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Assessing Conceptual Models for Subsurface Reactive Transport of Inorganic Contaminants

J.A. Davis
U.S. Geological Survey, jadavis@usgs.gov

S.B. Yabusaki
Pacific Northwest National Laboratory

C.I. Steefel
Lawrence Berkeley National Laboratory

John M. Zachara
Pacific Northwest National Laboratory, john.zachara@pnl.gov

G.P. Curtis
U.S. Geological Survey

See next page for additional authors

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Authors

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In many subsurface situations where human health and environmental quality are at risk (e.g., contaminant hydrogeology, petroleum extraction, carbon sequestration, etc.), scientists and engineers are being asked by federal agency decision-makers to predict the fate of chemical species under conditions where both reactions and transport are processes of first-order importance.

In 2002, a working group (WG) was formed by representatives of the U.S. Geological Survey, Environmental Protection Agency, Department of Energy, Nuclear Regulatory Commission, Department of Agriculture, and Army Engineer Research and Development Center to assess the role of reactive transport modeling (RTM) in addressing these situations. Specifically, the goals of the WG are to (1) evaluate the state of the art in conceptual model development and parameterization for RTM, as applied to soil, vadose zone, and groundwater systems, and (2) prioritize research directions that would enhance the practical utility of RTM.

The WG is addressing issues related to the fate of reactive solutes in complex field systems, where spatially and temporally subsurface properties directly influence not only the physical processes of flow and transport, but also the rates and extent of biogeochemical reactions. Of particular interest is the interplay between physical and reaction processes, and how this coupling could be efficiently and realistically accounted for in RTM. The WG has focused on the evaluation of conceptual models; improvement of numerical approaches and comparison of computer codes are outside the scope of WG activities.

The activities of the WG to date have included a literature review, internal meetings, and sponsorship of a workshop (see: www.iscmem.org for the full membership and background of the WG, and information on other interagency environmental modeling groups). The workshop included agency representatives and federal and academic specialists in model development, geochemistry, hydrology, and microbiology. This article summarizes findings of the WG to date with respect to the status of RTM for inorganic contaminants.

Technical Issues

A conceptual model for RTM represents the scientific understanding of processes controlling the movement and transformation of system components, including contaminants, for a specific water-rock system. For example, a conceptual model for a groundwater contaminant plume might include knowledge of (1)

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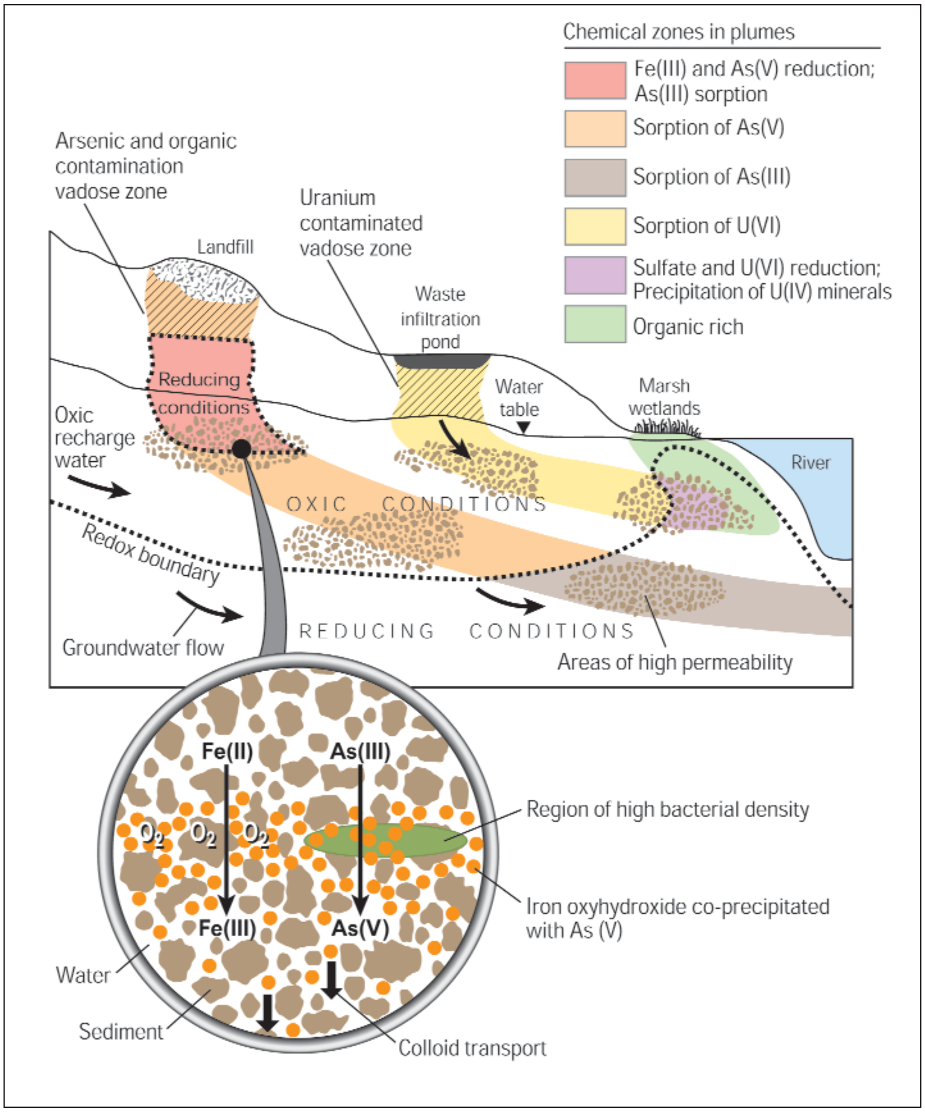

