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THE MATHEMATICAL MODELING OF Ca AND Fe DISTRIBUTION IN PEAT LAYERS

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Abstract. *Bogs have been formed by an accumulation of peat - a light brown-to-black organic material, built up from partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees under waterlogged conditions. The total peatlands area in Latvia covers 698 918 ha or 10.7% of the entire territory.*
Knowledge's of peat metals content are important for any kind of peat using. Experimental determination of metals in peat is very long and expensive work. Using experimental data mathematical model for calculation of concentrations of metals in different points for different layers can help to very easy and fast to find approximately concentration of metals or trace elements.
The results of the research show that concentrations of trace elements in peat are generally low. Concentrations differ between the superficial, middle and bottom peat layers, but the significance decreases depending on the type of mire.
The mathematical model for calculation of concentration of metals in different points for different 3 layers in peat blocks is developed. As an example, mathematical models for calculation of Ca and Fe concentrations have been analyzed.

Keywords: *finite difference method, heavy metals, peat bog.*

Introduction

Peat is a mixture of plant remains in different stages of decay consisting in five main groups of organic compounds: proteins, lipids, hydrocarbons, pigments and lignin [1]. Peat can be totally or poorly humified, depending on the level of decomposition and formation that its parent plants have undergone. Peat is classified primarily as fibric, hemic or sapric peat. With fibric peat being the least decomposed and containing large amounts of undecomposed fibers, hemic peat is being moderately decomposed, and sapric peat being the most decomposed. Peat has ability to bind trace elements which depends of peat structure and composition. Climatic conditions may be the principal factor favouring peat formation. Regional climate, the nature of the vegetation, water pH, and degree of metamorphosis may affect the characteristics of the peat. [2]

Trace elements accumulated in peatlands have two main natural sources:

1) atmospheric deposition of soil dusts and aerosols (the only source in ombrotrophic mires); and
2) the incorporation as particulate matter or in solution via runoff and ground waters (by mineral dissolution or desorption of compounds previously accumulated in the environment). [1]

Main anthropogenic pollution sources are atmospheric particles, wastewaters, results of changes in environmental conditions such as changes in pH value [1]. Although at trace levels some heavy metals are essential for plants and animals, at higher concentrations they become dangerous for any form of life [3].

The mechanisms for sorption of metal ions on peat include physical adsorption, ion exchange, chelating, lone pair electron sharing, chemical reaction with phenolic hydroxyls and similar species [4, 5]. There are some limitations in the use of peat as sorbent material. Natural peat has a low mechanical strength, a high affinity for water, poor chemical stability and tendency to shrink.

Experimental chemical analyses of heavy metals in peat usually are expensive and not always easy to use. Mathematical models which based on real results are more easy to use for practical determination of necessary elements.

Using experimental data the mathematical model for calculation of concentration of metals in different points for different 3 layers (peat blocks) is developed. In study was considered averaging and finite difference methods for solving the 3-D boundary-value problem in multilayered domain. A specific feature of these problems is that it is necessary to solve the 3-D boundary-value problems for elliptic type partial differential equations (PDEs) of second order with piece-wise diffusion coefficients in three layer domain.

In study process was developed a finite-difference method for solving of above mentioned boundary-value problem of the type with periodical boundary condition in x direction. This procedure allows reducing the 3-D problem to a system of 2-D problems by using circulant matrix [6].

Materials and methods

Peat. Peat samples have been carried out in Knavu peat bog in East Latvia, Vilani district. Total area of Knavu bog is 1240.6 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.

The peat samples (0.34 m long monoliths) were put in polyethylene film. 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 ($\varnothing = 0.08$ m). Excess surface vegetation was removed *in situ* to facilitate penetration of the peat surface. Samples of peat were taken to a depth of 3 m.

Study of metals in peat samples has been carried out using air dry peat. All analysis has been performed using A class vessels, calibrated measuring instruments and equipment. Analytical quality reagents have been used without further purification.

