

Spreading of Chemical Substance after its Accidental Spillage onto the Soil Surface under Unsaturated Conditions and Variable Porosity

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Abstract— In this paper we study a mathematical model of soil moisture transport with variable porosity. The problem is set for the case of highly concentrated solute spilled onto soil surface. We investigate the way solute transfer, adsorption of contaminant by soil particles and variable porosity influence infiltration of solute into the soil profile. For that purpose, two models are used: a classical one and the one with consideration of mentioned factors. By comparing the results of both models, we established that high concentration of solute causes moisture transport to transpire more slowly, and the pollutant to remain on the soil surface for longer time. Numerical results indicate that porosity can vary considerably under the conditions of intensive contamination with salts.

Keywords— mathematical model, porous medium, moisture transfer, solute transport, finite elements method.

I. INTRODUCTION

In the case of accidental spillage of chemical pollutant onto the soil surface, a problem of predicting its movement into the porous medium arises. Besides the diffusive process of pollutant spreading into the soil, also a convective flow is present, which is related to the moisture transport.

The difficulty of soil water flow modelling lies in the fact it is influenced by a considerable number of other factors and processes. Presence of chemical solutes, transfer of solutes between the phases of the soil, heat transfer, net radiation, precipitation dynamics, plant growth, root water uptake, soil erosion by surface and underground waters are some of them [2, 8]. They cause changes in water content rate and soil properties, which, in their own turn, influence mentioned processes. For instance, porosity depends greatly on soil salts content and solute transport dynamics; hydraulic conductivity is influenced by temperature, chemical content and soil moisture [4]. These dependencies are complex and often not uniquely defined, e.g. hysteresis [11].

Such properties of heterogeneous porous media are currently actively studied. For example, mathematical models of mentioned processes for the purpose of crop yield forecasting has been built in [11]. References [6, 10] proposed models describing transport of water, vapor and air in the soil under non-isothermal conditions. Modelling of solute transport

during the wetting of saturated-unsaturated soil has been done in [12]. Also, the impact of anthropogenic factors on the water flow is being studied. Authors of [13] studied the influence of temperature on evaporation and the combined moisture and solute transfer. The likelihood of acid rains causing landslides has been discussed in [14].

The aim of this study is to establish the effect of variable soil porosity, since it influences water capacity of porous medium, and so indirectly impacts moisture transport. The model built in this paper is based on the model proposed in [5], which is implemented to solve a three-dimensional problem of pollutant spillage on the soil surface. Described problem is relevant from the perspective of ecosystems, agriculture and hydrology.

II. MATHEMATICAL MODEL OF THE PROBLEM

A. Governing equations

Let us consider a problem of contaminant migration in finite three-dimensional domain $\Omega \supset \mathbf{X} \in (x_1, x_2, x_3)$ with boundary Γ . Hence, we have the following nonlinear mathematical problem consisting of four equations (for one-component chemical solution):

1) Moisture transport equation

$$\begin{aligned} & \left(\frac{\partial \rho_l}{\partial c} \frac{\partial c}{\partial t} + \frac{\partial \rho_l}{\partial T} \frac{\partial T}{\partial t} \right) (s(\sigma - \theta_{\min}) + \theta_{\min}) + \\ & + \rho_l (c - \theta_{\min}) \frac{\partial s}{\partial t} + \rho_l s \left(\frac{\partial \sigma}{\partial t} + \frac{\partial \sigma}{\partial N} \frac{\partial N}{\partial t} + \frac{\partial \sigma}{\partial T} \frac{\partial T}{\partial t} \right) = \\ & = \nabla \cdot (\rho_l \mathbf{D}((\sigma - \theta_{\min}) \nabla s + s \nabla \sigma)) + \\ & + \nabla \cdot (\rho_l (\mathbf{K}_l \nabla x_3 - \mathbf{K}_c \nabla c - \mathbf{K}_T \nabla T)), \mathbf{X} \in \Omega, t > 0. \end{aligned} \quad (1)$$

