MATHEMATICAL MODELING OF CONVECTIVE DIFFUSION OF SOLUBLE COMPOUNDS IN THE SOIL AT NONISOTHERMAL MOISTURE TRANSFER

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This paper presents a mathematical model of solute transport in a soil with account for nonisothermal moisture transfer. The model is based on the equations of convective diffusion, sorption kinetics, and two-phase filtration, on the isotherms of water sorption by the soil, and on the thermodynamic laws. A numerical analysis of the influence of various physical mechanisms on the process of mass transfer in the soil has been performed.

Introduction. At present, investigations of the quantitative laws of vertical transport of solutes in the soil are needed for solving a wide spectrum of agroecological problems and developing nature-protective measures, such as evaluation of the threat of groundwater pollution by toxic substances, including radionuclides; evaluation of ingress of radionuclides and other toxic substances into plants; analysis of their getting into open water bodies due to surface run-off; analysis of the mechanisms of formation of the water-salt regime of irrigated soils; forecast of ecological consequences of measures to control the mass transport processes.

The present-day theory of solute transport in natural disperse systems is based on the application of the equations of convective diffusion and motion of moisture under isothermal conditions [1–3]. However, a change in the moisture content of the soil, which strongly influences the transport of solutes, can be caused not only by the capillary motion of moisture, but also by the recondensation of water vapor into cold parts of the soil. Therefore, the use of the equation of isothermal motion of moisture can lead to significant errors in calculating the convective diffusion of solutes under nonisothermal conditions. Note that at present the most widely used approach in describing the nonisothermal motion of moisture is, as before, the approach based on A. V. Luikov's works [4]. But in A. V. Luikov's moisture transport theory, because of the difficulty of determining the "the phase transition criterion" [5], it is practically impossible to determine what part of the change in the moisture content of a portion of soil has been caused by the capillary flow and what part is due to the vapor recondensation. This problem may not be so important in modeling the processes of convective drying, for which A. V. Luikov proposed his model. However, in calculating the convective diffusion of solutes in the soil, it is necessary to know what part of the moisture moves in the liquid phase and what part moves in the gaseous phase. This is due to the fact that it is the convective flow of the liquid phase that realizes the transport of solutes, and at the same time the water vapor recondensation causes a change in the thickness of water films on the surface of the solid phase of the soil, influencing the processes of diffusion and sorption of solutes. Therefore, in describing the convective diffusion of solutes in the soil mathematically, it is expedient to use the equations of two-phase filtration with separation of vapor and liquid flows.

It should be noted that in the Republic of Belarus after the accident at the Chernobyl NPP, the problem of predicting the migration of radionuclides in the soil became particularly urgent. Therefore, in the last twenty years, a large number of works in this field have appeared [6, 7]. However, most mathematical models presented in them are semiempirical and do not take into account the physics of the process of mass transfer in capillary-porous media, whose theoretical foundations were stated several decades ago [2, 8]. As is known [9], the nonlinearity of the considered process and the influence on its proceeding of a large number of factors make it difficult to use empirical models which hold only within the framework of the conditions and spatial-temporal scales in which they were obtained.

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In the present work, the authors aimed at developing a mathematical model and investigating the convective diffusion of solutes in the soil in their nonisothermal moisture transfer with account for the separate motion of the liquid and the water vapor.

Convective Diffusion of Solutes in the Soil with Account for the Nonequilibrium Sorption under the Conditions of a Change in the Saturation of the Soil with Moisture. Consider the mechanisms of motion of a solute through the pore space of a moisture-containing soil. The soil therewith is represented as a heterogeneous multiphase disperse system having the properties to accumulate, transform, and conduct matter and energy [10]. For the elementary volume ΔV of the soil, whose linear scale l is much less than the external scale L of the problem but much greater than the characteristic size of the capillaries r, of which the investigated medium consists (i.e., $L \gg l \gg r$), the balance equation

$$\frac{\partial (\theta_{liq}C)}{\partial t} = \nabla J_s \tag{1}$$

holds.

In the mass transfer by the flow of the soil moisture, processes connected with the absorption of solutes may proceed [8]. The following basic mechanisms of substance absorption in the soil are distinguished. First, it is adsorption of solutes on the surface of the solid phase of the soil [11]. Second, a change in the substance concentration in the soil can be due to its absorption by plants, the chemical and radioactive transformation, etc. The third type of absorber are zones of the so-called inactive porosity [8, 10], in which the velocity of liquid flow is close to zero. The substance that has entered this zone can stay there for a rather long time, which will lead to a delay in its return into the main stream. Whereas for taking into account the last mechanism it is necessary to divide the whole pore space of the soil into two subspaces, with the introduction for them of their own concentration as well as the intensity of substance exchange (this issue was considered in [3]), for taking into account the adsorption the intensity of substance absorption at the interface between the solid and liquid phases is given. This quantity is related to the solute concentration in the liquid phase by the sorption kinetics equation

$$\rho_b \frac{\partial a}{\partial t} = \beta (C - S) . \tag{2}$$

To take into account the change in the concentration caused by the processes of chemical and radioactive transformation and due to the substance absorption by plants, one can introduce into the balance equation (1) the function F characterizing the intensity of these processes [10].