For preparation of solutions high purity deionized water has been used throughout. All chemicals used in study were of high purity. 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. Peat samples were digested heating 1.5 g of peat with 15 mL conc. HNO_3 at 95 ^{0}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. Ca and Fe 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
$\Omega = \{(x, y, z): 0 \le x \le l, 0 \le y \le L, 0 \le z \le Z\}.$

The domain Ω 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

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

Where $H_i = z_i - z_{i-1}$ is the height of layer Ω_i, $z_0 = 0$, $z_N = Z$.

We will find the distribution of concentrations $c_i = c_i(x,y,z)$ in every layer Ω_i at the point $(x,y,z) \in \Omega_i$ by solving the following partial differential equation (PDE):

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

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 continues on the contact lines between the layers $z = z_i, i = \overline{1, N-1}$:

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

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:

$c_1(x,y,0) = C_0(x,y)$, $c_N(x,y,Z) = C_a(x,y)$ - the boundary conditions of the first type (3)

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

$$c_i(0,y,z) = c_i(l,y,z), \partial c_i(0,y,z)/\partial x = \partial c_i(l,y,z)/\partial x, \qquad (4)$$

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

$$\partial c_i(x,0,z)/\partial y = \partial c_i(x,L,z)/\partial y = 0. \qquad (5)$$

For solving the problem (1 - 5) 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) is averaged along the heights H_i of layers Ω_i and quadratic integral splines along z coordinate in following form one used [7]:

$$c_i(x,y,z) = C_i(x,y) + m_i(x,y)(z - \bar{z}_i) + e_i(x,y)G_i\left((z - \bar{z}_i)^2 / H_i^2 - 1/12\right) \qquad (6)$$

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

After averaging the system (1) along every layer Ω_i, we obtain system of N equations of 2-D PDE

$$D_{ix}\partial^2 C_i / \partial x^2 + D_{iy}\partial^2 C_i / \partial y^2 + 2H_i^{-1}e_i + F_i(x,y) = 0, \qquad (7)$$

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 (3) follows

$$3m_1 H_1 = 6(C_1 - C_0) + e_1 G_1 \qquad (8)$$

$3m_3H_3 = 6(C_a - C_3) - e_3G_3$

From (2), (6) we obtain following system of $N-2$ algebraic equations for determining e_i:

$$2e_{i-1}G_{i-1}(G_i + G_{i+1}) + e_i((G_i + 3G_{i-1})(G_i + G_{i+1}) + (G_i + 3G_{i+1})(G_i + G_{i-1})) + \\ + 2e_{i+1}G_{i+1}(G_i + G_{i-1}) = 6(C_{i+1} - C_i)(G_i + G_{i-1}) - 6(C_i - C_{i-1})(G_i + G_{i+1}) \quad (9)$$

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

From the system of algebraic equations (2 - 9) can be obtained e_i depending of $C_i, i = \overline{1, N}$. In the case $N = 3$ (three layers) we have:

$$e_i = e_{i,1}C_1 + e_{i,2}C_2 + e_{i,3}C_3 + e_{i,0} \quad (10)$$

$m_i = m_{i,1}C_1 + m_{i,2}C_2 + m_{i,3}C_3 + e_{i,0}$, $i = 1;2;3$,

From (7), (10) follows the system of three PDE

$$\begin{cases} D_{1x}\partial^2 C_1(x,y)/\partial x^2 + D_{1y}\partial^2 C_1(x,y)/\partial y^2 + 2H_1^{-1}e_1(x,y) + \hat{F}_1(x,y) = 0 \\ D_{2x}\partial^2 C_2(x,y)/\partial x^2 + D_{2y}\partial^2 C_2(x,y)/\partial y^2 + 2H_2^{-1}e_2(x,y) + \hat{F}_2(x,y) = 0, \\ D_{3x}\partial^2 C_3(x,y)/\partial x^2 + D_{3y}\partial^2 C_3(x,y)/\partial y^2 + 2H_3^{-1}e_3(x,y) + \hat{F}_3(x,y) = 0 \end{cases} \quad (11)$$

where $\hat{F}_i(x,y) = F_i(x,y) + 2H_1^{-1}e_{i,0}$, $i = 1;2;3$.