2) Solute transport equation

$$\begin{aligned} & \theta \left(1 - \frac{c}{\rho_l} \frac{\partial \rho_l}{\partial c} \right) \frac{\partial c}{\partial t} = \nabla \cdot (\theta \mathbf{D}_c \nabla c) - \mathbf{q}_1 \cdot \left(1 - \frac{c}{\rho_l} \frac{\partial \rho_l}{\partial c} \right) \nabla c + \\ & + \frac{c}{\rho_l} \frac{\partial \rho_l}{\partial T} \left(\theta \frac{\partial T}{\partial t} + \mathbf{q}_1 \nabla T \right) - \frac{\partial N}{\partial t}, \mathbf{X} \in \Omega, t > 0. \end{aligned} \quad (2)$$

3) Heat transfer equation

$$c_T \frac{\partial T}{\partial t} + T \left(c_N \frac{\partial N}{\partial t} - \rho_{m0} c_{m0} \frac{\partial \sigma_0}{\partial t} + c_{m0} (1 - \sigma_0) \frac{\partial \rho_{m0}}{\partial T} \frac{\partial T}{\partial t} \right) = \nabla \cdot (\lambda \nabla T) - \rho_l c_l \mathbf{q}_l \nabla T, \mathbf{X} \in \Omega, t > 0. \quad (3)$$

4) Equation of solute transport kinetics between the soil phases, describing adsorption and desorption of dissolved salts under Henry isotherm (Verigin et al., 1977)

$$\frac{\partial N}{\partial t} = f(c, N), \mathbf{X} \in \bar{\Omega}, t > 0. \quad (4)$$

In equations above the following notations are used: $s = (\theta(\mathbf{X}, t) - \theta_{\min}) / (\sigma(\mathbf{X}, t) - \theta_{\min})$ – degree of saturation; θ – volumetric water content; σ – porosity; σ_0 – porosity of indissoluble solid soil skeleton; θ_{\min} – residual (minimum) water content; c – solute concentration in soil water; N – salt concentration in the solid soil component; T – temperature; $\mathbf{q}_l = -\mathbf{D} \nabla \theta - \mathbf{K}_l \nabla x_3 + \mathbf{K}_c \nabla c + \mathbf{K}_T \nabla T$ – soil water flux rate; ρ_l – pore water density; \mathbf{D} – soil moisture diffusion coefficient; \mathbf{K}_l – unsaturated soil hydraulic conductivity; \mathbf{K}_c – chemical osmosis coefficient; \mathbf{K}_T – thermal osmosis coefficient; \mathbf{D}_c – dispersion coefficient; c_T – volumetric heat capacity of porous medium; λ – thermal conductivity; c_N – density of salt in the solid soil component; ρ_{s0}, c_{s0} – density and specific heat capacity of solid soil skeleton, γ_1 – adsorption and desorption rate constant, $\alpha = 1/\Gamma$ – distribution ratio, $\Gamma = N_0/\sigma c_0$ – Henry coefficient, N_0, c_0 – balance concentrations of the salt in solid and liquid phases respectively, t – time.

B. Modelling of nonlinear parameter dependency

Coefficients $\mathbf{D}, \mathbf{K}_l, \mathbf{K}_c, \mathbf{K}_T, \mathbf{D}_c$ in equations (1), (2) are tensors in the general case. We henceforth consider the soil isotropic, and treat mentioned coefficients as scalar functions. This assumption can be made without loss of generality. In this study, we chose certain methods to identify some variable characteristics of the medium and the moisture transfer process, as described below.

As proposed in [7], dependence of NaCl solution density on salt concentration c and temperature T is defined as

$$\rho_l(c, T) = \sum_{i=1}^3 \sum_{j=1}^3 a_{ij} c^{j-1} T^{i-1}, \quad (5)$$

where a_{ij} are empirical coefficients as specified in their work.

