**Special Section:
Reactive Transport Modeling**

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The guest editors summarize the eight studies in this issue's Special Section: Reactive Transport Modeling. The studies represent the diverse application of reactive transport modeling at a range of scales. This modeling work addresses the fate and transport of both reactive solutes and colloidal material, with potential for synthesizing diverse data, evaluating competing biogeochemical processes, identifying research gaps, and ultimately improving our understanding of biogeochemical processes.

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Reactive Transport Modeling

This special section in the *Vadose Zone Journal* focusing on reactive transport modeling was developed from a special symposium jointly sponsored by the Soil Physics and Soil Chemistry Divisions of the Soil Science Society of America at the 2010 annual meetings held in Long Beach, CA. It contains eight contributions reflecting a diverse range of reactive transport modeling applications that address the fate and transport of both reactive solutes and colloidal material (i.e., viruses). Further, the eight studies range in scale from laboratory batch and column experiments to the regional scale. Three of the submissions reflect efforts to model experimental data that were already reported in the literature, providing additional insight concerning underlying physical and chemical processes. In addition to the obvious predictive applications, the eight contributions to this special section illustrate the additional advantages to including reactive transport modeling as an active component within a diverse research agenda. In addition to scenario testing, reactive transport modeling provides a framework for synthesizing diverse experimental data, evaluating the relative importance of various competing and interrelated biogeochemical processes, and identifying important data gaps and research priorities under more natural conditions at multiple temporal and spatial scales.

Abbreviations: AWI, air–water interfaces; CCM, constant capacitance model; CW, constructed wetlands; MCL, maximum concentration level; OM, organic matter; SOTS, second-order two site [model]; SWI, solid–water interfaces.

This special section focusing on reactive transport modeling was developed from a special joint symposium of the Soil Physics and Soil Chemistry Divisions at the 2010 annual Soil Science Society of America meetings held in Long Beach, CA. This section consists of eight studies illustrating a diverse range of reactive transport modeling applications evaluating the interrelated nature of various biogeochemical processes from the laboratory to the regional scale. Initially, reactive solute transport modeling efforts focused on improving our understanding of water movement in the subsurface environment, with less attention placed on the coupled biological and geochemical reactions that impact solute behavior, where solute partitioning was generally treated in a simplistic manner that can be easily implemented within a hydrologic flow model. And, while considerable progress has been made in recent years, addressing the scale-dependency of reactive transport processes attributable to both physical and biogeochemical heterogeneities remains a challenge.

The most widely used approach for predicting reactive solute partitioning in advective systems has been the linear distribution coefficient, K_d (Davis et al., 2004; Steefel et al., 2005; Tebes-Stevens et al., 2001). Although reasonable for certain applications, numerous studies have demonstrated the inherent limitations in applying simplistic empirical expressions (e.g., K_d and linear kinetic terms) to describing contaminant migration at the field scale (Davis et al., 2004; Steefel et al., 2005). For example, the K_d approach to predicting solute partitioning neglects the impact of limited sorption sites and competitive effects induced by the presence of other solute species. In part, the quest for more robust modeling applications reflects the need to make accurate predictions of subsurface processes for the protection of both human health and environmental quality.

From an experimental point of view, much of the recent environmental research has focused on isolated processes at a micro-scale under well-defined conditions. Such an approach eliminates issues associated with mass transfer or localized micro-environments, factors that are often encountered as experimental scale increases. In contrast, reactive transport modeling provides a framework for synthesizing experimental data (i.e., coupling processes studied in isolation), evaluating the relative importance of various biogeochemical processes, and identifying important data gaps and research priorities under more natural conditions at multiple relevant temporal and spatial scales (Steefel et al., 2005). Beyond

the obvious predictive applications, the eight contributions to the current special section illustrate the diverse nature of reactive transport modeling and its place within an active research agenda.