Thus, the substance balance in the soil can be written as a system of equations

$$\frac{\partial (\theta_{liq}C)}{\partial t} + \rho_b \frac{\partial a}{\partial t} = \nabla J_s + F , \quad \rho_b \frac{\partial a}{\partial t} = \beta (C - S) . \tag{3}$$

Consider the solute flow in the soil. To describe the solute transfer in porous media, one usually employs the convective diffusion equation

$$J_s = \theta_{liq} D_{eff} \nabla C - \mathbf{u}C , \tag{4}$$

in which the first term defines the contribution of the diffusion flow of the substance under the action of the concentration gradient, and the second term defines the convective transfer of dissolved substances. Since mass transport in the soil occurs through the pore space filled with water, volume humidity of the soil θ_{liq} was introduced into the convective diffusion equation (4).

However, in real porous media smearing of the concentration front occurs not only due to the molecular diffusion, but also due to the inhomogeneity of the pore space leading to a change in the liquid velocity compared to the mean velocity. Velocity variations at microscopic level can occur due to the difference in the thickness of capillaries, the friction between the soil particles and the liquid, the curvature of the streamlines, etc. Velocity fluctuations lead to changes in the solute concentration. To take into this mechanism, in the equation of solute flow in the soil instead of the diffusion coefficients D_{eff} the hydrodynamic dispersion tensor $\mathbf{D}$ is used. At present, there exist several approaches for its determination, but the following expression has found the widest use [8, 12]:

$$\mathbf{D} = (\alpha_x - \alpha_y) \frac{u_x u_y}{|\mathbf{u}|} + \alpha_y \, |\mathbf{u}| \, \delta_{xy} + \tau D_m \,. \tag{5}$$

Note that in Eq. (5) $\alpha_y/\alpha_x \approx 0.1$, i.e., the longitudinal dispersion is greater than the transverse dispersion, since the latter is controlled by the molecular transition of particles from one streamline to another.

It should be noted that, as was shown in [13–15], hydrodynamic dispersion depends on the velocity of mass transport by the liquid flow not linearly but in the form of a power law:

$$\mathbf{D} = \frac{\mathbf{u}^2 \theta_{liq}^2}{K_d \beta} \,. \tag{6}$$

Note also that the molecular diffusion coefficient depends on the medium temperature

$$D_m = D_0 \exp\left(\frac{-E}{RT}\right). \tag{7}$$

The velocity of mass transport $\mathbf{u}$ by the liquid flow is related to the liquid velocity in the soil $\mathbf{v}_{liq}$ calculated by the Darcy law by the equation

$$\mathbf{u} = \frac{\mathbf{v}_{liq}}{\theta_{liq}} \,. \tag{8}$$

Representing the left-hand side of the mass balance equation (3) as

$$\frac{\partial\,(\theta_{liq} C)}{\partial t} + \rho_b \frac{\partial a}{\partial t} = \theta_{liq} \frac{\partial C}{\partial t} + C \frac{\partial \theta_{liq}}{\partial t} + \rho_b \frac{\partial a}{\partial t} \tag{9}$$

and taking into account that the solute flow in the soil is determined by the hydrodynamic dispersion and convection, we obtain a system of equations describing mathematically the solute transport in the soil with account for the sorption kinetics under the conditions of a change in the soil saturation with moisture:

$$\theta_{liq} \frac{\partial C}{\partial t} + C \frac{\partial \theta_{liq}}{\partial t} + \rho_b \frac{\partial a}{\partial t} = \nabla\,(\theta_{liq} \mathbf{D} \nabla C - \mathbf{u} C) + F \,, \quad \rho_b \frac{\partial a}{\partial t} = \beta\,(C - S)\,. \tag{10}$$

The above derivation of the convective diffusion equation with account for the sorption kinetics shows that the process of solute transport in the soil depends explicitly on its moisture content θ_{liq}, the rate of change in the moisture content $\partial\theta_{liq}/\partial t$, and the moisture flow, whereas in many works the equation

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} - v_{av} \frac{\partial C}{\partial x} \tag{11}$$

is widely used to describe the processes of vertical migration of salts, heavy metals, and radionuclides [16, 17]. Equation (11) does not explicitly take into account the moisture content of the soil and the sorption kinetics, but assumes that the coefficients of effective diffusion D_{eff} and average velocity of mass transport by the soil v_{av} have an empirical character and their values indirectly take into account a number of features of transport in the sorbed medium. In this connection, many problems connected with experimental determination of the parameters D_{eff} and v_{av} arise.

At the same time, writing the effective diffusion coefficient in terms of the moisture content, the sorption coefficient, and the hydrodynamic dispersion tensor permits optimal planning of the experiment on the determination of this coefficient [13–15]. Since the molecular diffusion coefficients in the solution for most cations and anions are now known, their values can be obtained from the reference literature [18]. And the porous medium parameters α and τ determining the dispersion are practically independent of the kind of the soluble compound, i.e., their values calculated

on the basis of the diffusion of one compound can be used to estimate the diffusion coefficients of other compounds [13–15].