We also consider porosity to be variable due to adsorption of salts by solid soil particles. Such variations are neglected in most moisture transport models, including HYDRUSS [9]. According to [6], and in the case of one-component chemical solution, we have the following relation for porosity:

$$\sigma = \sigma_0 - \frac{N}{\rho_c}. \quad (6)$$

Assuming the porosity of soil skeleton σ_0 and the salt density ρ_c are constant, we get $\frac{\partial \sigma}{\partial N} = \frac{1}{\rho_c}$.

Numerous methods to determine hydraulic properties of the soil are described in the literature. For our problem, we use a widely known approach called Brooks and Corey model [1]:

$$K_l(c, T, s, \sigma) = K_0(c, T, \sigma) s^{\frac{2+3\lambda}{\lambda}}, \quad (7)$$

$$D(c, T, s, \sigma) = D_0(c, T, \sigma) s^{2+\frac{1}{\lambda}}, D_0 = \frac{K_0(c, T, \sigma) \psi_b}{\lambda(\sigma - \theta_{\min})},$$

where $K_0(c, T, \sigma)$ – permeability coefficient, λ – pore-size distribution index, ψ_b – pore air pressure.

Further, we use Kozeny-Carman empirical formula as one of the simplest relations between the coefficient of permeability and void ratio e :

$$K_0 = k_0 \frac{1 - e_0}{1 - e} \left(\frac{e}{e_0} \right)^3, \quad (8)$$

where k_0, e_0 are initial values of the coefficient of permeability and void ratio, respectively.

Other parameters (coefficients of osmosis, dispersion, heat capacity etc.) are considered constant.

C. Setting of the problem

Assume we have a spatial soil domain, as shown on fig. 1. The upper boundary contacts with the atmosphere. Lower boundary is for some reasons impermeable – lies either on a bedrock or on low-permeable clays. We will consider moisture transport in the case when highly concentrated chemical substance was spilled on the part of upper boundary, denoted as Γ_p .

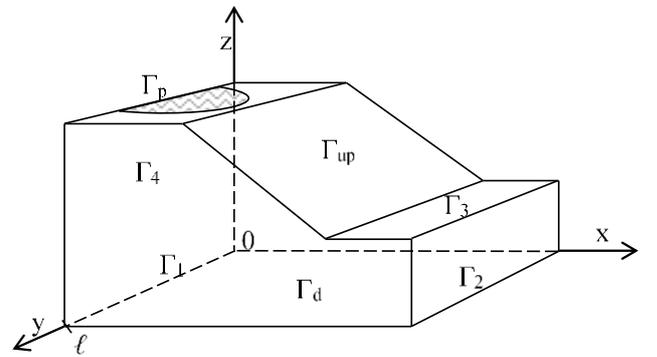


Figure 1. The domain of the problem

Boundary conditions for side boundaries $\Gamma_s = \Gamma_1 \cup \Gamma_2 \cup \Gamma_3 \cup \Gamma_4$ are symmetry conditions, for the lower

(Γ_d) and upper (Γ_{up}) boundaries are the following, according to the setting of the problem:

$$\left. \frac{\partial s}{\partial n} \right|_{\Gamma_s} = \left. \frac{\partial c}{\partial n} \right|_{\Gamma_s} = \left. \frac{\partial T}{\partial n} \right|_{\Gamma_s} = 0, \quad \mathbf{X} \in \Gamma_s, t \geq 0. \quad (9)$$

$$\left. \frac{\partial s}{\partial n} \right|_{\Gamma_d} = \left. \frac{\partial c}{\partial n} \right|_{\Gamma_d} = 0, \quad \mathbf{X} \in \Gamma_d, t \geq 0. \quad (10)$$

$$\left[D_c \frac{\partial c}{\partial n} - (\mathbf{q}_1, \mathbf{n})(c - C_1) \right]_{\Gamma_{up}} = 0, \quad (11)$$

$$-D \left. \frac{\partial s}{\partial n} (\sigma - \theta_{\min}) \right|_{\Gamma_{up}} = q_E, \quad \mathbf{X} \in \Gamma_{up}, t > 0, \quad (12)$$

$$s(\mathbf{X}, t)|_{\Gamma_p} = 1, \quad c(\mathbf{X}, t)|_{\Gamma_p} = C_2, \quad \mathbf{X} \in \Gamma_p, 0 \leq t \leq t_p. \quad (13)$$

where q_E is evaporation rate from the soil surface, \mathbf{n} is outward normal vector to Γ_{up} , t_p is ponding time.