Summary of Contributions

Bea et al. (2012) used reactive transport modeling to improve our understanding of CO_2 sequestration during the weathering of ultramafic mine tailings initially containing minerals such as serpentine [$Mg_3Si_2O_5(OH)_4$] and brucite [$Mg(OH)_2$] at a site near Mount Keith, Australia. This work is based on the observation that hydrated magnesium carbonate minerals (e.g., hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$]) commonly form during the weathering of serpentine-rich mine wastes (Wilson et al., 2006, 2009; Wilson, 2009). Although hydromagnesite is considered meta-stable under exposed surficial conditions, it persists under neutral to alkaline conditions that can serve as sink for capturing atmospheric CO_2 (Bea et al., 2012; Palandri and Kharaka, 2004).

Bea et al. (2012) use the MIN3P-D multicomponent reactive transport code of Henderson et al. (2009) to describe processes occurring within a mine tailing impoundment. The MIN3P-D code was further enhanced to include energy balances and water vapor transport, the application of which is documented in detail. These enhancements are essential to adequately describe evaporation at the surface of the tailings impoundment. Additionally, reactive transport modeling considers unsaturated flow, solute transport, gas diffusion, and the requisite geochemical reactions under critical atmospheric boundary conditions associated with the arid mine tailing site. The geochemical reactions include the dissolution of serpentine, the dissolution and precipitation of brucite, and the precipitation of primary carbonates and other associated minerals. The dissolution and precipitation of primary minerals are modeled using kinetic rate expressions from the literature. Simulations were conducted for a 30-yr span to predict the level of future carbon mineralization.

A unique aspect of the Bea et al. (2012) contribution is the limited role that water flow plays in the geochemical reactions under consideration. Initially, the tailings are deposited in a saturated state; however, arid conditions at the Mount Keith site result in evaporation that causes an efflorescent salt crust to form at the mine tailing surface. With time the evaporation front is driven deeper, with the dissolution of serpentine and brucite serving as the source of Mg and alkalinity to support hydromagnesite precipitation. The partial pressure of CO_2 eventually declines with depth due to hydromagnesite precipitation, with continued precipitation limited by the downward diffusion of CO_2.

Model simulations were generally consistent with field observations for tailings that have been weathered for 10 yr. Laboratory-derived serpentine dissolution rates were decreased considerably to be consistent with field observations, possibly due to mineral crust

formation (i.e., hydromangesite) that reduced the reactive surface area. Long-term simulations indicate that 17 kg m^{-2} of CO_2 is trapped in the tailings after 30 yr of impoundment, mostly in the form of hydromagnesite. However, field data reflecting the first 10 yr of weathering indicate that current model predictions underestimate hydromagnesite formation, suggesting more rapid CO_2 diffusion than predicted. Such discrepancies may be attributed to any combination of several factors, including gas advection due to barometric pressure fluctuations, temperature-dependent diffusion gradients not incorporated in the model, advective displacement of gas during infiltration events, and wind effects (Bea et al., 2012). Increasing the CO_2 diffusion coefficient within the model as a surrogate for the processes noted above increased the amount of CO_2 trapped over 30 yr to 31 kg m^{-2}. Further, the limited degree of serpentine consumption and the high pH maintained by continued mineral dissolution suggest the mine tailing may act as a significant long-term sink for CO_2 sequestration, with the ingress of atmospheric CO_2 playing an important role in controlling the rate of carbon fixation.

The modeling efforts described in Chang et al. (2012) focus on evaluating the potential efficacy of using Fe(II)-containing solutions ($FeCl_2$ and $FeSO_4$) as an in situ means of reducing toxic hexavalent chromium, Cr(VI), to Cr(III), which subsequently coprecipitates with Fe(III) to form a mixed Fe(III)/Cr(III) oxyhydroxide. The modeling efforts are based on a series of laboratory batch and column experiments conducted using Fe-oxide-rich Atlantic Coastal Plain sediments that display a high capacity for Cr(VI) sorption (Seaman et al., 1999). Initial laboratory column experiments indicated that substantial Cr(VI) retardation would make aquifer reclamation unfeasible using conventional pump-and-treat extraction, despite the aquifer sediments lack of inherent reduction capacity. Batch experiments using Fe(II) solutions indicated that in situ reduction was a feasible alternative based on the rapid loss of Cr(VI) using the diphenylcarbazide colorimetric analysis method. However, Cr$_{total}$ remained elevated in solution, well above the USEPA maximum concentration level (MCL), presumably due to the acidic conditions associated with Fe(II) oxidation and the subsequent hydrolysis of Fe(III). When acetate buffer (pH 5.6) was added to the Fe(II) treatments, both Cr(VI) and Cr$_{total}$ decreased below USEPA MCLs in batch experiments.

