The HPx Reactive Transport Models: Summary of Recent Developments and Applications

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Abstract

The HPx reactive transport codes were developed to simulate flow and transport processes in variably-saturated porous media subject to a variety of low-temperature geochemical processes. The codes combine the HYDRUS models for flow and transport (HYDRUS-1D version 4.16, and HYDRUS 2D/3D version 2.02) with the generic thermodynamic and kinetic model PHREEQC-2.17. As such, HPx expands significantly the capabilities of the individual codes for multicomponent one-dimensional (HP1) and two-dimensional (HP2) transport problems. This paper provides a brief summary of recent developments and applications of HPx, such as (i) the inclusion of gas diffusion, (ii) extension to two-dimensional problems, (iii) inverse optimization, and (iv) feedback between changes in geochemical variables and transport properties. HPx is a flexible tool which can be applied to flow and transport problems involving relatively complex geochemical processes. A typical example is the geochemistry of mercury, which in a contaminated soil may be present in different forms and phases.

1. Introduction

The fate and transport of nutrients and contaminants in variably-saturated porous media is influenced by a range of interacting physical, chemical, and biological processes (Jacques et al., 2008). Transport in soil systems is often further complicated by a multitude of coupled biogeochemical reactions, the presence of spatially and temporally variable flow velocities, and spatial heterogeneities at different scales (for a review see Mallants et al., 2011). A numerical tool that integrates these various processes offers unique possibilities for advanced model building and improving process understanding, ranging from sensitivity analyses of processes and parameters, designing experiments, hypothesis testing by running virtual laboratories, conceptual model validation using experimental data, and evaluation of different management or remediation practices. Based on the HYDRUS suite of models for one-dimensional (Šimůnek et al., 2008) and multi-dimensional problems (Šimůnek et al., 2011), and the generic thermodynamic and kinetic geochemical model PHREEQC (Parkhurst and Appelo 1999), the HP1 (Jacques and Šimůnek, 2005) and HP2 (Šimůnek et al., 2012) modules were developed to handle water flow, multi-component solute transport, heat transfer, and biogeochemical reactions for a range of environmental soil quality applications. In this paper we provide a brief summary of recent developments and various applications of the HPx modules.

2. Conceptual Basis of HPx

The HPx codes considerably extend upon the capabilities of the individual codes. For example, the full range of water flow and solute transport formulations available in the standard HYDRUS codes are now combined with the different geochemical models available in PHREEQC.

Contrary to the conventional advection-dispersion-reaction equations forming the basis of the standard HYDRUS-1D and HYDRUS 2D/3D codes, the HPx modules account for interactions between different aqueous components to simulate intra-aqueous degradation, transformation or production processes, as well as heterogeneous equilibrium and kinetic processes. Using the capabilities of PHREEQC, HPx allows thermodynamic equilibrium calculations for

- aqueous speciation with different activity correction models (Davies, extended Truesdell-Jones, B-Dot, Pitzer, SIT - Specific ion Interaction Theory),
- multi-site ion exchange sites for different conventions (Gaines-Thomas, Vanselow, Gapon, or accounting for different selectivities considering the equivalent fraction occupied by the cation by the Rothmund-Kornfeld or the active fraction model),
- multi-site surface complexation sites with a non-electrostatic, the Dzombak and Morel, or the CD_MUSIC model and different options to calculate the composition of the diffuse double layer,
- mineralogical assemblages,
- solid-solutions consisting of multiple end members in an ideal solid solution or a binary non-ideal solid solution using the Guggenheim approach for determining the activity coefficients of the end members (Glynn and Reardon, 1990), and
- gas exchange.

Kinetic calculations are furthermore used to describe mineral dissolution/precipitation (e.g., based on transition state theories as shown by Lasaga (1998) and Brantley (2003)), non-equilibrium sorption processes, biogeochemical reactions, including first-order degradation networks (e.g., C-sequestration, see below), Monod kinetics, and Michaelis-Menten kinetics (e.g., solute-dependent plant uptake coupled with root exudation as shown by Raji et al. (2013)).

