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THE MOTION OF IONS AND CHEMICAL COMPOUNDS IN SOIL SOLUTIONS*

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Analytic solutions are presented for a system of equations of a model of chemical compounds motions in soils that take into account the filtration heterogeneity effect, sorption and, also, the action of biological processes or chemical transformation. Examples are given of the application of models for describing the motion of nitrate fertilizers in soil.

Some models of mass transfer of interstatial solute components of soils were previously investigated /1,2/. In the analysis of models and checking programs for modelling on computers, an analytic solution of boundary value problems for the system of equations of models proved to be useful.

The one-dimensional filtration of soil solute is considered. The direction of the x axis is the same as the macroscopic motion of water. The filtration inhomogeneity of soils is described by introducing two zones of interstatial space: a stagnation one, where the solute is immobile, and a running zone, where convective transfer of migrants takes place (of ions and chemical compounds), and hydrodynamic dispersion appears. Subsequently subscripts 1 and 2 are attributed to quantities in the running and stagnation zones, respectively, c_1 and c_2 represent the migrant concentration in the solute, s_1 and s_2 are the contents of adsorbed migrants per unit weight of soil, and ε_1 and ε_2 are the moisture contents, as fractions of unit volume. The equation of conservation of mass is of the form

$$\frac{\partial(\varepsilon_1 c_1)}{\partial t}+\frac{\partial(\varepsilon_2 c_2)}{\partial t}+\rho\frac{\partial}{\partial t}(s_1+s_2)+\frac{\partial(qc_1)}{\partial x}=\frac{\partial}{\partial x}\left(D_1\frac{\partial c_1}{\partial x}\right)-I_1-I_2 \tag{1}$$

where q is the solute stream through unit cross section per unit time, D_1 is the coefficient of hydrodynamic dispersion, ρ is the soil structure density, and I is the migrant rate of transformation in a unit of volume per unit of time. The supplementary relations are

$$\begin{gathered}
\frac{\partial(\varepsilon_2 c_2)}{\partial t}+\rho\frac{\partial s_2}{\partial t}+I_2=k_{12}(c_1-c_2) \\
I_1=k_{t,1}(c_1-c_e),\quad I_2=k_{t,2}(c_2-c_e) \\
\frac{\partial s_1'}{\partial t}=\mu'\frac{\partial c_1}{\partial t},\quad \frac{\partial s_2'}{\partial t}=\mu_2'\frac{\partial c_2}{\partial t} \\
\partial s_1''/\partial t=k_{s,1}(\mu_1''c_1-s_1''),\quad \partial s_2''/\partial t=k_{s,2}(\mu_2''c_2-s_2'') \\
s_1=s_1'+s_1'',\quad s_2=s_2'+s_2''
\end{gathered} \tag{2}$$

The first equation of system (2) defines the mass exchange between the stagnation and running zones (k_{12} is the constant of the zones mass exchange kinetics), the second and third define the dynamics of migrant transformation (c_e is the migrant equilibrium concentration, and $k_{t,1}$ and $k_{t,2}$ are constants of transformation kinetics), the remaining equations are equations of sorption dynamics, as assumed in /3/ namely: the sorption centers are divided in two types, one with equilibrium (the respective quantity is denoted by a prime) and non-equilibrium (denoted by two primes) adsorption.

Let us consider now the system of equations

$$\frac{\partial y}{\partial t}+\beta\frac{\partial y}{\partial x}+\gamma\frac{\partial z}{\partial t}=\alpha^2\frac{\partial^2 y}{\partial x^2}-\sigma y,\quad \frac{\partial z}{\partial t}=\lambda(y-z) \tag{3}$$

One can verify that system (1), (2) with constant $\varepsilon_1, \varepsilon_2, q, D_1, \rho$ reduces to (3) in two cases: first, in the absence of stagnation zone ($\varepsilon_2=c_2=s_2=0$)

$$\begin{gathered}
y=c_1-c_e,\ z=s_1''/\mu_1''-c_e,\ \beta=q/R_1,\ \alpha^2=D_1/R_1 \\
\gamma=\rho\mu_1''/R_1,\ \sigma=k_{t,1}/R_1,\ \lambda=k_{s,1},\ R_1=\varepsilon_1+\rho\mu_1'
\end{gathered} \tag{4}$$

and, second, in the presence of stagnation zone, when we have only an equilibrium adsorption

