

Modelling and numerical simulation of water and solute transport in the non-isothermal, near surface, vadose zone

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A complete water and volatile organic compound transport model for the unsaturated soil zone under non-isothermal conditions has been developed and implemented in a numerical code. The model includes four different mass balances equations: one for the liquid water, one for the vapor water, one for the gaseous phase as a whole and, finally, one for the organic compound as well as an energy balance. The liquid water movement is modeled by means of Richards' equation subject to dynamic surface boundary conditions that consider either evapotranspiration or rain infiltration. The water vapor movement is modeled considering the dependence of the vapor pressure with temperature and the decrease of vapor pressure with capillary pressure of the liquid water. No empirical enhancing factors of the water vapor diffusion process were used. The movement of the gaseous phase as a whole is due mainly to liquid water displacement and change of gas density with temperature. In addition to the classical

mechanisms and processes that governs the chemical transport (convection, dispersion, diffusion, sorption to the organic matter and partition between liquid and gas phases) the model includes chemical vapor/mineral surfaces adsorption as an equilibrium process, which depends on water vapor pressure and temperature. The energy balance equation considers local thermal equilibrium, conduction in all phases, and convective and dispersive transport in the fluid phases. The top boundary condition for the energy equation takes into account downwards and upwards radiative fluxes and convective heat flow to the atmosphere at the soil surface. The accounting of the radiation processes includes for the short wave the dependence respect the sun declination, local latitude, hour angle of the sun, the actual earth-sun distance, atmospheric transmission, soil reflection as well as incoming and outgoing long wave radiation.

A one-dimensional version of the five coupled partial differential equations that compose the model was discretized using the finite volume formulation for the balance equations, central difference scheme for the fluxes and fully implicit time integration to ensure numerical stability. The grid spacing and the time step were non uniform to provide enough numerical description of the space-temporal variations of the different dependent variables. The local compliance of the classical restrictions when solving numerically linear transport equations (Courant and Peclet number limits) was monitored. Moreover, in all simulations was checked that further decrease of the grid and time steps did not change appreciably the results.

Simulation results agree well with experimental results concerning the water movement measured by different authors under natural bare soil conditions. After soil irrigation and in a drying period, both experimental and simulation results show a volumetric water content (hereafter VWC) daily cycle oscillation with decreasing amplitude with soil depth. The detailed accounting of all significant transport

mechanisms and processes is shown to be enough to describe quantitatively the drying phenomena without the help of any empirical parameter adjust. In addition to the water movement in soils, the model has also shown its ability to reproduce qualitatively well experimental data for the organic compound transport and volatilization fluxes under natural soil conditions. Under such conditions both experimental and simulation results exhibit important diurnal variations for the volatilization flux.

Several test cases have been simulated to show the coupling effect between water movement and organic compound transport during a progressively soil drying episode under natural conditions. Results obtained are used to explore the relative role and importance of the different phases and transport mechanisms in the migration of the organic compound near the soil surface. Three organic compounds of different volatilization, ethanol, 1,3-dichlorobenzene and lindane have been selected to provide a self consistent set of compounds with physicochemical parameters that span a reasonable range of three orders of magnitude for the Henry's law constant. In addition two different soil scenarios have been studied. The first one, the wet scenario, corresponds to the initial stage of a soil drying process (when the VWC of the soil is still high) while the other one, the dry scenario, corresponds to a later stage of the drying process, (when the VWC near the surface is very low). In all simulations it was supposed that, initially, there was a near surface fringe with constant concentration of the chemical.

Simulation results for the water evaporation flux and organic compound volatilization rates obtained under natural conditions exhibit markedly diurnal variations cycles controlled by the soil temperature with maximum and minimum values located when the soil temperature is at its highest and lowest value, respectively. The results suggest that large diurnal variations in volatilization rates are higher for slightly volatile

organic, being these variations greater when the soil is dryer.

Results obtained for the organic compounds and soil scenarios selected suggest that the influence of the water liquid dynamics to the chemical migration and volatilization is stronger for those compounds with relatively low Henry's law constant (i.e. ethanol and lindane). On the other hand, results for the 1,3-dichlorbenzene show that, for this specific compound, the transport in the vadose zone occurs mostly in the gas phase. The liquid and gas phase contribution to the organic compound transport from the inner to the atmosphere can all be significant, to varying degrees, during different hours of the day. In the case of organic compounds like ethanol, with a high water solubility and relatively low Henry's law constant, dispersion mechanism dominates the transport in the liquid phase, while for organic compounds with a stronger tendency to volatilize, like 1,3-dichlorbenzene, diffusion and dispersion dominates the transport in the gas phase.

Changes of the organic compound adsorption from the vapor to the soil phase may affect the organic compound diffusion through the unsaturated zone as well as the volatilization rates at the top soil dry surface. These adsorption changes are due to variations in the adsorption affinity caused by daily temperature and soil dryness. This is specially significant for organic compounds like the 1,3-dichlorbenzene with a relatively high Henry's law constant. Results obtained for this compound indicates that this mechanism can be responsible of differences on mass remaining in soil as high as 12% after a period of 5 days simulation.