HPx allows one to select uniform or dual-porosity models for water flow, and uniform, mobile/immobile, or dual-porosity models for solute transport (Figure 1), as well as diffusive processes in the gas phase. As opposed to many other reactive transport codes, HPx also provides an option to account for the effects of root water and nutrient or contaminant uptake, including compensated water uptake and root growth (Šimůnek and Hopmans, 2008). Furthermore, the HPx simulators can accommodate complex boundary conditions including water and chemical exchange with streams and groundwater. Because geochemical gradients (e.g. changing redox conditions) are especially strong along such interfaces, only simulators that provide proper coupling between the various hydrological, geochemical and biological processes involved are capable of providing accurate system descriptions.
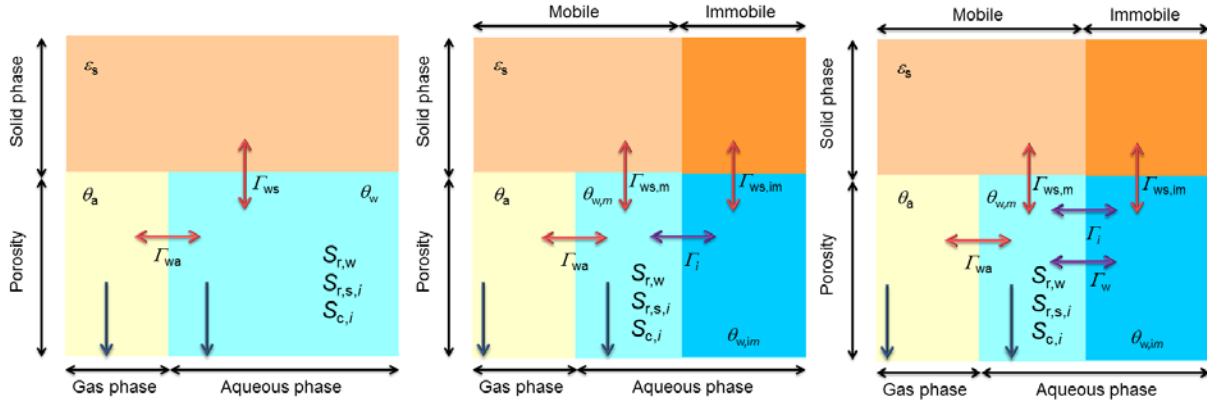
Figure 1. Schematic of possible coupled flow–transport–reaction models available within HPx: a uniform water flow and solute transport model (left), a uniform water flow model with a mobile/immobile solute transport model (middle), and a dual-porosity water flow model with a dual-porosity transport model (right). In the figure, ε_s is the volume fraction of solid phase, θ_a is the air content, θ_w is the water content, $\theta_{w,m}$ is the mobile water content, $\theta_{w,im}$ is the immobile water content, $S_{r,w}$ represents root water uptake, $S_{r,s,i}$ represents root uptake of solute i, $S_{c,i}$ is a sink or source term for solute i resulting from aqueous degradation or transformation processes, Γ_i and Γ_w are solute and water mass exchange terms between the mobile and the immobile water phases, respectively, and Γ_{wa}, Γ_{ws}, $\Gamma_{ws,m}$, and $\Gamma_{ws,im}$ are heterogeneous mass exchange terms between the water and air phases, the water and solid phases, the mobile water and solid phases, and the immobile water and the solid phases, respectively (after Šimůnek and van Genuchten, 2008).
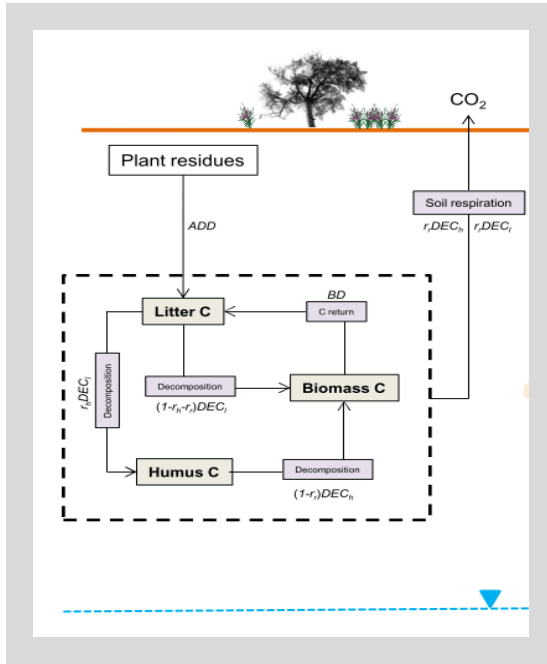
3. Recent Developments and Applications