It should be noted that the problem of determining the moisture velocity in the soil runs into great difficulties [2, 3, 10]. In natural conditions, in the soil there occurs a periodic change in the temperature and moisture regimes which influence, in a complex manner, the velocity of motion of the soil moisture. A. V. Luikov [4] has established that in the presence of a temperature gradient in a moist capillary-porous material there appears an additional moisture flow directed from a portion with a higher temperature to a portion with a lower temperature. The temperature field will also produce a strong effect on the intensity of water-to-vapor phase transformations and the moisture transfer in the vapor form, which leads to a change in the thickness of moisture films on which molecular diffusion of the substance occurs. Thus, the processes of moisture transfer in non-water-saturated soils have a complex form and it is necessary to take into account the moisture transfer in two forms: in the form of a liquid flow and in the form of water vapor. Therefore, the use of the average velocity of mass transport of the soil moisture is incorrect. Therefore, to model the solute transport in a soil, it is necessary to know the soil moisture velocity and the change in the water-saturation of the soil which are due to the capillary motion of the moisture and the water vapor recondensation. These values are very difficult to obtain experimentally, since they are functions of coordinates and time. Therefore, one has to complement the convective diffusion equation by nonisothermal moisture transfer equations, which make it possible to calculate, on the basis of the hydrological properties of soils and climatic factors, the dynamics of the moisture-content fields and the water velocity in the soil.

One example of such an approach to the solution of the nonisothermal moisture transfer equation is the model developed by the authors based on the heat conduction and two-phase filtration equations [19–21]

$$C_{\mathrm{eff}} \frac{\partial T}{\partial t} = \nabla \left(\lambda_{\mathrm{eff}} \nabla T \right) + h_{\mathrm{v}} I_{\mathrm{v}} + h_{\mathrm{liq}} I_{\mathrm{liq}} ,\tag{12}$$

$$\frac{\partial \left(\rho_{\mathrm{v}} \theta_{\mathrm{v}} \right)}{\partial t} = \nabla \left(\rho_{\mathrm{v}} \frac{K K_{\mathrm{v}} \left(\theta_{\mathrm{v}} \right)}{\eta_{\mathrm{v}}} \nabla \left[P_{\mathrm{v}} \left(\theta_{\mathrm{v}}, T \right) - \rho_{\mathrm{v}} g x \right] \right) + I_{\mathrm{v}} ,\tag{13}$$

$$\frac{\partial \left(\rho_{\mathrm{liq}} \theta_{\mathrm{liq}} \right)}{\partial t} = \nabla \left(\rho_{\mathrm{liq}} \frac{K K_{\mathrm{liq}} \left(\theta_{\mathrm{liq}} \right)}{\eta_{\mathrm{liq}}} \nabla \left[P_{\mathrm{liq}} \left(\theta_{\mathrm{liq}}, T \right) - \rho_{\mathrm{liq}} g x \right] \right) - I_{\mathrm{liq}} .\tag{14}$$

The liquid velocity in the soil therewith is determined from the Darcy law

$$\mathbf{v}_{\mathrm{liq}} = - \frac{K K_{\mathrm{liq}} \left(\theta_{\mathrm{liq}} \right)}{\eta_{\mathrm{liq}}} \nabla \left[P_{\mathrm{liq}} \left(\theta_{\mathrm{liq}}, T \right) - \rho_{\mathrm{liq}} g x \right] .\tag{15}$$

Note that the theory of two-phase flows, where the liquid and vapor motion is considered, is based on the equations of mass conservation of both phases, which cause no doubt. In this connection, the authors of [19–21] have shown that to determine the dependence of the liquid pressure on the moisture content and temperature, one can use the isotherms of sorption (desorption) of moisture by the soil at various temperatures and the Kelvin equation.

The sorption isotherm is an experimentally obtained dependence of the equilibrium moisture content of the soil on the relative humidity: $\theta_{\mathrm{e}} = f(\varphi, T)$. It should be noted that to model the nonisothermal moisture transfer, one needs data on sorption isotherms at various temperatures (Fig. 1) which can be approximated by a function of the form

$$\theta_{\mathrm{e}} = \left(p_1 + p_2 \varphi^{p_3} \right) \left(p_4 + p_5 T \right) .\tag{16}$$
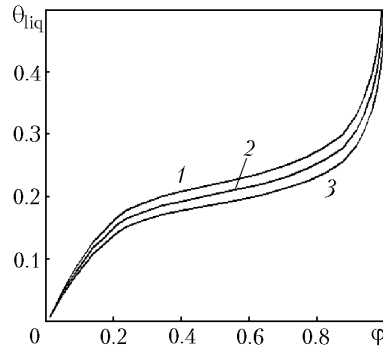
Fig. 1. Isotherms of moisture sorption by the soil at various temperatures: $T =$ 275; 2) 295; 3) 315 K.

In the region of relative humidity from 0 to 0.95, the simplest and most popular method of determining the water sorption curve is keeping soil samples over saturated solutions of various salts [10]. Using a capillary meter or a membrane press, we can obtain the dependence of the capillary-sorption potential on the moisture content of the soil in the region of relative humidities exceeding 0.95 [10]. In so doing, with the aid of the Kelvin equation we can calculate the dependence of the moisture content of the soil on the relative humidity, i.e., the sorption isotherm.