As observed in the batch experiments, effluent Cr$_{total}$ levels [i.e., Cr(III)] generally remained elevated for unbuffered Fe(II) treatments due to the acidity associated with the oxidation and subsequent hydrolysis of applied Fe. Further, the $FeSO_4$ treatment increased the mobility of Cr(VI) when compared with $FeCl_2$, presumably due to SO_4 competition for sorption sites, resulting in two diverging plumes that limited the potential efficacy of Fe(II) additions. Buffered Fe(II) treatments, however, resulted in an increase in Cr(VI) mobility regardless of the Fe(II) source (i.e., $FeCl_2$ or $FeSO_4$), a result that could not be anticipated based on laboratory batch results (Seaman et al., 1999). Therefore, the

objective of Chang et al. (2012) was to determine if laboratory batch and column results could have been predicted based on reactive transport modeling that accounted for the temporal and spatial dynamics of competitive Cr(VI) sorption and the shifts in pH that accompanied Fe(II) oxidation and hydrolysis.

Using the PHREEQC-2 geochemistry modeling code (Parkhurst and Appelo,1999), Chang et al. (2012) described Cr partitioning behavior on the basis of two major mechanisms: (i) competitive Cr(VI) sorption to weak binding sites on Fe oxides using the diffuse double layer model (DDLM) based on surface complexation constants derived from the published literature and (ii) the precipitation of a mixed Cr(III)/Fe(III) hydroxide. Chang et al. (2012) used only two optimized parameters in model development, apparent sorption site density and the solubility of the Cr(III)/Fe(III) precipitate. The reactive transport modeling was successful in qualitatively simulating the dynamic column experiments, including the enhanced transport of Cr(VI) in the presence of SO_4 that limited interaction with Fe(II), and the enhanced solubility and continued migration of Cr(III) due to the acidity generated in unbuffered Fe(II) treatments. However, the reactive transport modeling overpredicted shifts in effluent pH that could be attributed to Cr(VI) sorption, which Chang et al. (2012) attributed to the inherent soil buffering capacity that wasn't fully realized in the model system. Furthermore, column results indicated that acetate was successfully competitive for Cr(VI) sorption sites, which can reduce the efficacy of Fe(II) treatments by limiting Cr(VI) interaction with Fe(II) in advective systems. The appropriate surface complexation constants for including such competition in the current model were not available in the published literature. Additional discrepancies between experimental results and model simulations were largely attributed to the kinetics associated with Cr(VI) sorption reactions and redox processes.

Metal retention at high pH in calcareous soils has been attributed to the formation of carbonate salts with ion exchange becoming more important as carbonates dissolve and pH decreases (Elbana and Selim, 2012; Elzahabi and Yong, 2001). In previous experiments, Selim and Ma (2001) characterized Cu retention in soils over a wide range of conditions, describing the nonlinear kinetics of sorption and desorption using the second-order two site (SOTS) model within the multireaction model code developed by Selim and Amacher (1997). The SOTS model assumes that a limited number of sites are available for reactive solute retention, a portion of which are rate limited with the remaining fraction reacting instantaneously with the aqueous phase. The full version of the SOTS model includes six fitting parameters, four kinetic terms, a partitioning factor, and the sorption maximum (Selim and Amacher, 1997).