Fig. 1. Schematic diagram illustrating how complex subsurface environments may affect the fate and transport of arsenic and uranium contaminants.

spatial distribution of chemical species, sediment texture, and mineralogy; (2) hydrologic sources and sinks, porosity, and spatial dependence of hydraulic conductivity; (3) aqueous solute speciation and chemical reactions controlling phase distribution; and (4) microbial controls on aqueous chemistry and elemental speciation. The conceptual model provides the biogeochemical reaction network and parameters, the hydrologic properties and geologic structure, and initial/boundary conditions (e.g., water saturation and pore water concentrations, surface site and organism identities and concentrations, etc.).

Although there have been successful applications of complex conceptual models for RTM at the laboratory scale, application of scientifically based RTM to the field scale has been limited by difficulties in defining appropriate conceptual models.

A principal difficulty in conceptual model development is the identification of appropriate process models in the presence of multiscale heterogeneities. Spatially variable permeability and porosity can result in preferential flow paths that control supply rates and residence times of chemical components. Nonuniform distributions of chemical concentrations arising from these conditions are subject to diffusive mixing enhanced by dispersion processes that are linked to the heterogeneous pore network. These mixing processes bring into contact solutes, surfaces, and solids that are not in chemical equilibrium. While the resulting reactions may be fast, the rate may be limited by mass transfer between adjacent zones with differing chemistries and microbial populations. Examples of this kind of behavior can be found at all length scales, but especially in the case of transport between fractures and matrix in fractured rock, and between mobile and immobile zones in sediments.

Multiscale heterogeneities in chemical properties are typically associated with spatially variable mineral assemblages, contaminant sources, or microbial populations. Mineral reactions can create nonuniform component distributions even in the absence of physical heterogeneities. Reactive surface area is a critical parameter controlling rates and extents of reactions, but the values of reactive surface area for individual minerals/phases that are required by mechanistic submodels are very difficult to measure in natural samples.

Contaminant transport and fate can be strongly influenced by redox reactions that are mediated by microorganisms (see examples for arsenic and uranium in Figure 1). Modeling the dynamics of subsurface microbial communities and their temporal and spatial impacts on system geochemistry is a major challenge in implementing RTM. The difficulty results from a limited understanding of the varied factors that control in situ metabolic activity and uncertainty in how to describe the community dynamics and interrelationships of multiple functional groups of micro-organisms (e.g., sulfate and iron reducers). Microbial growth and decay are typically not included in RTM or are based on an implicit, but unproven, assumption that microbial activity is proportional to microbial biomass.

Working Group Outlines Needs

In the absence of mechanistic understanding at the field scale, the WG concludes that it is best to refine process-level models developed from laboratory-scale experiments with field materials rather than to attempt to fit global parameters to a "standard" process model without a scientific basis (e.g., fitting a constant K_d to field observations of contaminant migration). This approach should be done with the expectation that process models and parameterizations developed under idealized conditions at the laboratory scale (e.g., using an homogenized < 2 mm sediment fraction) are not likely to accurately depict the field-scale situation, which must address multiple scales of physical (e.g., hydraulic conductivity) and geochemical (e.g., mineralogy) heterogeneity.

The challenge is to develop field-scale parameterizations that accurately address the combined impact of physical and chemical heterogeneities on flow and reaction processes. Sufficient detail in the understanding of hydrologic and biogeochemical processes is needed to resolve transport- and reaction rate-limited behaviors associated with physically and chemically heterogeneous domains. Furthermore, small-scale processes and properties below the resolution of computational grids must be addressed if their influence is significant. Subgrid variability in hydrologic and biogeochemical parameters such as dispersivity, multiregion mass transfer, sorption site multiplicity, and microbial community location are important to consider. Appropriate representation of fingering phenomena and the homogenizing behavior that results from spatially correlated physical and chemical heterogeneities requires this level of modeling detail.