This section describes several recent improvements and applications of HPx. Additional examples are included in these proceedings for mercury transport and fate in soils (Leterme and Jacques, 2013), CO_2 production and transport in bare and planted mesocosmos (Thaysen et al., 2013), and active root nutrient uptake accounting for solution composition effects (Raji et al., 2013). The extension of the HPx code to two-dimensional flow and transport problems is described in another contribution to these proceedings (Šimůnek and Jacques, 2013).

3.1. Gas Diffusion Coupled to Organic Matter Degradation

A recent addition to HPx is diffusion of components in the gas phase. We present here an illustrative example that includes a process-based soil organic matter degradation model with three immobile organic carbon pools (litter, humus, and biomass), external input of C into the system, and an inorganic pool (CO_2). The model is based on previous work by Porporato et al. (2003) as illustrated in Figure 2 (see also Batlle-Aguilar et al., 2011). The model consists of a number of coupled nonlinear ordinary differential equations (see Fig. 2). There are several differences with the original model of Porporato et al. (2003). For example, water flow is modeled using the Richards equation with a root water uptake term (versus a probabilistic modeling approach in Porporato et al., 2003), while heat transport is also considered. Two inorganic pools are further included: $CO_{2(g)}$ and dissolved C, with thermodynamic exchange

between the two pools. We additionally consider the temperature dependence of rate parameters, and also included transport of inorganic C in the aqueous and gaseous phases.

$$\frac{\mathrm{d}C_l}{\mathrm{d}t} = k_1 + k_2 C_b - k_3 C_b C_l$$

$$\frac{\mathrm{d}C_k}{\mathrm{d}t} = r_h k_3 C_b C_l - k_4 C_b C_k$$

$$\frac{\mathrm{d}C_b}{\mathrm{d}t} = (1 - r_h - r_r) k_3 C_b C_l + (1 - r_r) k_4 C_b C_k - k_2 C_b$$

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = r_r k_3 C_b C_l + r_r k_4 C_b C_k$$

C_l	Concentration of litter pool (gC / dm³)
C_h	Concentration of humus pool (gC / dm³)
C_b	Concentration of biomass pool (gC / dm³)
C_i	Concentration of CO_2 (gC / dm³)
k_1	Added litter
k_2	First-order biomass decay coefficient
k_3	First-order litter pool decomposition coefficient
k_4	First-order humus pool decomposition coefficient
r_r	Respiration coefficient
r_h	Humification coefficient

Figure 2. Schematic of the soil organic matter model (left), the set of coupled non-linear ordinary differential equations, and a list of symbols (after Porporato et al., 2003).