The Finite Difference method

For solving 2-D problems we consider a 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. The PDEs (11) can be rewritten in following vector form:

$$D_x \partial^2 C/\partial x^2 + D_y \partial^2 C/\partial y^2 - AC + \hat{F} = 0 \quad (12)$$

where D_x, D_y are the 3-d order diagonal matrices with elements D_{1x}, D_{2x}, D_{3x} and D_{1y}, D_{2y}, D_{3y}, C is the 3 order vectors-column with elements C_1, C_2, C_3, $\hat{F}$ is also the vectors-column with elements $\hat{F}_1, \hat{F}_2, \hat{F}_3$, and matrix A is in following form:

$$A = -2\begin{pmatrix} e_{1,1}/H_1 & e_{1,2}/H_1 & e_{1,3}/H_1 \\ e_{21}/H_2 & e_{22}/H_2 & e_{23}/H_3 \\ e_{3,1}/H_3 & e_{3,2}/H_3 & e_{3,3}/H_3 \end{pmatrix}.$$

The equation (12) with periodical conditions for vector function C in the uniform grid (x_i, y_j) is replaced by vector difference equations of second order approximation:

$$AA_j W_{j-1} - CC_j W_j + BB_j W_{j+1} + \hat{F}_j = 0, \quad (13)$$

where $W_j, \hat{F}_j, i = \overline{2, N_y}$ are the $M \times N, (M = N_x)$ order vectors-column with elements $C_{k,i,j} \approx C_k(x_i, y_j)$, $\hat{F}_{k,i,j} = \hat{F}_k(x_i, y_j)$, $i = \overline{1, M}, k = 1; 2; 3$, $AA, CC, BB = AA$ are the 3 block-matrices of M order circulant symmetric matrix. The circulant matrix

$$A = \begin{pmatrix} a_1 & a_2 & \dots & a_M \\ a_M & a_1 & \dots & a_{M-1} \\ \dots & \dots & \dots & \dots \\ a_2 & a_3 & \dots & a_1 \end{pmatrix}$$

can be given with its first row in the form $A = [a_1, a_2, ..., a_M]$. The calculation of circulant matrix (matrix inversion and multiplication) can be carried out with MATLAB using simple formulae for obtaining the first M elements of matrix.

The boundary conditions (5) are replaced by difference equations of first order approximation:

$C(x, h_y) = C(x,0) + O(h_y)$, $C(x, L) = C(x, L - h_y) + O(h_y)$.

The vectors-column W_j from (15) is calculated by Thomas algorithm [8] in the matrix form using MATLAB.

The numerical methods

The vectors-column W_j from (13) is calculated by Thomas algorithm in the matrix form using MATLAB.

$$W_j = X_j W_{j+1} + Y_j = 0,\ j = N_y(-1)1 \qquad (14)$$

where X_j, Y_j are corresponding matrices and vectors, obtaining of following expressions

$$X_j = (CC_j - AA_j X_{j-1})^{-1} BB_j\ ,\ Y_j = (CC_j - AA_j X_{j-1})^{-1}(AA_j Y_j + F_j), \quad j = 2(1)N_y \qquad (15)$$

Here $X_1 = E\ \ Y_1 = 0\ \ W_{\widehat{N}+1} = (E - X_{\widehat{N}})^{-1} Y_{\widehat{N}}$, $(\widehat{N} = N_y)$

where

$$E = \begin{pmatrix} [1,0,\ldots,0] & 0 & 0 \\ 0 & [1,0,\ldots,0] & 0 \\ 0 & 0 & [1,0,\ldots,0] \end{pmatrix}.$$

The inverse matrix of

$$A = \begin{bmatrix} A11 & A12 & A13 \\ A21 & A22 & A23 \\ A31 & A32 & A33 \end{bmatrix}$$

$B = A^{-1}, (BA = AB = E)$ is in the form

$$B = \begin{bmatrix} B11 & B12 & B13 \\ B21 & B22 & B23 \\ B31 & B32 & B33 \end{bmatrix}$$

where is obtained from the following MATLAB file [8]:

function[B11,B12,B13,B21,B22,B23,B31,B32,B33]=apg3(A11,A12,A13,A21,A22,A23,A31,A32,A33).