Elbana and Selim (2012) used batch and column experiments to characterize Cu fate and transport in calcareous soils, with greater retention observed with increasing $CaCO_3$ content, presumably in a nonexchangeable form. Batch equilibrium results were described using the Freundlich and Langmuir isotherms to depict the non-linear partitioning behavior and differences in sorption affinity for the test soil materials. For describing Cu transport in a column system, a linear equilibrium partitioning model within the advection–dispersion equation, including a first-order decay term to operationally account for irreversible retention, failed to describe Cu breakthrough or extensive tailing in the current study. In contrast, the SOTS model that accounts for both reversible and irreversible (both concurrent and consecutive) solute partitioning effectively described Cu transport in column experiments, including the diffuse initial Cu arrival and the limited, slow release during extensive leaching. Copper retention also coincided with release of Ca into solution (Elbana and Selim, 2012).

Langergraber and Šimůnek (2012) illustrated the use of reactive transport modeling with the publically available wetland module within the HYDRUS software code as a tool for evaluating complex physical and chemical processes occurring within wetland systems constructed for the treatment of various contaminants. As they noted, the complex reactions occurring within constructed wetlands (CW) have largely been treated empirically. In subsurface flow wetlands, the water level remains below the soil surface, with horizontal flow generally restricted to the "saturated zone" to simplify modeling. For vertical flow CW systems experiencing intermittent loading, the ability to mimic dynamic flow under variably saturated conditions is essential (Langergraber, 2011).

To fully describe CW systems, the reactive transport modeling must describe water flow and reactive solute transport, including solute partitioning reactions, biochemical transformations and degradation processes, plant processes (i.e., growth, decay, nutrient uptake, oxygen release), and matrix clogging processes (Langergraber et al., 2009). Version 2 of the HYDRUS wetland module, the focus of Langergraber and Šimůnek (2012), includes two biokinetic models for simulating biochemical transformations and degradation processes, CW2D and CWM1 (Langergraber et al., 2009; Langergraber and Šimůnek, 2005). Model CW2D, developed mainly for vertical flow wetlands, includes both the aerobic and anoxic transformation and degradation of organic matter (OM), while accounting for nitrogen and phosphorus. However, model CW2D does not consider anaerobic processes, making it more appropriate for use in describing vertical flow wetlands under low to moderate nutrient loading rates. Model CWM1, developed for both horizontal and vertical flow wetlands, accounts for aerobic, anaerobic, and anoxic processes related to OM transformations, while also considering the fate of nitrogen and sulfur.

In addition to the two biokinetic models, HYDRUS considers many critical processes occurring within a CW, with the exception of porous media clogging and certain plant responses (Langergraber and Šimůnek, 2011). HYDRUS is unable to simulate the growth and decomposition of wetland plants, and the

transport and deposition of suspended particulates that may adversely impact hydraulic conductivity, factors that can impact the long-term efficacy of CW systems. HYDRUS describes water movement under variably saturated conditions using Richards' equation, and heat and solute migration by the convection–dispersion equation, with a sink term to account for water uptake by plants (Šimůnek et al., 2011).

Langergraber and Šimůnek (2012) verified the two biokinetic models using a simplified example, i.e., the hydrolysis and mineralization of OM by heterotrophic bacteria, as well as cell lysis with no flow into or out of the model domain. Such a simplified example is required for comparison because inherent differences in the specific processes within the two models prohibit more complex comparisons. Langergraber and Šimůnek (2012) provided a more complex comparison of CWM1 implemented within HYDRUS and within the two-dimensional, finite element RETRSO code under initial conditions originally defined by Llorens et al. (2011a,b). Since the RETRSO requires introduction of bacteria as soluble species at unrealistically high inlet concentrations, implementation of CWM1 within the HYDRUS model resulted in more realistic, complex bacteria distribution profiles despite the use of the same biokinetic model (i.e., CWM1) parameters. As a result the concentration profiles for various solute compounds were very different as well.

In the last reactive transport modeling scenario, Langergraber and Šimůnek (2012) considered the impact of plants for the two biokinetic models under conditions similar to those described above, assuming that roots are largely restricted to the upper layers of the CW and decrease with depth. Such an assumption restricts direct water uptake to the upper portions of the CW. Water uptake is assumed constant, and oxygen release from the roots is based on reported values (5 g m^{-2} d^{-1}) for common reed (Kadlec and Wallace, 2009). The presence of plants provides a constant release of oxygen that facilitates the persistence of aerobic microorganisms, resulting in a different bacterial distribution profile. Further, the HYDRUS model can be expanded to include plant uptake of nutrients in addition to water.