The relative humidity and the water vapor pressure are interrelated by the expression

$$\varphi = \frac{P_v}{P_{sat}} . \tag{17}$$

The temperature dependence of the saturated vapor pressure therewith is described by the simple analytical equation [22]

$$P_{sat} = 10^5 \left(\frac{T}{373}\right)^{15} . \tag{18}$$

Then, using the sorption isotherm (16) and expressions (17), (18), we can obtain the functional dependence determining the change in the vapor pressure caused by the change in the moisture content and temperature: $P_v = f(\theta_{liq}, T)$. Using it, we can write the Kelvin equation in the following form:

$$P_{liq} (\theta_{liq}, T) = P_{sat} + \frac{RT\rho_{liq}}{M} \ln \frac{f(\theta_{liq}, T)}{P_{sat}} . \tag{19}$$

The obtained relation (19) takes into account the physicochemical properties of the liquid and the structural characteristics of the porous body and is needed to solve the transfer equation of the liquid phase (14) as a relation between the liquid pressure, the moisture content, and the temperature. The vapor density therewith is determined by its pressure in accordance with the ideal gas law

$$\rho_v = \frac{MP_v}{RT} , \tag{20}$$

and the volume vapor content is calculated in the following way:

$$\theta_v = m - \theta_{liq} . \tag{21}$$

As for the mass transfer intensities between the phases I_v and I_{liq}, in accordance with the local thermodynamic equilibrium principle and the mass conservation law they can be calculated from the moisture sorption isotherm

$$I_{liq} = \frac{\partial (\rho_{liq}, \theta_e)}{\partial t} , \quad I_v = \frac{\partial (\rho_v \theta_e)}{\partial t} . \tag{22}$$

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Thus, with the use of the two-phase filtration equations (13), (14), the expressions for the source terms (22), and the closing relations (16)–(22) relating the liquid pressure and the volume vapor content to the volume moisture content and temperature, we can calculate the dynamics of the moisture content and liquid velocity fields under nonisothermal conditions. In so doing, the change in the soil temperature is determined by means of the heat conduction equation (12), and the obtained values of the moisture content and liquid velocity are used to calculate the convective diffusion of solutes in the soil under nonisothermal moisture transfer in accordance with equation (10).

For a complete statement of the problem of solute transport in the soil with account for the nonisothermal moisture transfer, it is necessary to formulate the initial and boundary conditions for the obtained system of differential equations. The initial conditions define the temperature, moisture, and solute fields in the soil at the initial instant of time:

$$C_{t=0} = C_0 , \quad T_{t=0} = T_0 , \quad \theta_{\text{liq}t=0} = \theta_{\text{liq}0} .$$ (23)

Knowing the temperature and moisture content distributions over the soil profile, from the sorption isotherm we can find the value of the vapor pressure in the soil: $P_{t=0} = f(\theta_{\text{liq}0}, T_0)$.

For the boundary conditions on the soil surface, it is necessary to define the change with time in the temperature of the near-surface layer of air, the intensity of taking in rain water, and the intensity of evaporation from the soil surface, i.e., these boundary conditions define the influence of climatic factors on the solute transport in the soil. Also, since the migration of soluble substances from the soil into the air and vice versa is insignificant or is absent altogether, for the convective diffusion coefficient at the boundary the equality to zero of the mass flow

$$\nabla (\theta_{\text{liq}} \mathbf{D} \nabla C - \mathbf{u} C) = 0$$ (24)

is taken.

For the heat conduction equation, the following boundary condition is given:

$$T_{x=0} = T_{\text{env}} (t) .$$ (25)

The infiltration of atmospheric precipitation (absorption intensity) can be determined as follows. At the beginning of a rainfall, when the soil is not saturated with moisture, the moisture flow from the soil surface is equal to the rainfall intensity (H):

$$\rho_{\text{liq}} \frac{KK_{\text{liq}} (\theta_{\text{liq}})}{\eta_{\text{liq}}} \nabla [P_{\text{liq}} (\theta_{\text{liq}}, T) - \rho_{\text{liq}} gx] = H \quad \text{at} \quad \theta_{\text{liq}} < \theta_{\text{sat}} .$$ (26)

When the near-surface layer of the soil approaches the saturated state $\theta_{\text{liq}} = \theta_{\text{sat}}$, i.e., the pores in the soil are completely filled with moisture, on the soil surface the boundary condition can be written in the form

$$P_{\text{liq}x=0} (t) = P_{\text{sat}} + \frac{RT\rho_{\text{liq}}}{M} \ln \frac{f (\theta_{\text{sat}}, T)}{P_{\text{sat}}} .$$ (27)

The evaporation intensity from the soil surface in the proposed mathematical model can be given knowing the relative humidity of the air near the soil surface:

$$P_{vx=0} = \varphi_{\text{env}} (t) P_{\text{sat}} (T) .$$ (28)

The above system of equations cannot be solved analytically. Therefore, it is necessary to use for mathematical modeling numerical methods (finite element method, finite difference method, etc.) [23]. To solve the obtained system of differential equations, we used a Femlab program complex that permits solving systems of equations of mathematical physics by the finite element method [24].

Thus, one can carry out, with the use of the proposed method, numerical investigations of the motion of water-soluble compounds in the soil at nonisothermal moisture transfer and with account for the change in climatic factors.
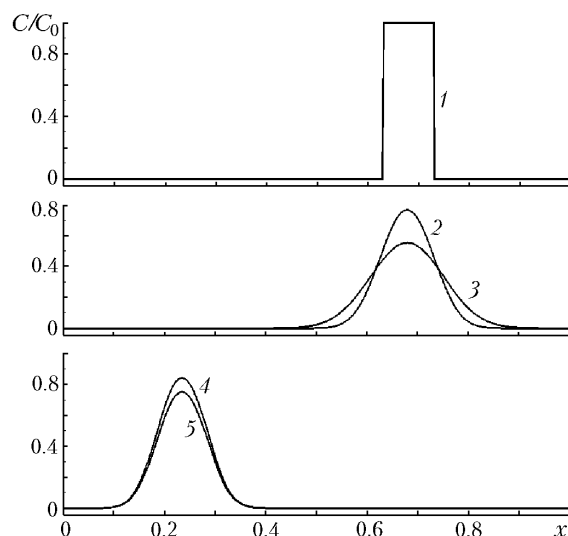
Fig. 2. Influence of various physical mechanisms on the solute transport in the soil: 1) convection; 2) molecular diffusion; 3) hydrodynamic dispersion; 4) equilibrium sorption; 5) solute decay.