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$(\mu_1'' = \mu_2'' = 0)$

$$y = c_1 - c_e,\ z = (c_2 - c_e)(1+\xi),\ \beta = q/R_1,\ a^2 = D_1/R_1 \qquad (5)$$
$$\gamma = R_2/[R_1(1+\xi)^2],\ \sigma = [k_{t,1} + k_{12}\xi/(1+\xi)]/R_1$$
$$\lambda = k_{12}(1+\xi)/R_2,\ R_1 = \varepsilon_1 + \rho\mu_1',\ R_2 = \varepsilon_2 + \rho\mu_2',\ \xi = k_{t,2}/k_{12}$$

Let us obtain solutions of system (3) in the semi-infinite interval $0 \leqslant x < \infty$ with initial conditions $y(x, 0) = y_0(x)$, $z(x, 0) = z_0(x)$ and boundary conditions of the first and third kind

$$y(0, t) = y_1 \quad \text{or} \quad y(0, t) - \frac{\alpha^2}{\beta}\frac{\partial y}{\partial x}\bigg|_{x=0} = y_1 \qquad (6)$$

when $y_1 = \mathrm{const}$ expressing the constancy at $x = 0$ of concentration or the stream of migrant mass, respectively. We effect the substitution

$$\bar{y} = y - y_1,\ \bar{z} = z - y_1 \qquad (7)$$

and reduce the problem to solving the integral equation with respect to $\bar{y}(x, t)$. Expressing $\bar{z}(x, t)$ from the second of Eqs. (3) we obtain

$$\bar{z}(x, t) = [z_0(x) - y_1]e^{-\lambda t} + \lambda\int_0^t \bar{y}(x, \tau)e^{-\lambda(t-\tau)}d\tau \qquad (8)$$

From the first of Eqs. (3) we have

$$L[\bar{y}] \equiv \frac{\partial\bar{y}}{\partial t} - \alpha^2\frac{\partial^2\bar{y}}{\partial x^2} + \beta\frac{\partial\bar{y}}{\partial x} + (\sigma + \gamma\lambda)\bar{y} = -\sigma y_1 + \gamma\lambda\bar{z}$$

which formally is an inhomogeneous linear equation of the parabolic type. Its solution can be written with the use of the influence function $G(x, \xi, t)$ of the homogeneous equation $L[\bar{y}] = 0$, which corresponds to the selected boundary condition

$$\bar{y}(x, t) = \int_0^\infty \left\{G(x, \xi, t)[y_0(\xi) - y_1] + \int_0^t G(x, \xi, t-\tau)[-\sigma y_1 + \bar{z}(\xi, \tau)]d\tau\right\}d\xi$$

Substituting here $\bar{z}(\xi, \tau)$ from (8), we obtain the sought integral equation

$$\bar{y}(x, t) = Y_{y_0-y_1}(x, t) + \gamma\lambda\int_0^t Y_{z_0-y_1}(x, \tau)e^{-\lambda\tau}d\tau - \qquad (9)$$
$$\sigma\int_0^t Y_{y_1}(x, \tau)d\tau + Q[\bar{y}(x, t)],\quad Y_h(x, t) = \int_0^\infty G(x, \xi, t)h(\xi)d\xi$$
$$Q[\bar{y}(x, t)] = \Lambda\int_0^t d\tau\int_0^\infty G(x, \xi, t-\tau)d\xi\int_0^\tau \bar{y}(\xi, \tau_1)e^{-\lambda(\tau-\tau_1)}d\tau_1,\quad \Lambda = \gamma\lambda^2$$

where $Y_h(x, t)$ denotes the solution of the homogeneous equation $L[Y] = 0$ on the semi-infinite straight line with initial $Y(x, 0) = h(x)$ and boundary condition (6) at $y_1 = 0$.