CWM1 generally produces better results than CW2D because of its ability to consider anaerobic degradation processes. These modeling efforts also demonstrated the importance of considering the influence plants can have in controlling wetland processes, such as the subsurface release of oxygen from plant roots.

Lichtner and Hammond (2012) used PFLOTRAN to evaluate geochemical processes controlling the aqueous phase distribution and solid phase speciation of the hexavalent uranium [i.e., U(VI)] plume underlying the Hanford 300 Area bordering the Columbia River, Hanford, WA. The PFLOTRAN reactive transport code was executed on Oak Ridge National Laboratory's Jaguar XT5 Cray supercomputer. The goal of the present study is to estimate the flux of U(VI) to the Columbia River. Much of the U(VI) underlying the Hanford 300 Area is thought to reside within the vadose zone, where fluctuations in the water table can result in the continued release of U(VI) to groundwater.

The current modeling effort extended Hammond and Lichtner (2010) to predict cumulative U(VI) flux for the next 100 yr in the presence and absence of both labile and nonlabile U(VI) phases. The aqueous phase U(VI) speciation has been updated to take advantage of more recent estimates that are consistent with field conditions (Dong and Brooks, 2006). Simulations designed to estimate the initial plume distribution were extended.

In the current context, Lichtner and Hammond (2012) defined sorption as surface complexation reactions that can be described using simple partitioning isotherms, excluding U(VI) bearing precipitates. The previous study of Hammond and Lichtner (2010) indicated that such sorption reactions had a relatively minor impact on U(VI) flux into the Columbia River, with equilibrium and multirate approaches to describing sorption yielding results that were almost identical to the no sorption model. Model results also agreed with field estimates for both U and water flux into the Columbia River (Peterson et al., 2009).

Solid-phase U(VI) was considered in two forms—labile U(VI) subject to surface complexation reactions and a nonlabile U(VI) form for which metatorbernite, a uranium bearing phosphate mineral [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$], was used as a surrogate—as the exact solid-phase U speciation is still in dispute. Initial model conditions were based on current plume distributions due to the lack of historical data related to the initial generation and discharge of the waste stream. Therefore, the initial condition was the same as in Hammond and Lichtner (2010), reflecting present-day conditions. The cumulative flux of U(VI) to the Columbia River was evaluated for model simulations considering equilibrium and multirate controlled sorption, as well as no sorption, in the presence and absence of the nonlabile U(VI), i.e., metatorbernite. Model simulation indicated that the presence of nonlabile U(VI) was critical in explaining the longevity of the U(VI) plume.

The Lichtner and Hammond model includes aqueous phase complexation/speciation, nonelectrostatic surface complexation (Bond et al., 2008), the multirate model of Liu et al. (2008), and reactions with metatorbernite and calcite included as solid phases. Oxidation reduction reactions were not considered, based on observed field data. Despite the obvious complexity, the reactive transport modeling included only two parameters that are not based on field or laboratory estimates: the conductance coefficient for the river water interface representing the hyporheic zone and the effective rate constant for the nonlabile source term. As expected the U is rapidly flushed from the system in the no sorption case. Similar results were observed for the equilibrium and multirate sorption cases, with a much larger inherent U inventory observed for

both cases, when compared to the no sorption case (232 vs. 14 kg). Adding the nonlabile phase results in an extended linear flux of U reaching the river, with "no sorption" producing the least U flux; followed by the multirate condition; and, finally the equilibrium condition that provides the highest flux to the river.

After accounting for the impact of river stage fluctuations, the major conclusion from Lichtner and Hammond (2012) is that, including labile U (i.e., sorbed) alone is insufficient to explain the longevity of the plume, regardless of whether sorption in assumed to be in equilibrium or kinetically controlled. When sorption alone is considered, the aqueous phase U falls below the MCL within a relatively short time period, well before all of the U(VI) has been removed. When a nonlabile phase is present, the aqueous phase concentration of U(VI) is maintained at a much higher level that remains above the EPA MCL. Similar to Chang et al. (2012), Lichtner and Hammond (2012) further asserted that the slow release slow of U from the nonlabile phase, in this case a U-bearing precipitate, is the primary cause of the failure of pump-and-treat remediation strategies.

