Reactive transport in unsaturated soil: Comprehensive modelling of the dynamic spatial and temporal mass balance of water and chemical components

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Computer methods for simulating environmental processes of water, flow solute transport and geochemical reactions have greatly advanced during recent years. However, there is still demand for the development of programs that a capable of simulating the numerous interactions between physical transport processes and biogeochemical reactions in natural soils.

We are presenting a new tool for simulating transient vadose zone flow and solute transport according to the moisture-based form of Richards' equation within the widely used geochemical software PHREEQC. The direct implementation into the geochemical framework provides access to comprehensive geochemical models, giving capabilities beyond existing software for unsaturated flow and reaction. Possible reactions include complex aqueous speciation, cation exchange, equilibrium phase dissolution and precipitation, formation of solid solutions, redox reactions, gas phase exchange, surface adsorption considering electrostatics and kinetic reactions with user-defined rate equations, among others. As a result of the close coupling procedure the influence of geochemical reactions on water contents, e.g. through dissolution or precipitation of water containing phases can be investigated. For the solution of partial differential equations of flow and transport, an explicit finite difference formulation with second order space discretization and first order time discretization was employed. The use of integrated diffusivities transforms Richards' equation into a sim-

ple advection-diffusion equation. Changes in water contents and solute concentrations were conceptualized as local kinetic reactions of individual elements where changes in moisture contents result from fluxes of oxygen and hydrogen across cell boundaries. Reactions and element transport are coupled via sequential two-step operator splitting. The scheme was implemented into PHREEQC without any source code modification such that it can be applied by the experienced user with nothing but the existing freely available software.

On this poster, we show exemplary results from extensive code verification and demonstrate the unique capabilities of the model for simulating surface sorption to variable charge surface sites including the development of a diffuse double layer as well as dissolution reactions with effects on soil moisture.