The rate parameters in Figure 2 for first-order decay and decomposition depend on the soil water content (described with the formulations of Porporato et al. (2003) and Manzoni and Porporato (2007)) and soil temperature. The latter effect is described using the temperature stress function from the RothC model of Coleman and Jenkinson (2005). The effects of water content and temperature stress were modeled as a multiplication of both factors. The combined effect of transient variations in the water content and temperature in a soil profile during one year on the stress factors is illustrated in Figure 3. Multiplication of the temperature and water content stress factors leads to considerable variation in organic matter decomposition rates during the year (Figure 3). Decomposition rates, relative to the reference rate value, range from zero (during dry periods near the surface) up to 3.5 (during wet and warm periods).

Evolutions of the organic C pools during one year are shown in Figure 4. The different curves follow smoothly the seasonal trends in temperature (and water content). The transformation and decomposition of the organic C pools is also reflected in the general trend of soil CO_2 gas. On the other hand, water content changes on the shorter temporal scale seem to influence variations in the soil CO_2 partial pressure.
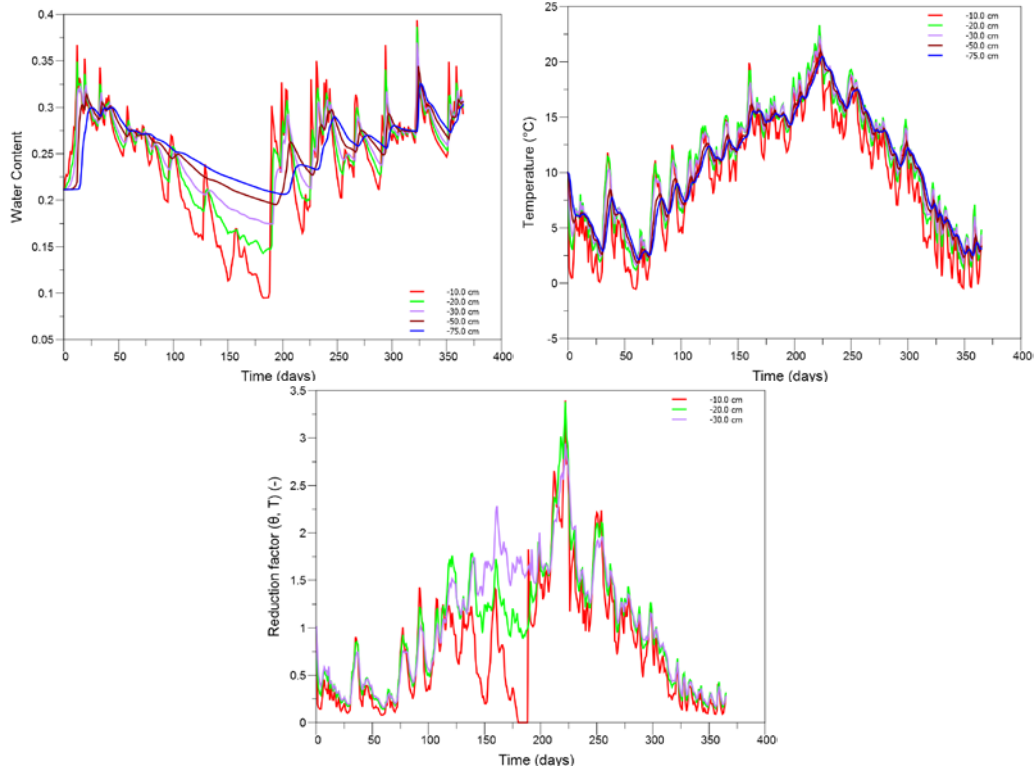
Figure 3. Temporal variations of water contents (top, left) and temperatures (top, right) in a soil profile during a one year simulation. Resulting stress factors (bottom) for the decay and decomposition rates.

