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EDITORIAL: Recent developments in surface complexation modeling

This special section on surface complexation modeling contains papers presented during the special session “Recent developments in surface complexation modelling: Trace element speciation and reactive transport modelling” at the 12th International Conference on the Biogeochemistry of Trace Elements (ICOBTE), which took place 16–20 June 2013 in Athens, Georgia, USA.

Ion-binding and surface complexation models have been developed during the past 2 decades to describe equilibrium trace element binding to complex reactive components of the surface and near-surface environments, including natural organic matter, hydrous metal oxides, and clay minerals. Because of their semi-mechanistic and process-based nature, these models are applicable over a wide range of conditions and have potentially powerful uses in hazard and risk assessment of metals and metalloids.

In the past, such models largely have been used to increase understanding of trace element complexation and adsorption processes, although there also have been important applications in hazard and risk assessment, particularly the biotic ligand model (BLM), and in multimedia fate and transport modeling. With this special section, we aimed to stimulate broader application of these models by establishing the state of the art and highlighting recent developments in the field.

The state of the art is established in two reviews, each of which deals with one of the two main approaches for applying ion-binding models to natural systems comprising multiple reactive components [1, 2]. The review by Goldberg [1] describes the generalized composite approach, in which binding to the reactive components of a natural material such as a soil, sediment, or aquifer is simulated using a single composite binding phase whose binding sites represent the overall binding properties of the natural material. This requires separate fitting of conditional model parameters for each natural material. The approach may be adapted for predictive purposes by regressing model parameters against natural material properties such as cation exchange capacity, surface area, organic carbon content, inorganic carbon content, aluminum oxide content, and iron oxide content.

The review paper by Groenenberg and Lofts [2] describes the component additivity approach, whereby the total binding of elements to the assemblage of reactive components is computed by simulating and summing binding to the individual components. Model parameters, including binding constants and site densities for each component, are determined a priori from binding experiments with the specific components. The approach has the advantage of wide applicability in principle, provided that ion binding to the in situ reactive components may be sufficiently well characterized. Groenenberg and Lofts [2] describe the development of models for specific components and review the literature on the application of such models to both artificial and natural composites. “The characterization of natural assemblages in terms of their components (active organic matter, reactive oxide surface) is key to successful model applications. Improved methods for characterization of reactive components in situ will enhance the applicability of assemblage

models. Collection of compositional data for soil and water archetypes, or the development of relationships to estimate compositions from geospatially available data, will further facilitate assemblage model use for predictive purposes" [2].

Of the four research studies included in the section, three focus on modeling the adsorption of oxyanions to soils. The study by Gabos et al. [3] is an example of the application of the generalized composite approach to a series of tropical soils with a broad range in soil properties. The study demonstrates how application of the generalized composite approach results in a range of conditional binding parameters that could be related to soil properties to provide a framework for predictive modeling of new soils. The two studies by Perez et al. [4, 5] describe oxyanion sorption to a ferralic soil using the charge distribution surface complexation model with goethite as a proxy for the reactive surface; thus, the modeling is a limiting case of the component assemblage approach. Modeling takes into account the competitive adsorption of organic matter onto the soil and its effect on reducing the available site density for oxyanion sorption. The first study [4] describes the modeling of phosphate adsorption to soil using standard binding constants but with optimization of the soil surface characteristics, which yielded fitted values of the amount of phosphate reversibly bound to the surface, the reactive surface area, and the site density of adsorbed organic matter on the soil surface. The parameters obtained in the first study were used to model binding of chromate, selenite, molybdate, and arsenate adsorption to the soil, described in the second study [5].

In recent years, ion-binding modeling—specifically, binding to natural organic matter in surface waters—has found a significant application in improved understanding and prediction of how metal bioavailability and toxicity vary with exposure medium chemistry. Development and application of bioavailability models, particularly the BLM, has reached a stage where the knowledge gained is in the process of being applied to set site-specific environmental quality standards for certain metals in some legislatures. This represents a significant success for speciation modeling in practical application to risk assessment and chemical management. Research into the relationships between speciation, bioavailability, and toxicity continues to develop. The final study in this section, by Antunes and Kreager [6], shows how chemical speciation modeling can aid the description of dose-response relations for biota under laboratory conditions.

Overall, advancements in the mechanistic modeling of ion-binding to natural surfaces mean that, in many cases, models are sufficiently advanced to be "ground–truthed" against real field data, which is necessary for their robust application in hazard and risk assessment. The next stage is to establish how well models can perform in application to the field, particularly in relation to data availability at different scales, and to assess how well current methods for field characterization provide suitable data for modeling. Depending on the desired timescales of application, the need to incorporate models into transport frameworks that can consider slower, non-equilibrium processes alongside ion-binding needs to be considered.

Jan E. Groenenberg

Alterra, Wageningen UR, The Netherlands

Department of Soil Quality, Wageningen University, Wageningen, The Netherlands
Stephen Lofts
NERC Centre for Ecology and Hydrology, Lancaster Environment Centre, Lancaster, United Kingdom

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