Reading et al. (2012a) used reactive transport modeling to address issues associated with irrigation and management of sodic soils, where chemical ameliorants are often used to improve infiltration and hydraulic conductivity and enhance the leaching of excess salts from the root zone. Describing such a system requires a model that accommodates solute transport and the requisite chemical reactions (i.e., cation exchange and mineral dissolution/precipitation). As Reading et al. (2012a) noted, however, the model must also describe physical changes in soil properties that accompany changes in soil chemistry; more specifically, changes in hydraulic conductivity that occur when sodium dominates the cation exchange complex. While several available models can be used to describe such basic chemical reactions, only UNSATCHEM and HYDRUS-1D can address changes in hydraulic conductivity associated with shifts in soil chemistry (Šimůnek et al., 1996, 2008). However, the hydraulic conductivity reduction function (K_{red}) included within Richards' equation for the two models is based on a limited range of soils (Suarez et al., 1984; McNeal, 1968) and may not be generally applicable to all soil types due to differences in texture, clay mineralogy, and bulk density.

In their study, Reading et al. (2012a) compared simulations using HYDRUS-1D (ver. 4.14) to a series of recent laboratory experiments reported in Reading et al. (2012b) that evaluated the use of gypsum to ameliorate a nonsaline sodic clay soil from North Queensland, Australia. The HYDRUS model including the "major ion chemistry" option was used to simulate cation exchange, carbonate chemistry, and carbon dioxide transport (Šimůnek et al., 2008), with cation exchange capacity and initial composition of the exchange complex based on soil characterization data (Reading et al., 2012b). For comparison, HYDRUS simulations were run with and without the K_{red} factor, to evaluate how failure to consider changes in hydraulic conductivity can impact the duration of soil amelioration.

Initial column leachates displayed electrical conductivity values that were much higher than the inlet solution. This was attributed to dissolution of salt that had precipitated within the soil profile. The initial salt concentration within the model profile was increased to mimic this observation. The HYDRUS model simulated general experimental trends, including the order in which exchangeable cations were leached from the column (i.e., Na and then Mg and Ca). Including the K_{red} function improved cation leaching simulation results; without including the K_{red} factor, the decrease in exchangeable Na occurred more rapidly at the higher initial sodicity levels.

Cation exchange reactions depended on the soil bulk density, indicating the importance of pore structure and exchange site accessibility in limiting observed kinetics of cation exchange, a factor not considered by the model. Model-predicted changes in hydraulic conductivity generally followed measured trends, but reached a simulated maximum more rapidly than observed for the experimental columns, resulting in more rapid Na leaching in the simulated columns. Reading et al. (2012a) attributed this discrepancy to the fact that K_{red} reached a maximum when the sodium adsorption ratio falls below 10, while the observed hydraulic conductivity of the experimental columns continued to change as additional Na and Mg were leached from the column. Reading et al. (2012a) further asserted that enabling the user to modify the K_{red} function for a specific soil could greatly enhance the model's predictive capabilities, and they noted that additional model flexibility with respect to transport boundary conditions, more specifically adding an upflow condition often required for leaching fine-textured materials, could improve transport simulations.

Understanding the reactions controlling the fate and transport of boron in soils is critical to the appropriate management of B-containing waste waters in arid systems (Suarez et al., 2012). Boron partitioning in the soil environment depends on both soil and pore-water properties in a complex manner that limits the validity of using empirical sorption isotherms for describing the pH dependence of partitioning (Goldberg and Glaubig, 1986; Goldberg et al., 2000). Version 3.1 of the UNSATCHEM code used the constant capacitance model (CCM) to describe B sorption behavior with model constants estimated based on average soil parameters and the specific surface area for the soil in question (Suarez and Šimůnek, 1996, 1997). Version 4.1 of USATCHEM, however, incorporates the equations of Goldberg et al. (2000) for estimating soil specific CCM parameters based on readily available soil properties (i.e., organic and inorganic carbon contents and extractable Al) and surface area, with surface area determined experimentally or estimated based on clay content and mineralogy.