3.2. Inverse Optimisation with UCODE

Coupled codes such as HP1 allow simultaneous optimization of various flow, transport, and geochemical parameters using inverse methods. A recent application with HP1 is given by Jacques et al. (2012), who combined HP1 with the general optimization tool UCODE (Poeter et al., 2005). The experimental data resulted from previously published laboratory experiments (Smiles and Smith, 2004) about the transport of major cations (Na, K, Mg, and Ca) during water absorption into horizontal soil columns, which were terminated at different times. Experimental data consisted of spatial distributions of the water content (θ), the Cl concentration, and total aqueous and sorbed concentrations of the major cations. In addition to selected flow and transport parameters (i.e., those describing the water retention and hydraulic conductivity functions, as well as the dispersivity), cation exchange coefficients for the major cations and the cation exchange capacity were estimated. Another new aspect of this study was that two different exchange models could be tested: the Gapon approach and a variable-selectivity model based on the Rothmund-Kornfeld approach. The latter enables stronger binding of a species at lower equivalent sorbed fractions (e.g., Bond, 1995). Calibrated profiles for Mg are shown in Figure 5. The Rothmund-Kornfeld approach was found to perform slightly better than the Gapon approach.
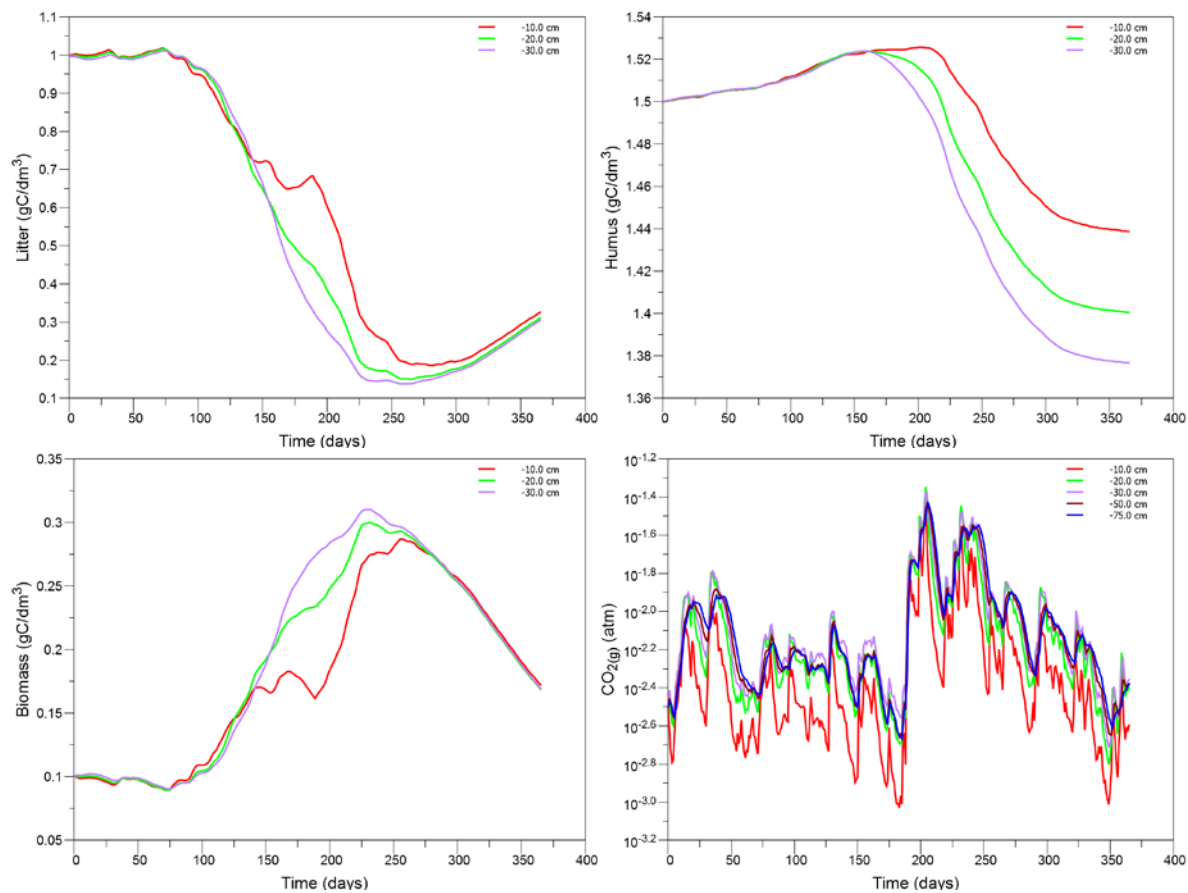
Figure 4. Time evolution of organic C pools (litter: top, left; humus: top, right; and biomass: bottom, left) and of gaseous CO_2 concentrations (in atm, bottom, right) in a soil profile during a one year simulation.
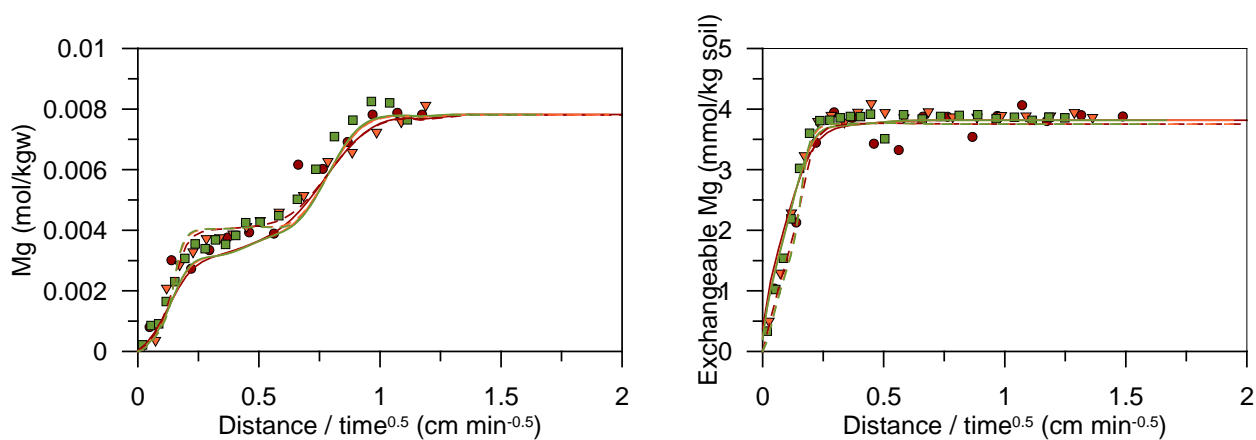