Results and discussion

Average concentrations of Ca and Fe in peat of the Knavu bog are shown in Fig. 1. The profile of concentration changes for metals at first may be influence their biogenic recycling and low mobility of these elements considering also the changes of the water table. Changes of concentrations of studied elements in all points have similar characters - concentrations very fast decreases with depth increasing.

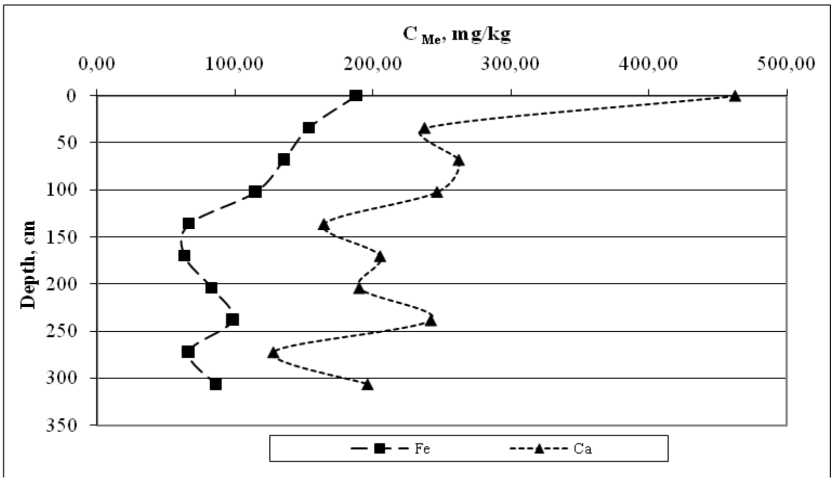

Fig. 1. **Fe and Ca concentrations (mg/kg) in peat core**

The numerical results

On the top of the earth (*z* = *Z*) we have the measured concentration ***c*** *mg/kg* x10^2 of metals in the following nine points in the (*x; y*) plane:

1) for **Fe:**

c(01., 0.2) = 1.69*;* *c*(0.5, 0.2) = 1.83*;* *c*(0.9, 0.2) = 1.72*;* *c*(0.1, 0.5) = 1.70*;* *c*(0.5, 0.5) = 1.88*;* *c*(0.9, 0.5) = 1.71*;* *c*(0.1, 0.8) = 1.71*;* *c*(0.5, 0.8) = 1.82*;* *c*(0.9, 0.8) = 1.73,

2) **for Ca:**

c(0.1, 0.2) = 3.69*;* *c*(0.5, 0.2) = 4.43*;* *c*(0.9, 0.2) = 3.72*;* *c*(0.1, 0.5) = 4.00*;* *c*(0.5, 0.5) = 4.63*;* *c*(0.9, 0.5) = 4.11*;* *c*(0.1, 0.8) = 3.71*;* *c*(0.5, 0.8) = 4.50*;* *c*(0.9, 0.8) = 3.73.

This date are smoothing by 2D interpolation with MATLAB operator, using the spline function.

We use following diffusion coefficients in the layers:

1) **for Fe** (C0 = 0.66):

D1z = 10^{-3}; D2z = 0.38 10^{-3}; D3z = 0.22 10^{-3};

2) **for Ca** (C0 = 1.30) :

D1z = 10^{-3}; D2z = 1.875 10^{-3}; D3z = 0.1333 10^{-3}:

The diffusion coefficients in (x, y) directions are:

D1x = D1y = 310^{-4}; D2x = D2y = 410^{-4}; D3x = D3y = 510^{-5}.