Numerical Modeling of the Solute Transport in the Soil. Consider the influence of various mechanisms of convection, hydrodynamic dispersion, molecular diffusion, sorption, and decomposition on the pollutant transport in the soil and other porous media. Suppose that at the initial instant of time ($t = 0$) in the region of $0 \le x \le 0.1$ m of the soil a pollutant is contained (Fig. 2) and it is necessary to calculate how this substance will be distributed in the soil after one year ($t = 3.1536 \cdot 10^7$ sec). The parameters of Eqs. (3) and (4) describing the mass transport in the soil, at which the calculation was performed, are given in Table 1.

As the numerical analysis has shown, in the case of representing the porous medium as an ideal capillary (only the convection mechanism is taken into account), the pollutant will move in the form of an ideal step (Fig. 2, curve 1). In the presence of the process of molecular diffusion the front of the moving solution will be "smeared" by the diffusion processes (Fig. 2, curve 2). In so doing, the front width of the moving solution will characterize the diffusion process — the wider the front the more intensive the diffusion.

The presence of dispersion processes "smears" the front of the moving substance to an even greater extent (Fig. 2, curve 3). But if the migrating substance is sorbed by the soil (account of equilibrium sorption), then due to the adsorption processes it will be "detained" in the soil, i.e., the front of the moving solution will be shifted backwards compared to the nonsorbed substance (Fig. 2, curve 4). And, finally, in the presence of processes associated with a decrease in the solute concentration in the soil (chemical or radioactive decay, absorption by plants, precipitation, etc.) the front maximum of the moving solution will decrease (Fig. 2, curve 5). And the smaller the front maximum of the moving solution, the more intensive the processes of degradation of the soluble substance in the soil.

Thus, the ability of the soil to accumulate (adsorb the substance) and conduct the substance can already be determined by the migrating substance distribution over the soil profile alone. The intensity of these processes is evidenced by the maximum position and the front width of the moving solution.

Of interest is also the analysis of the influence on the solute transport in the soil of the sorption kinetics and the rate of change in the moisture content, which are not taken into account in the classical convective diffusion equation (11). To this end, we have performed calculations at various values of the sorption rate β and of the rate of change in the moisture content $\partial\theta_{liq}/\partial t$ (Table 1). As is seen from Figs. 3 and 4, the sorption kinetics and the rate of change in the moisture content of the soil influence the process of solute transport in the soil. Therefore, since the degree of influence of particular processes may differ for different geological media, soluble substances, instants of time, and spatial coordinates, to conduct a reliable analysis and forecast the transport of soluble substances in the soil, it is necessary in each particular case to adopt a well-grounded (by means of numerical estimation) approach to the choice of factors to be and not to be taken into account.

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TABLE 1. Values of the Coefficients in the Convective Diffusion Equation

| Physical mechanisms taken into account	Value of parameters
Convection	$\theta_{\text{liq}} = 0.5$ m³/m³, $J_{\text{liq}} = 1 \cdot 10^{-8}$ m/sec
Convection and molecular diffusion	$D_{\text{m}} = 5 \cdot 10^{-11}$ m²/sec, $\tau = 0.7$
Convection, molecular diffusion, and hydrodynamic dispersion	$\alpha_x = 0.002$ m, $\theta_{\text{liq}} D_x = \alpha_x u_x / |\mathbf{u}| + \theta_{\text{liq}} \tau D_{\text{m}}$
Convection, molecular diffusion, hydrodynamic dispersion, and equilibrium sorption	$\rho_{\text{b}} = 1200$ kg/m³, $K_{\text{d}} = 0.001$ m³/kg, $\partial a/\partial t = K_{\text{d}} \partial C/\partial t$
Convection, molecular diffusion, hydrodynamic dispersion, equilibrium sorption, and decay of solute	$\lambda = 7.66 \cdot 10^{-9}$ 1/sec, $F = -(\lambda \theta_{\text{liq}} C + \lambda \rho_{\text{b}} a)$
Nonequilibrium sorption	$\beta = 10^{-6}$ 1/sec, $\partial a/\partial t = \beta(C - a/K_{\text{d}})$
Rate of change in the moisture content	$\theta_{\text{liq}} = 0.25(1 + \cos(16\pi t/(3600 \cdot 24 \cdot 365)))$ $\partial \theta_{\text{liq}}/\partial t = -0.25 \sin(16\pi t/(3600 \cdot 24 \cdot 365))$
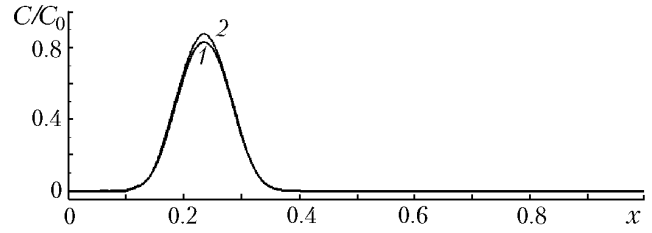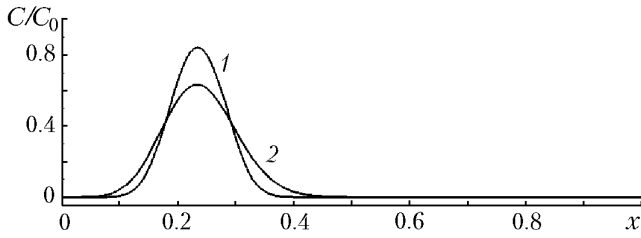
Fig. 3. Influence of the sorption kinetics on the solute distribution in the soil: 1) equilibrium sorption; 2) the sorption rate is 10^{-6} sec^{-1}.