Figure 5. Simulated profiles of aqueous (left) and sorbed (right) Mg concentrations obtained with the Gapon approach [solid lines] or the Rohtmund-Kornfeld approach [dashed lines], compared with experimental data [symbols: circles - 36 min, triangles - 106 min, and squares - 144 min] from water absorption and solute transport experiments using piggery effluent (Smith and Smiles, 2004) (adapted from Jacques et al., 2012).

The HP1-UCODE study was supplemented with information content (Hill and Tiedeman, 2007) and surface contour analyses. As illustrated in Figure 6, the parameters of the Gapon exchange approach were better identifiable as compared to the parameters of the Rothmund-Kornfeld approach. Several parameters in the latter approach showed strong correlations. We refer to Jacques et al. (2012) for details.
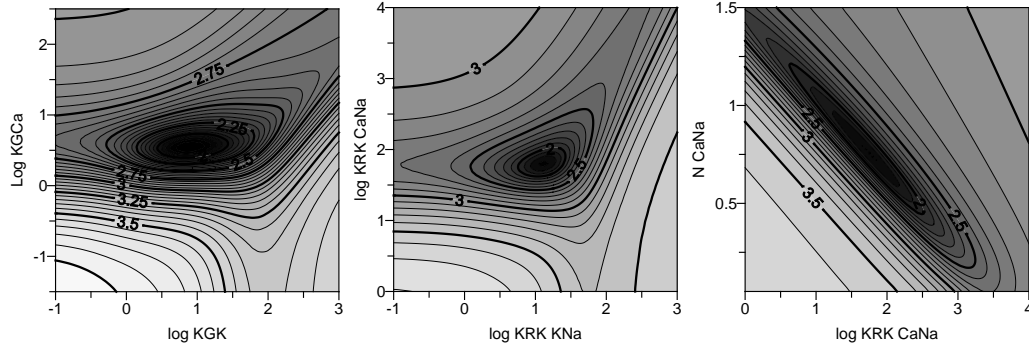