Mechanistic descriptions of microbial processes will continue to be the focus of important research, but translating the basic science to field-scale models is the current challenge. New techniques are needed that directly probe the reactivity of subsurface microbial communities, particularly in relation

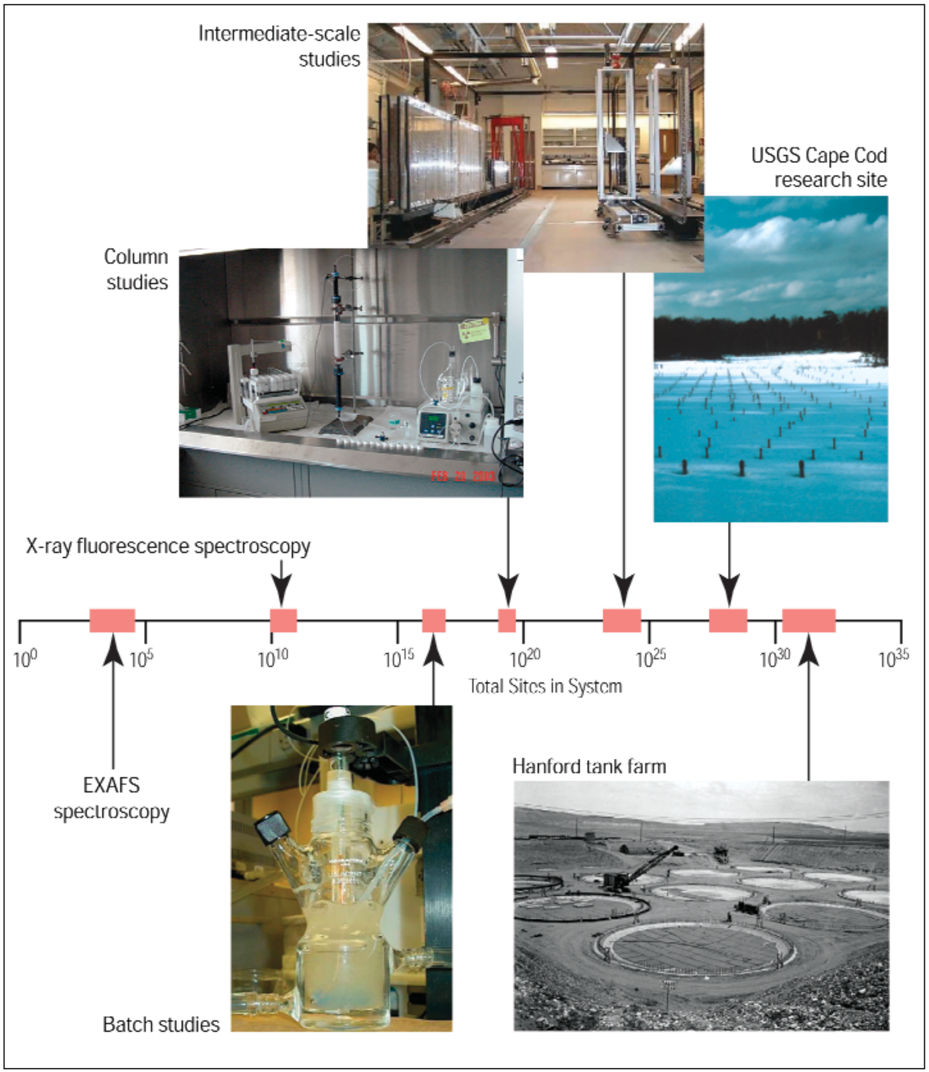

Fig. 2. Relationship between the number of surface reactive sites and the scale of experimental measurements. Based on fine-grained porous media with 0.1 moles of sites per m^3. Figure courtesy of Bruce D. Honeyman, Colorado School of Mines.

to the reactions that are mediated. Spectroscopic techniques can help to identify biosynthesized compounds and phases in order to formulate stoichiometrically balanced reactions for modeling. Field-scale studies are particularly important in this regard, because environmental conditions that are difficult to simulate in the laboratory profoundly affect microbial populations and activity.

An improved understanding is needed of (1) the factors that control the activity of specific bacterial populations in a particular environment, and (2) the explicit relationships that exist between microbial activity, reaction kinetics, and the chemical speciation of redox-sensitive elements. Using key environmental parameters, including nutrient availability and flux, the models need to simulate consumption of multiple terminal electron acceptors and the biosynthesis of reactive products, without the use of empirical constants. The adaptation of physiological functions that occur in response to evolving geochemical conditions must eventually be implicit to the modeling approach.