To calculate the time t_p , until which the spilled substance is ponded on the soil surface, we consider that the volume of spilled solution Q infiltrates into the soil at the rate of \mathbf{q}_1 , and evaporates at the rate of q_E . That yields the following rule for calculating remaining volume of ponding:

$$Q^k = Q^{k-1} + ((\mathbf{q}_1, \mathbf{n}) - q_E) \cdot \Delta t, \quad k = 0, 1, 2, \dots \quad (14)$$

where Q^k – remaining volume of substance on the soil surface on k^{th} time step, Δt – time step. The time step k , at which Q^k is reaching 0, i.e. the surface ponding it gone, will correspond to the sought ponding time t_p . After this time, the boundary Γ_p will become the boundary of contact with the atmosphere, same as the rest of upper boundary Γ_{up} .

For the heat transfer equation, we set first type boundary conditions on both lower and upper boundaries:

$$T(\mathbf{X}, t)|_{\Gamma_d} = T_1, \quad T(\mathbf{X}, t)|_{\Gamma_{up}} = T_{atm}, \quad \mathbf{X} \in \Gamma_{up}, t > 0, \quad (15)$$

where T_1 – temperature of underlying soil layer; T_{atm} – mean daily soil surface temperature, affected by the atmospherical conditions (in general case can include also daily temperature variations).

In this study, we also consider two principal cases of the problem and compare their solutions:

1) *classical moisture transport problem with only the Richard's water flow equation and Brooks-Corey model (7) taken into consideration;*

2) *moisture transport problem with regard to heat and solute transport and all coefficient dependencies mentioned above.*

III. RESULTS OF NUMERICAL EXPERIMENTS

The given problem is solved for a period of 30 days with a one-day time step. The finite elements method and the software package FreeFem++ are used to solve partial differential equations [3]. As said above, solutions of the classical moisture transport problem s and of the problem considering heat and solute flow s^* are compared in this paper. Fig. 2 presents the dynamics of changes in water content with time.

As fig. 2 shows, in the case of classical problem spilled substance is infiltrating into the soil much faster. The number of days until ponding is dissolved is $t_p = 6$ days for classical problem, and $t_p = 13$ days if we consider solute transport and variable porosity. After t_p , water content on the surface is also decreasing noticeably faster in the first case.

Let us also consider the distribution plots on the last time step $t = 30$ for both cases and their relative difference (built in FreeFem++), calculated as follows (providing $s \neq 0$):

$$\Delta_s = \frac{|s^* - s|}{s} \cdot 100\%. \quad (16)$$

As we see from the figure, in classical problem the spilled substance has infiltrated into the whole soil layer, with resulting water content ranging from 0.66 to 0.72. Conversely, in the case where solute transport was taken into account,