Figure 6. Contour plots of the objective function for (left) the exchange coefficient of K and Ca in the Gapon approach (K_{GK} and K_{GCa}), (middle) the exchange constant between K and Na (K_{RKKNa}), and between Ca and Na (K_{RKCaNa}) in the Rothmund-Kornfeld approach, and (right) the exchange constant (K_{RKCaNa}) and the nonlinear coefficient (N_{CaNa}) for exchange between Ca and Na in the Rothmund-Kornfeld approach (adopted from Jacques et al., 2012).

3.3. Coupling Between Geochemical Variables and Transport Properties

A useful new feature recently included in HP1 is an option to change the hydraulic and solute transport properties as a function of evolving geochemical state variables. HP1 makes it possible to account for changes in (i) the porosity (and hence the saturated water content), (ii) the hydraulic conductivity, (iii) a scaling factor for the pressure head, (iv) aqueous and gaseous phase pore geometry factors for calculating pore diffusion coefficients, (v) the dispersivity, (vi) the thermal capacity, (vii) the thermal conductivity, and (viii) the thermal dispersivity. HP1 does not provide any pre-defined conceptual or mathematical model to update the flow and transport parameters, but uses the flexibility of the embedded BASIC interpreter for this purpose. This permits users to define any user-specific relationship between the geochemical state variables and the transport properties.