Fig. 4. Influence of the rate of change in the moisture content on the solute distribution in the soil: 1) the term in the equation is taken into account; 2) not taken into account.

Let us investigate the influence of taking into account the nonisothermal moisture transfer on the calculation error. Suppose that at the initial instant of time in a 0–0.1 m layer of the soil a solution of a nonsorbed substance-marker is contained. Consider two cases of vertical migration of this substance. In the first case, rain falls to the surface of the soils with an intensity $H = 5 \cdot 10^{-7}$ m/sec; the initial moisture therewith is $\theta_{\text{liq0}} = 0.15$ m³/m³, and the temperature in the soil was taken to be equal to $T_{\text{top}} = 293$ K near the surface and $T_{\text{bot}} = 273$ K at a depth of 1.5 m. In the second case, moisture evaporation occurs with a relative humidity of the air φ_{env} near the soil surface of 10%, and the initial moisture and temperature distributions are as in the first case.

The system of nonisothermal moisture transfer equations (12)–(14) is solved therewith with the following boundary conditions. In the case of a rainfall at $x = 0$, for the equation of motion of moisture (14) we write the boundary condition of the form

$$\rho_{\text{liq}} \frac{K K_{\text{liq}}(\theta_{\text{liq}})}{\eta_{\text{liq}}} \nabla [P_{\text{liq}}(\theta_{\text{liq}}, T) - \rho_{\text{liq}} gx] = H, \quad \theta_{\text{liq}} < \theta_{\text{sat}} ; \tag{29}$$

$$\theta_{\text{liq}} = \theta_{\text{sat}}, \quad \theta_{\text{liq}} \geq \theta_{\text{sat}},$$

for the equation of motion of vapor (13)

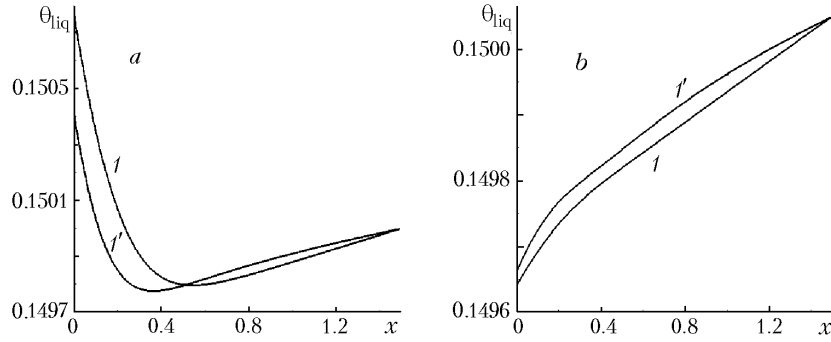$$\nabla [P_{\text{v}}(\theta_{\text{v}}, T) - \rho_{\text{v}} gx] = 0 \tag{30}$$

Fig. 5. Moisture distribution over the soil profile for different instants of time: 1) after 10 days; 1′) after 5 days; a) in the case of a rainfall; b) in the case of evaporation.

and for the heat transfer equation (12)

$$T_{x=0} = T_{top} . \tag{31}$$

At $x = 1.5$ m for the nonisothermal moisture transfer equations (12)–(14) the boundary conditions

$$\nabla [P_{liq} (\theta_{liq}, T) - \rho_{liq} gx] = 0 , \quad \nabla [P_v (\theta_v, T) - \rho_v gx] = 0 \quad \text{and} \quad T_{x=1.5} = T_{bot} \tag{32}$$

are written.

In the case of moisture evaporation from the soil surface at $x = 0$, the boundary condition is written for the equations:

of motion of moisture (14)

$$\nabla [P_{liq} (\theta_{liq}, T) - \rho_{liq} gx] = 0 , \tag{33}$$

of motion of vapor (13)

$$P_{vx=0} = \varphi_{env} T_{sat} (T) , \tag{34}$$

and of heat transfer (12)

$$T_{x=0} = T_{top} . \tag{35}$$

At $x = 1.5$ m for the nonisothermal moisture transfer equations (12)–(14) the same boundary conditions as in the case of a rainfall are written.

With the aid of the mathematical model of nonisothermal moisture transfer [19–21] the change in the fields of moisture and liquid flow in the soil was calculated (Figs. 5, 6). The hydrological and thermophysical properties of soils at which the calculation was made are given in Table 2. The other parameters defining the process of nonsorbed substance-marker transfer were given as follows: the solid phase density of the soil $\rho_b = 1200$ kg/m^3, the molecular diffusion coefficient $D_m = 4 \cdot 10^{-8}$ m^2/sec; the soil parameters defining the hydrodynamic dispersion are $\alpha_x = 0.005$ m and $\tau = 0.75$.

