2$

### Conclusions

The biggest concentrations of heavy metals are at the top layers of peat. Concentrations of trace elements are low. Metals concentration in peat profiles confirms with respect to the possibility of using metals concentration as indicator of the region and global environmental pollution. Data of metal concentration in peat bogs in different levels have been got not only by chemical analysis but using mathematical model as well. On practical analysis based mathematical model functionate. Modeling and practical data are very similar it means that model have practical application in real determination of metal concentrations.

The 3D diffusion problem in  $N$  layered domain described by a boundary value problem of the system of PDEs with piece-wise constant diffusion coefficients are approximate on the boundary value problem of a system of  $N$  PDEs.

The problem of metal concentration in the 2 layered peat block as an example of this algorithm is considered.

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