There is also a great need for advancements in understanding processes that are coupled to changes in permeability, such as dissolution/precipitation reactions of mineral phases of both biotic and abiotic origin. Development of conceptual models that describe metastable phases and co-precipitates and their transformation to more stable phases with time is important. Detailed field observations are needed to identify indicators of system change and to determine correlations with existing mineral phases; these observations will help clarify significant scientific issues that require further research in the laboratory.

A key consideration in developing robust, field-scale RTM is the ability to compare predictions with observations during perturbations of physical and chemical conditions that exercise as much of the field-relevant range of parameters as possible. In this respect, a series of history matching studies ranging from laboratory to field scales can provide both a strong basis for understanding scale-up issues and the resulting field-scale predictions, and better tests of the validity of alternative conceptual models. Laboratory-scale experiments must remain a fundamental component in building a field-scale model, but equally important are intermediate-scale experiments that provide essential links between small-scale analyses of limited dimensionality and field-scale behavior (see Figure 2). By studying the transitions in system behavior across a range of scales, process and parameter upscaling can be understood in multidimensional systems with realistic degrees of freedom and variability.

The WG has also concluded that quantitative measures of uncertainty are needed to compare alternative conceptual models, recognizing that RTM prediction uncertainty consists of both conceptual model uncertainty and parameter uncertainty. Many practitioners believe that complex models with many model parameters may yield greater uncertainty than simpler models with substantially fewer parameters. However, when conceptual model uncertainty is included, models in which multiple, interacting chemical and physical processes are poorly represented by a few empirical constants can have a relatively large total model uncertainty. A large uncertainty in predictions can lead to significant costs to federal agencies in long-term remediation projects. The costs of additional data collection to support a more advanced reaction model need to be weighed against realistic evaluations of the total uncertainty of model predictions. RTM studies can be conducted in parallel with data collection to help determine whether a simple or complex conceptual model is more useful in reducing total model uncertainty.

Major Recommendations

The WG concludes that federal agencies must support long-term research at field sites, specifically for the purposes of conceptual model development for RTM. While several field sites have been developed for reactive transport science (see Web sites: http://ma.water.usgs.gov/CapeCodToxics/default.htm; http://www.nrc.gov/reading-rm/doc-collections/nuregs/contract/cr6820/cr6820.pdf; http://mn.water.usgs.gov/bemidji; and http://www.lbl.gov/NABIR), the sites were generally not selected to examine which conceptual models provide the most robust, mechanistic description of reactive transport processes, while remaining feasible in terms of data and modeling requirements.

It is recommended that a modeling research site be carefully chosen to strike a balance between complexity and tractability, targeting a range of observable length scales of physical and chemical heterogeneity. Hydrologic and chemical transients are critical to the elucidation of system response, and allow more rigorous evaluation of the robustness of alternative conceptual models.

There also should be a spectrum of scales and measurable biogeochemical processes operating in the system (e.g., mineral precipitation/dissolution, redox and microbial environments, aqueous and surface complexation) to maximize relevance to problems faced by the multiple participating agencies.

It is envisioned that the field sites would form part of a broader research program that includes both laboratory and multiscale field experiments. By investigating conceptual models for subprocesses in the same system at various scales, it may be possible to provide independent constraints on the components of coupled models used to address field-scale reactive transport. Both laboratory "sand box" and in situ field experiments are recommended. This approach will provide insight into the limitations of conceptual models and parameterizations developed at the laboratory bench scale in accurately depicting a field-scale situation.

The need for calibration of field-scale reaction parameters in RTM should not be underestimated. Current limitations in characterizing multiscale variability in subsurface properties and observing in situ behavior result in knowledge gaps that will only be effectively addressed through process model calibration against field observations. While this may somewhat limit the robustness of model predictions, decisions based on RTM predictions can be justified if the conditions modeled are within the range of calibration conditions and the predicted outcomes can be bracketed to the extent that they clearly differentiate alternatives.

The WG concludes that addressing the research issues noted above would greatly improve the application of RTM to many public health issues where better predictions are needed, and ultimately result in cost savings to federal agencies.

Author Information

James A. Davis, U.S. Geological Survey, Menlo Park, Calif.; Steven B. Yabusaki, Pacific Northwest National Laboratory, Richland, Wash.; Carl I. Steefel, Lawrence Berkeley National Laboratory, Berkeley, Calif.; John M. Zachara, Pacific Northwest National Laboratory, Richland, Wash.; Gary P. Curtis, U.S. Geological Survey, Menlo Park, Calif.; George D. Redden, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho; Louise J. Criscenti, Sandia National Laboratory, Albuquerque, New Mex.; and Bruce D. Honeyman, Colorado School of Mines, Golden, Colo.

For additional information, contact J. Davis; E-mail: jadavis@usgs.gov