From the results of modeling (Figs. 5, 6) it is seen that the moisture flow in the soil is due to the nonuniform distribution of moisture and temperature over the soil profile. In the case of a rainfall, the moisture of the surface layer of the soil increases and there will appear a moisture flow directed from the surface into the depth of the soil (Fig. 6a, curve 2). At the same time the temperature on the soil surface is higher than the temperature at a depth of 1.5 m by 10 K; consequently, the capillary-sorption pressure near the soil surface will be higher than in the depth (with account for the sign), and the moisture will move from a point with a higher temperature to a point with a lower temperature. This causes a thermocapillary liquid flow (Fig. 6a, curve 1). Note that in the case of a rainfall the thermocapillary flow makes a small contribution to the resulting liquid flow (Fig. 6a, curve 3). Therefore, the sub-
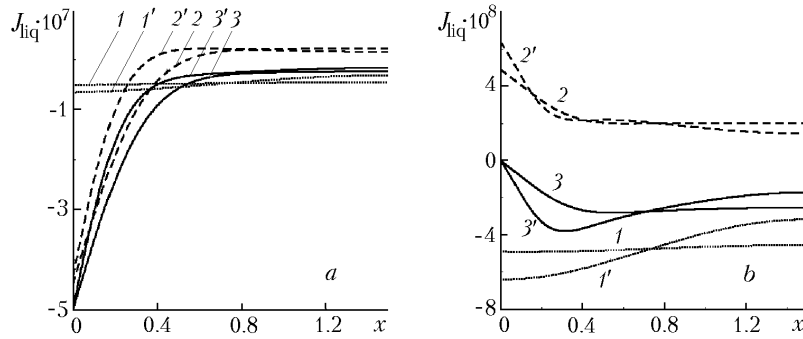
Fig. 6. Liquid flow distribution over the soil profile for different instants of time: 1 and 1′) liquid flow due to the temperature gradient after 10 and 15 days, respectively; 2 and 2′) liquid flow due to the moisture gradient after 10 and 5 days, respectively; 3 and 3′) resulting liquid flow after 10 and 5 days, respectively; a) in the case of a rainfall; b) in the case of evaporation.

TABLE 2. Values of Parameters in the Heat Conductivity and Moisture and Vapor Transfer Equations

Properties of soil	Value of parameters
Porosity	$m = 0.4$ m^3/m^3
Heat capacity	$C_{\text{eff}} = (1.92 \cdot 10^6 (1 - m) + 4.18 \cdot 10^6 \theta_{\text{liq}})$
Heat conductivity	$\lambda_{\text{eff}} = 0.925 + 1.68\theta_{\text{liq}} + 0.643 \exp(-\theta_{\text{liq}}^4)$
Penetrability	$K = 1.61 \cdot 10^{-12}$ m^2
Relative phase penetrability of:	
water	$K_{\text{liq}} = \left(\dfrac{\theta_{\text{liq}}}{m} \right)^{10.7}$
water vapor	$K_{\text{v}} = \left(1 - \dfrac{\theta_{\text{liq}}}{m} \right)^{10.7}$
Dependence of water vapor pressure on the moisture content and temperature	$P_{\text{v}} = P_{\text{sat}}(T) \exp\left[\dfrac{M}{R\rho_{\text{liq}}} \left(2.1 - \dfrac{1601}{T} \right) \left(\dfrac{m}{\theta_{\text{liq}}} \right)^{3.85} \right]$
Change in the liquid pressure depending on the moisture content and temperature	$P_{\text{liq}} = (2.1T - 1601) \left(\dfrac{m}{\theta_{\text{liq}}} \right)^{3.85}$

stance-marker distributions over the soil profile calculated with the use of the model taking into account the non-isothermal moisture transfer practically agree with the results obtained without account for the influence of temperature on the moisture redistributions (Fig. 7a).

However, in the case of moisture evaporation from the soil surface, an entirely different picture is observed. As a result of the evaporation, the moisture content of the top layer of the soil decreases. This causes a moisture flow from the bottom layers to the surface of the soil (Fig. 6b, curve 2). At the same time the nonuniform temperature distribution causes a thermocapillary moisture flow (Fig. 6b, curve 1) from the top layer of the soil into the depth. As is seen from the modeling results (Fig. 6b), in the case of moisture evaporation from the soil surface, the thermocapillary moisture flow makes a significant contribution to the resulting liquid flow in the soil.

It should be noted that in the model of mass transport in the soil developed by the authors of [1–3], in defining the liquid flow, the convective diffusion equation does not take into account the moisture flow caused by the temperature gradient and water vapor recondensation (for the case of moisture evaporation from the soil surface in
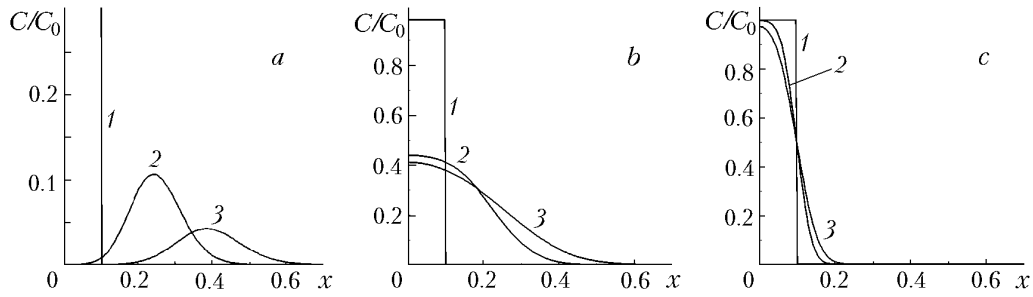
Fig. 7. Results of modeling the solute transport in the soil: 1) initial distribution; 2) distribution after 5 days; 3) distribution after 10 days; a) in the case of a rainfall; b, c) in the case of evaporation, respectively, with and without account for the nonisothermal moisture transfer.

these models, the liquid flow in the convective diffusion equation will be equal to zero). However, as is seen from the above modeling results (Fig. 7b and c), this may lead to large errors. Note also that under real natural conditions, along with the processes of in filtration of rain precipitation, the processes of moisture evaporation from the soil surface and thermocapillary motion of moisture always take place. All this definitively confirms that in modeling the process of solute transport in the soil the values of the moisture content and liquid flow in the convective diffusion equation should be calculated with account for the nonisothermal moisture transfer.