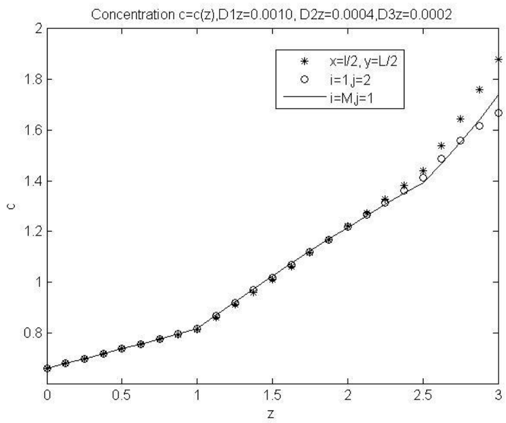

Fig. 2. **The distribution of Fe concentration *c* depending of vertical coordinate *z* in three points: *x = l/2, y = L/2; i=1, j=2; i=M (x=1), j=1***

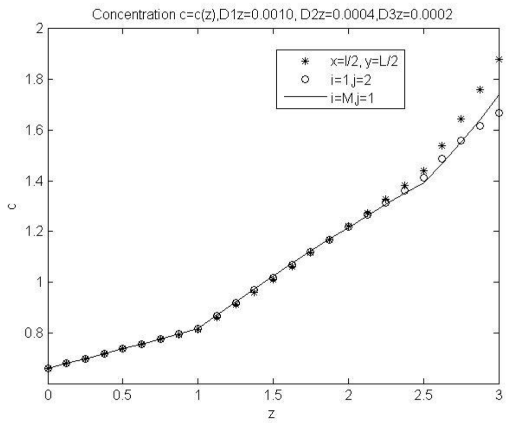

Fig. 3. **The distribution of Ca concentration *c* depending of vertical coordinate *z* in three points: *x = l/2, y = L/2; i=1, j=2; i=M (x=1), j=1***

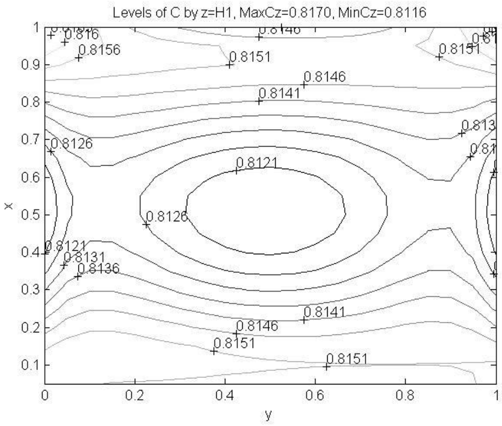

Fig. 4. **The distribution of Fe concentration *c* in the (*x; y*) plane (Levels of *c*) by *z* = *H*1**

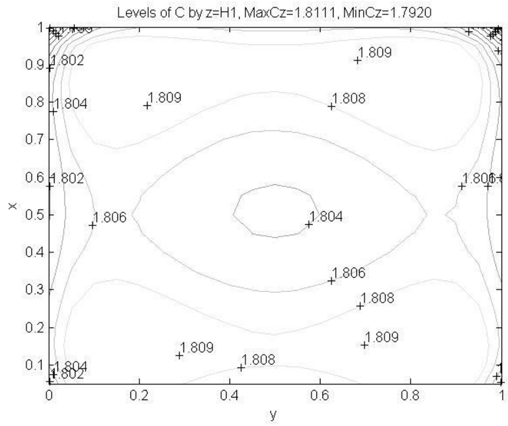

Fig. 5. **The distribution of Ca concentration *c* in the (*x; y*) plane (Levels of *c*) by *z* = *H*1**

In the Fig. 2 and Fig. 3 we can see the distribution accordingly of Fe and Ca concentration c depending of vertical coordinate z in three points, in Fig. 4 and Fig. 5 – the distribution of concentration c in the (x, y) plane by $z = H_1$ accordingly for Fe and Ca.