The solution of (9) may be presented in the form

$$\bar{y}(x, t) = u(x, t) + \gamma\lambda v(x, t) - \sigma w(x, t) \qquad (10)$$

where u, v, w satisfy the integral equation

$$u = Y_{y_0-y_1} + Q[u],\quad v = \int_0^t e^{-\lambda\tau}Y_{z_0-y_1}d\tau + Q[v],\quad w = \int_0^t Y_{y_1}d\tau + Q[w] \qquad (11)$$

Each of Eqs. (11) may be considered a Volterra's second order integral equation. On fairly general assumptions it is possible to seek their solution using the method of successive approximations. For this in effecting transformations, we use below the known property of the influence function

$$Y_h(x, t) = \int_0^\infty G(x, \xi, t-\tau)Y_h(\xi, \tau)d\xi \qquad (12)$$

and, when passing to limit, the representation of special functions in the form of series.

It can be shown that by virtue of (12)

$$Q[Y_h] = \Lambda\int_0^t \tau e^{-\lambda(t-\tau)}Y_h(x, \tau)d\tau$$

$$Q^{n+1}[Y_h] = Q[Q^n[Y_h]] = \frac{\Lambda^{n+1}}{n!(n+1)!}\int_0^t \tau^{n+1}(t-\tau)^n e^{-\lambda(t-\tau)}Y_h(x, \tau)d\tau$$

Then from (11) we have for u

$$u(x,t)=\sum_{n=0}^{\infty} Q^n[Y_{y_0-y_1}]=Y_{y_0-y_1}(x,t)+\int_0^t \sqrt{\frac{\Lambda\tau}{t-\tau}}\, I_1[2\sqrt{\Lambda\tau(t-\tau)}]\, e^{-\lambda(t-\tau)} Y_{y_0-y_1}(x,\tau)\, d\tau \tag{13}$$

Here and subsequently $I_n(x)$ are modified Bessel functions of the first kind. Similarly we obtain the formula

$$v(x,t)=\int_0^t I_0[2\sqrt{\Lambda\tau(t-\tau)}]\, e^{-\lambda(t-\tau)} Y_{z_0-y_1}(x,\tau)\, d\tau \tag{14}$$

To find w we denote beforehand

$$w_n'=\frac{(\gamma\lambda)^n}{n!}\int_0^t Y_{y_1}(x,\tau)\,\tau^n\, d\tau$$

$$w''_{n,m}=\frac{(\gamma\lambda)^n\lambda^m}{n!m!}\int_0^t Y_{y_1}(x,\tau)\, e^{-\lambda(t-\tau)}\tau^n(t-\tau)^m\, d\tau$$

Successive approximations yield

$$w_{(0)}=w_0',\ \ w_{(1)}+w_0'+Q[w_0']=w_0'+w_1'-w''_{1,0}$$

$$w_{(2)}=w_0'+Q[w_{(1)}]=w_0'+w_1'+w_2'-w''_{1,0}-w''_{2,0}-w''_{2,1}$$

and so on. At the limit we have

$$w(x,t)=\sum_{n=0}^{\infty} w_n'-\sum_{n=1}^{\infty}\sum_{m=0}^{n-1} w''_{n,m}=\int_0^t Y_{y_1}(x,\tau)\, e^{\gamma\lambda\tau} J_0[\gamma\lambda\tau,\lambda(t-\tau)]\, d\tau \tag{15}$$

Here we used the transformation

$$e^{-\lambda(t-\tau)}\sum_{n=1}^{\infty}(\gamma\lambda\tau)^n\sum_{m=0}^{\infty}\frac{\Lambda^m\tau^m(t-\tau)^m}{(n+m)!\,m!}=e^{-\lambda(t-\tau)}\sum_{n=1}^{\infty}(\gamma\lambda\tau)^n\frac{I_n[2\sqrt{\Lambda\tau(t-\tau)}}{[\sqrt{\Lambda\tau(t-\tau)}]^n}=e^{\gamma\lambda\tau}J_1[\lambda(t-\tau),\gamma\lambda\tau]$$

$$J_n(p,q)=\int_p^{\infty} e^{-\xi-q}\left(\frac{q}{\xi}\right)^{n/2} I_n(2\sqrt{\xi q})\, d\xi$$