Suarez et al. (2012) evaluated B transport in column experiments using three arid-land soils from southern California as a means of determining the ability of UNSATCHEM to predict B adsorption and desorption using both averaged and soil specific partitioning model constants. The B transport experiments were conducted at two pH conditions (pH 6.0 and 9.0). Boron transport as impacted by pH was generally well described using the B subroutine in UNSATCHEM with CCM constants based on specific soil properties. Significant model discrepancies were attributed to the inability to simulate initial pH conditions resulting from application of the high pH treatment solution. Using the averaged soil CCM partitioning constants combined with soil surface area yielded somewhat less satisfactory descriptions of experimental results, but indicated that reasonable predictions could be made based on average soil properties, without the need to extensively characterize parameters for each specific soil.

Studies evaluating virus transport have generally focused on steady-state flow at a uniform degree of saturation, failing to account for the dramatic remobilization of retained viruses often observed under transient flow conditions. Zhang et al. (2012) used reactive transport modeling to describe virus transport through porous media under variably saturated conditions, where fluctuating moisture regimes can impact both virus attachment and detachment, focusing on the influence of imbibition and drainage on the remobilization of viruses attached to both solid–water interfaces (SWI) and air–water interfaces (AWI). Further, virus transport mechanisms are also relevant to other contaminants that can be mobilized in colloidal form.

Zhang et al. (2012) used three modeling approaches to simulate a series of virus transport experiments reported in Torkzaban et al. (2006a,b) that included imbibition and drainage events. Torkzaban et al. (2006a,b) evaluated the fate and transport of viruses under steady-state flow conditions, the results of which they modeled using HYDRUS1D with attachment and detachment coefficients derived for different steady-state flow conditions; however, some of their initial virus transport studies were followed by transient flow conditions initiated by decreasing inlet flow and allowing the column to drain, or increasing flow to full saturation before allowing the column to drain. Both types of transient events resulted in a major increase in virus mobilization.

The first modeling approach used by Zhang et al. (2012) assumed an increased, yet constant, detachment coefficient for the duration of the transient flow event (e.g., drainage or imbibition). The authors referred to this as the "constant-detachment model." The remaining two modeling approaches reflected modifications of the model developed by Cheng and Saiers (2009), assuming virus detachment to be proportional to the rate of change in water content. The model of Cheng and Saiers (2009) was modified to include separate terms for attachment/detachment on the SWI and AWI (Zhang et al., 2012). The second modeling approach

accounted for virus attachment and detachment at the AWI, a process not specifically considered by Cheng and Saiers (2009), with desorption kinetics described as a function of changes in air or water content without explicitly accounting for the area of the AWI. This approach is called the "variable-coefficient model." The final modeling approach incorporated variations in the AWI as controlled by water content while assuming attachment–detachment to be an equilibrium process referred to as the "apparent linear partitioning model."

The best simulations of virus mobilization during both drainage and imbibition events reported in Torkzaban et al. (2006a,b) were achieved with the simpler, third modeling approach, which accounts for equilibrium based virus sorption on the available AWI. Zhang et al. (2012) noted that virus transport processes observed at the column scale may provide only limited information concerning the actual virus attachment–detachment mechanisms. The authors further admit that alternate virus partitioning expressions may be required for structured, finer textured soils.

Conclusions

This special section consists of eight studies illustrating a diverse range of reactive transport modeling applications evaluating the interrelated nature of various biogeochemical processes from the laboratory to the regional scale. In recent years, greater focus has been placed on improving our understanding of the coupled biological and geochemical reactions that impact solute behavior. Addressing the scale-dependency of reactive transport processes attributable to both physical and biogeochemical heterogeneities remains a challenge. While the contribution to the remediation and management of subsurface contamination is obvious, reactive transport models can also improve our understanding of fundamental biogeological processes, such as chemical weathering and nutrient and elemental cycling.

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