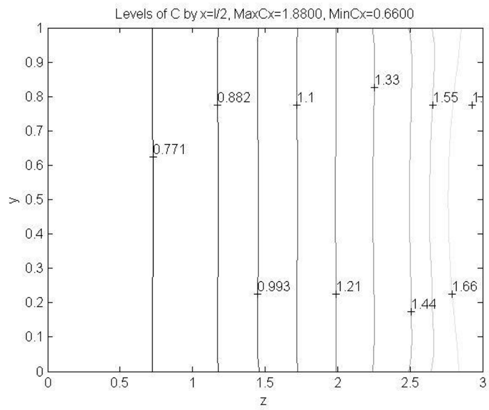

Fig. 6. **The distribution of Fe concentration *c* depending of vertical coordinate *z* by *x* = *l/2***

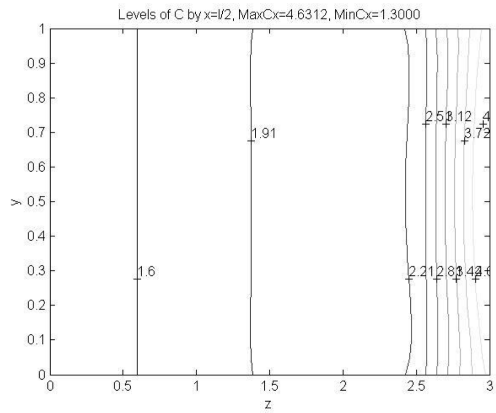

Fig. 7. **The distribution of Ca concentration *c* depending of vertical coordinate *z* by *x* = *l/2***

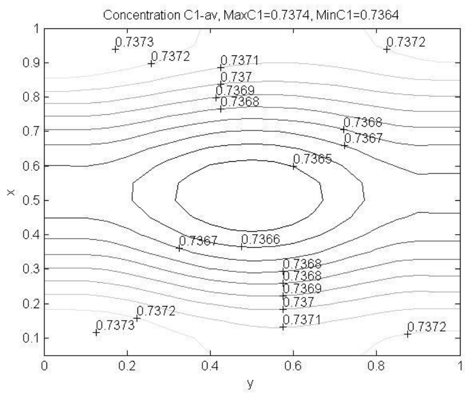

Fig. 8. **The distribution of averaged values C1 in first layer for Fe concentration**

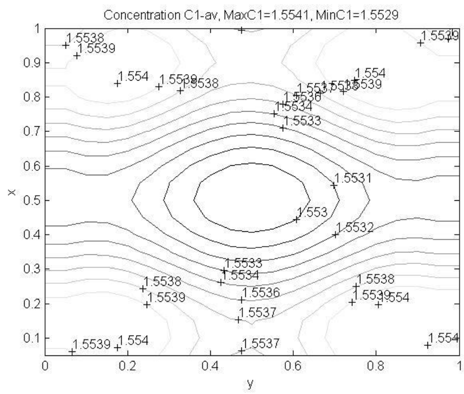

Fig. 9. **The distribution of averaged values C1 in first layer for Ca concentration**

In Fig. 6 and Fig. 7 – the distribution of c in the (z, y) plane by $x = l/2$ accordingly for Fe and Ca, and the distribution of averaged values C_1 in the first layer accordingly for Fe and Ca – in Fig. 8 and Fig. 9.

Conclusions

The biggest concentrations of heavy metals are at the top layers of peat. Concentrations of Ca and Fe very fast decreases with depth increasing. Elements concentration in peat profiles confirms with respect to the possibility of using trace elements concentration as indicator of the region and global environmental pollution.

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 2D boundary value problem of a system of *N* PDEs. This algorithm is used for solving the problem of metal concentration in the 3 layered peat block ($N = 3$). The total advantage and attainment of an averaged method for engineering calculations is determined from the number of grid points in every of three layers. The efficiency of this method is obtained due to simple algorithms for calculations of circulant matrix. Mathematical modeling results and practical data are very similar and it means that mathematical model have practical application in real determination of trace elements concentrations.

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