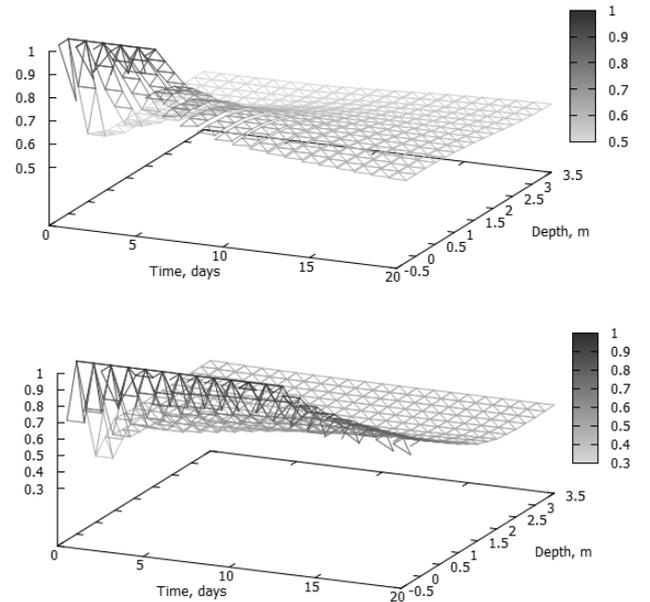


Figure 2. Distribution of volumetric soil water content by time and depth (on $x=0$ and $y = \ell/2$) in classical problem s (top) and in the problem considering solute transport s^* (bottom).

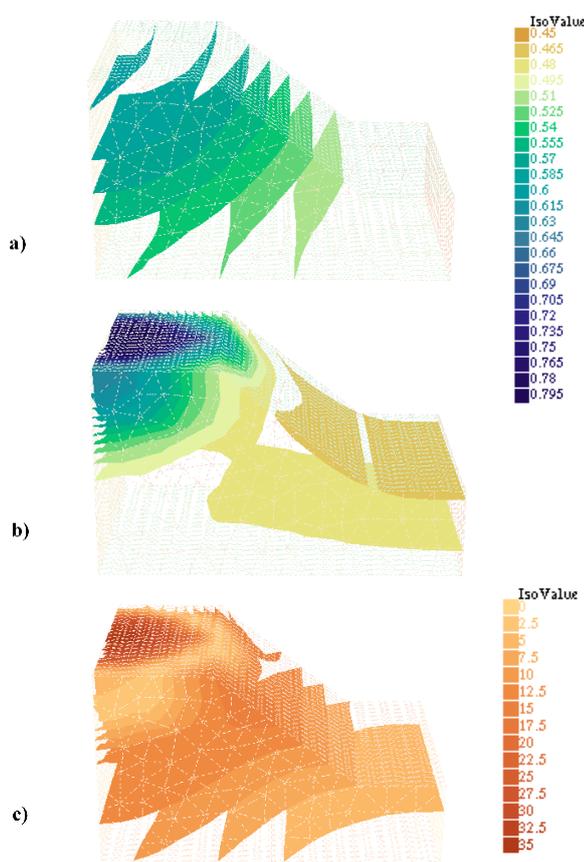


Figure 3. Solution of classical moisture transport problem s (a), solution of the described problem s^* (b) and their relative difference Δ_s , % (c)

the moisture does not reach lower boundary where the water content remains equal to the initial value. Relative difference of the results of those two problems amounts to 25% on the lower boundary. Such difference is caused by the high concentration of spilled solution – its density and viscosity are considerably higher, which slows solute flow. Besides, the effect of chemical osmosis forces pore solute to move along the gradient of concentration function – to the upper boundary. Moreover, adsorption of salt by solid soil particles causes their increase in volume and, consequently, reduces soil porosity. All mentioned factors result in decreased moisture flux rate.

IV. CONCLUSIONS

In this paper, we have investigated the mathematical model for moisture transport combined with heat and mass transfer. The four equations of the mathematical model are supplemented by the variable parameter definitions, reflecting the influence of the described processes on the porous medium.

The model has been used to model accidental spillage of highly concentrated solution on the soil surface. Modelling results showed that salts contained in the spilled liquid are slowing the process of moisture and mass transfer. Among the primary reasons for such behaviour is variable porosity.

Adsorption and crystallizing of salts by solid soil particles results in their increased volume and, therefore, decreased porosity. Comparing modelling results to the solution of the classical moisture transport problem demonstrated that variations of porosity and pore liquid density, which are often neglected in solute transport modelling, cause significant impact on the process of moisture transport under some problem settings.