Conclusions. We propose a mathematical model of solute transport in the soil with account for the nonisothermal moisture transfer which is based on the equations of convective diffusion, sorption kinetics, two-phase filtration, and on the isotherms of moisture sorption by the soil and the thermodynamic laws.

By means of the model developed, an analysis of the influence of various physical mechanisms (convection, hydrodynamic dispersion, molecular diffusion, and sorption) on the solute distribution in the soil has been performed. It has been shown that to obtain more reliable forecast results it is necessary in each particular case to adopt a well-grounded (by means of numerical estimation) approach to the choice of factors to be and not to be taken into account.

Analysis of the results of numerical studies shows that to obtain more reliable results of forecasting the mass transport in the soil, the mathematical models used should take into account the nonisothermal conditions of moisture transfer.

NOTATION

a, concentration of sorbed substance in the soil per mass unit of the soil, kg/kg; C, volume concentration of the solute in the liquid phase on a per-unit-volume basis of the porous medium, kg/m^3; C_{eff}, effective volume heat capacity of the soil, J/(m$^3\cdot$K); $\mathbf{D}$, hydrodynamic dispersion tensor, m^2/sec; D_x, component of the hydrodynamic dispersion tensor, m^2/sec; D_0, coefficient equal numerically to the diffusion coefficient in the absence of an energy barrier for diffusing ions, m^2/sec; D_{eff}, effective diffusion coefficient of the solute in the soil, m^2/sec; D_m, molecular diffusion coefficient of the solute in free liquid, m^2/sec; E, activation energy, J/mole; F, drain and source function of the solute in the soil due to the processes of chemical and radioactive transformation, absorption of the substance by plants, etc., kg/(m$^3\cdot$sec); g, gravitational acceleration, m/sec^2; H, rainfall intensity, m/sec; h_{liq}, specific enthalpy of the liquid, J/kg; h_v, specific enthalpy of vapor, J/kg; I_{liq}, mass transfer intensity between the liquid and gas phases, kg/(m$^3\cdot$sec); I_v, mass transfer intensity between the gas and liquid phases, kg/(m$^3\cdot$sec); J_{liq}, liquid flow in the soil, (kg/m^3)·(m·sec); J_s, solute flow, (kg/m^3)·(m·sec); K, penetrability coefficient of the soil, m^2; K_d, distribution coefficient between the liquid-soluble substance and the solid phase, m^3/kg; K_{liq}, relative phase penetrability of the liquid; K_v, relative phase penetrability of vapor; L, linear scale of the problem, m; l, linear size of the elementary volume of the soil, m; M, molar mass of water, kg/mole; m, soil porosity, m^3/m^3; P_{liq}, liquid pressure, Pa; P_{sat}, saturated vapor pressure over the water surface, Pa; P_v, vapor pressure, Pa; p_1, p_2, p_3, p_4, and p_5, empirical coefficients in the sorption isotherm equation; R, universal gas constant, J/(mole·K); r, characteristic size of the capillary, m; S, equilibrium concentration value at which the intensity of the solute flow between the liquid and solid phases goes to zero, kg/m^3; T,

temperature, K; t, time, sec; $\mathbf{u}$, velocity vector of solute transfer in the soil by the liquid flow, m/sec; u_x, u_y, components of the velocity vector of mass transfer in the soil by the liquid flow, m/sec; $\mathbf{v}_{liq}$, velocity vector of the liquid flow in the soil, m/sec; v_{av}, average velocity of mass transfer by the soil moisture, m/sec; x, y, Cartesian coordinates; ΔV, elementary volume of soil, m^3; α, dispersion parameter of the porous medium, m; β, sorption rate, liter/sec; δ, unit tensor; η_{liq}, dynamic viscosity coefficient of the liquid, Pa·sec; η_v, dynamic viscosity coefficient of vapor, Pa·sec; θ_e, equilibrium volume moisture content of the soil, m^3/m^3; θ_{liq}, volume moisture content of the soil, m^3/m^3; θ_{sat}, maximum volume moisture content of the soil, m^3/m^3; θ_v, volume content of water vapor in the soil, m^3/m^3; λ, decay constant, liter/sec; λ_{eff}, effective heat conductivity of the soil, W/(m·K); ρ_b, solid phase density of the soil, kg/m^3; ρ_{liq}, liquid density, kg/m^3; ρ_v, water vapor density, kg/m^3; τ, parameter characterizing the "windingness" of diffusion paths in the pore space; φ, relative humidity. Subscripts: av, average; b, basic mass; bot, bottom; s, soluble substance; d, distribution; e, equilibrium; eff, effective value; env, environment; liq, liquid; m, molecular; sat, saturated; top, top; v, vapor; 0, initial.

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