The influence function appearing in the expressions for Y_n for the boundary condition of the first and third kind are, respectively, of the form

$$G(x,\xi,t)=-\frac{1}{2}e^{-(\sigma+\gamma\lambda)t}\frac{\partial}{\partial\xi}\left[\operatorname{erfc}(\zeta_-)-\exp\left(\frac{\beta}{\alpha^2}x\right)\operatorname{erfc}(\zeta_+)\right] \tag{16}$$

$$G(x,\xi,t)=-\frac{1}{2}e^{-(\sigma+\gamma\lambda)t}\frac{\partial}{\partial\xi}\Big\{\operatorname{erfc}(\zeta_-)+$$

$$\exp\left(\frac{\beta}{\alpha^2}x\right)\left[\operatorname{erfc}(\zeta_+)-\frac{2\beta\sqrt{t}}{\alpha}\operatorname{ierfc}(\zeta_+)\right]\Big\},\quad \zeta_\pm=\frac{\beta t+\xi\pm x}{2\alpha\sqrt{t}}$$

The program in FORTRAN for the calculation using (7), (10), and (13)−(16) are given in /4/.

The solution of problem (3), (6) for arbitrary $y_1=y_1(t)$ can be obtained from (7), (10) and (13)−(16) in conformity with the Duhamel principle. Solution of problem (3), (6) with $\sigma=0$ was investigated and presented earlier /5−7/.

Using the derived formulas, it was possible to find parameters in (3) from data on water migration in columns with samples of soils. The cases of constant migrant concentration at entry were investigated, as well as its step-by-step variation. Parameters were determined from the condition of minimum square deviation from the calculated values of migrant concentration in the filtrate from the column, using measured values of these concentrations. Minimization was effected by the method of random search.

Examples of conformity of calculated parameters and measured concentration of nitrate ions in fertilizers are shown in Fig.1, where the experimental data, shown by dots, are taken from /8/. T is the quantity of filtrated solute relative to the volume interstice humidity,

c_0 is the concentration in the supplied solute. The basic processes were: transformations resulting from the activity of soil micro-organisms (reduction of nitrate), hydrodynamic dispersion and convective transport; sorption was not observed. The velocity of solute stream was 0.002 m/s, the total humidity $\theta = 0.37$, and the column length was 0.14 m.

In the first case (the solid curve relates to it in Fig.1) in the beginning the column was fed a layer of solute containing nitrates 0.0111 m thick, after which a solute without nitrate was fed. In the second case (the dash curve) the supply of nitrate was continuous during the whole of the experiment. In both cases parameters were sought in (3) for two model variants: without the stagnation zone ($\varepsilon_2 = \gamma = \lambda = 0$) and with it. In the first case (with stagnation zone) the quality of approximation was statistically reliably improved; in the second case such improvement did not take place.

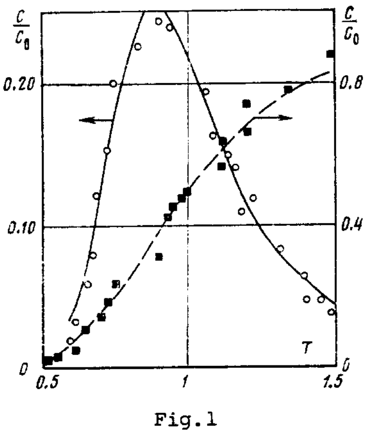

Fig.1

Values of parameters (3) with boundary condition of the third kind and the calculated subsequently in conformity with (5) values of some parameters (1) and (2) are listed below (the upper row of figures relates to the first case, the lower to the second)

$\alpha^2 \cdot 10^9$ m²/s	$\beta \cdot 10^7$ m/s	γ	$\lambda \cdot 10^6$ 1/s	$\sigma \cdot 10^5$ 1/s	ε_1	$k_{12} \cdot 10^7$ 1/s	$k_{t,1} \cdot 10^7$ 1/s
3,53	5,09	0,232	6,94	1,59	0,300	4,84	4,77
1,74	4,29	0	0	0,29	0,356	0	1,02

It should be noted that the quantity ε_1 in the second case was some-what smaller than θ, the migrant was not present in the whole volume of interstatial solute, and abrupt lowering of concentration of anions at the surface of the negatively charged particles was observed.

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