REFERENCES

- [1] R.H. Brooks and A.T. Corey, "Hydraulic Properties of Porous Media," Hydrology Paper, no. 3, Colorado State University, Fort Collins, pp. 1 – 27, 1964.
- [2] C. J. Harman, P. S. C. Rao, N. B. Basu, G.S. McGrath, P. Kumar, and M. Sivapalan, "Climate, soil, and vegetation controls on the temporal variability of vadose zone transport," *Water Resources Research*, vol. 47, W00J13, pp. 1-21, 2011.
- [3] F. Hecht, "FreeFem++. Third Edition, Version 3.60," accessed February, 19, 2019, from <https://github.com/FreeFem/FreeFem-docpdf/raw/master/freefem%2B%2Bdoc.pdf>.
- [4] D. Jacques, J. Simunek, D. Mallants, and M.Th. van Genuchten, "Modeling coupled water flow, solute transport and geochemical reactions affecting heavy metal migration in a podzol soil," *Geoderma*, vol. 145, pp. 449–461, 2008.
- [5] T.V. Kutya, V.A. Herus, and P.M. Martyniuk, "Soil moisture transfer equation in case of the chemical and thermal factors influence," *Mathematical Methods and Physicomechanical Fields*, vol. 60, no. 1, pp. 169–177, 2017 (in Ukrainian).
- [6] P.M. Martyniuk, M.T. Kuzlo, S.K. Matus, and T.P. Tsvetkova, "Mathematical model of nonisothermal moisture transference in the form of water and vapor in soils in the case of chemical internal erosion," *Far East Journal of Mathematical Sciences*, vol. 102, no. 12, pp. 3211–3221, 2017.
- [7] A. I. Simion, C.-G. Grigoras, A.-M. Rosu, and L. Gavrila, "Mathematical modeling of density and viscosity of NaCl aqueous solutions," *Journal of Agroalimentary Processes and Technologies*, vol. 21, no. 1, pp. 41–52, 2015.
- [8] J. Simunek and M.Th. van Genuchten, "Contaminant transport in the unsaturated zone," in *The handbook of groundwater engineering*, second edition, J. H. Cushman, D. M. Tartakovsky, Eds. Boca Raton: CRC Press, pp. 203-236, 2006.
- [9] J. Simunek, M.Th. van Genuchten, and M. Sejna, "HYDRUSS Technical Manual," Version 2, accessed March, 22, 2019, from https://www.pc-progress.com/en/.%5Cdownloads%5CPCgm_Hydrus3D2%5CHYDRUS3D%20Technical%20Manual.pdf, 2011.
- [10] W. Shao, Y. Su, and J. Langhammer, "Simulations of coupled non-isothermal soil moisture transport and evaporation fluxes in a forest area," *Journal of Hydrology and Hydromechanics*, vol. 65, no. 4, pp. 410–425, 2017.
- [11] J. C. van Dam et al., "Theory of SWAP version 2.0. Simulation of water flow, solute transport and plant growth in the Soil-Water-Atmosphere-Plant environment," Wageningen Agricultural University and DLO Winand Staring Centre, Tech. Doc. 45, 1997.
- [12] A.P. Vlasyuk and T.P. Tsvetkova, "Mathematical simulation of the transport of salt in the case of filtration and moisture transfer in saturated-unsaturated soils in a moistening regime," *Journal of Engineering Physics and Thermophysics*, vol. 88, no. 5, pp. 1062–1073, 2015.
- [13] R. Ren, J. Ma, Q. Cheng, L. Zheng, X. Guo, and X. Sun, "An investigation into the effects of temperature gradient on the soil water-salt transfer with evaporation," *Water*, vol. 9, no. 7, 456, 2017.
- [14] M. Zhang and M.J. McSaveney, "Is air pollution causing landslides in China?" *Earth and Planetary Science Letters*, vol. 481, pp. 284–289, 2018.