A typical example, illustrated in Figure 7, is diffusive leaching from a porous medium in contact with more or less aggressive water. The example concerns leaching of a small concrete beam in contact with three types of water as indicated in the top part of Figure 7: (i) Rain W (wet deposition only), (ii) Rain B (wet and bulk deposition), which has higher ion concentrations, and (iii) Soil water with a higher inorganic carbon content as a result of soil microbiological processes. In terms of concrete performance, the soil water type should be the most detrimental since portlandite ($Ca(OH)_2$) dissolution proceeds rapidly due to leaching and carbonation (i.e., portlandite dissolution followed by calcite precipitation as show by Jacques et al. (2010)). At the same time, chemical dissolution of portlandite and precipitation of calcite change the physical properties such as porosity and tortuosity (e.g., Perko et al., 2010; Jacques et al., 2011).
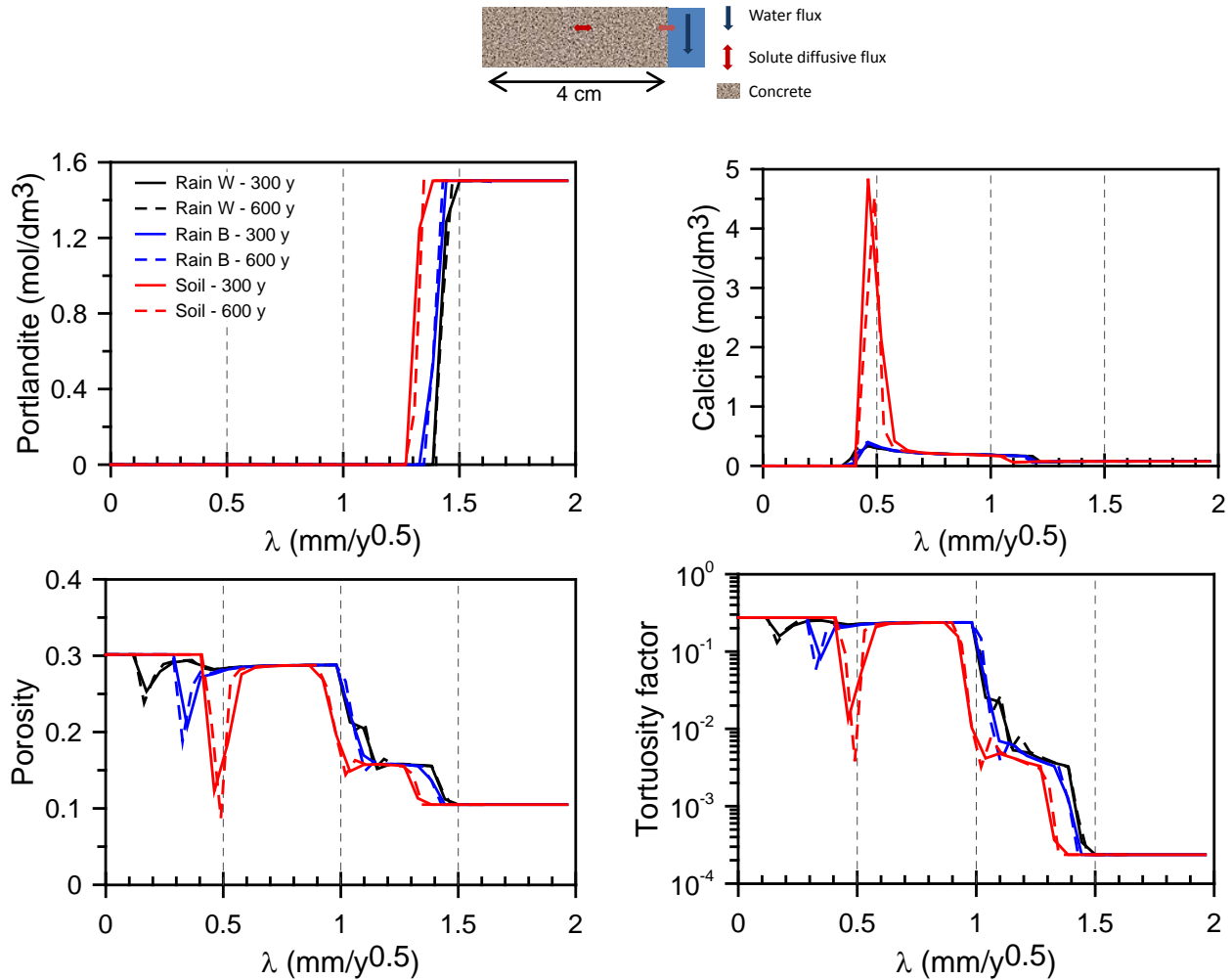
Figure 7. Example showing the effect of coupling transport parameters to geochemical variables. Results are for diffusive leaching of a small concrete beam. Shown are profiles of portlandite (top left), calcite (top right), porosity (bottom left), and the tortuosity factor (bottom right) as a function of the Boltzmann transform λ for three different water types and two different times.

Since calcite has a slightly larger molar volume than portlandite, porosity and tortuosity should decrease if calcite precipitation leads to pore blockage without generation of internal stresses and subsequent fracturing. Some of these processes are clearly evident from the results in Figure 7. The portlandite profiles as a function of the Boltzmann transform (which should collapse to a single curve in case of pure diffusive transport) are different among the three water types. In particular, the portlandite dissolution front has progressed slightly further for water with a presumably less aggressive solution composition (Rain W). On the other hand, enhanced calcite precipitation in the soil water case causes pore clogging and a strong reduction in the tortuosity and the diffusion coefficient. As a result, the portlandite dissolution front is retarded compared to the dissolution fronts when concrete is leached with the other two water compositions. A porosity decrease is also simulated for the Rain B case, mainly due to precipitation of Mg-bearing minerals.

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