Humic ion-binding modelling and its application to field processes and ecotoxicology

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WHAM/Model VI combines an ion-binding model for humic substances with an inorganic speciation code. Model VI uses a structured formulation of discrete, chemically-plausible, binding sites for protons, to allow the creation of regular arrays of bidentate and tridentate binding sites for metals, including relatively rare sites with high affinity. The (competitive) binding of each metal, and its first hydrolysis product, is characterised by a single intrinsic equilibrium constant. Account is taken of electrostatic interactions.

The catchment model CHUM-AM includes process descriptions of N and S uptake and release by the soil-plant system, percolation and evaporation of water, solid-solution partitioning of solutes (described with WHAM/Model VI), chemical interactions in solution (also described with WHAM/Model VI), and chemical weathering. The model operates on a yearly time-step and is driven by inputs of wet and dry deposition.

CHUM-AM has been applied to moorland catchments in northern England, to simulate acidification and its reversal, and heavy metal behaviour. By 1998, the catchment soils had retained 89-98% of previously deposited anthropogenic Cu, and 95-100% of Pb. Retention of the other metals, which sorb relatively weakly to the soil, depended on soil pH and varied from 5%, for Ni in the most acid soil, to 62%, for Zn in the least acid soil. Simulations of future metal behaviour suggest that weakly-sorbing metals (Ni, Zn, Cd) will respond on timescales of decades to centuries to changes in metal inputs or acidification status. More strongly-sorbing metals (Cu, Pb) will respond over centuries to millennia.

WHAM/Model VI provides estimates of free metal ion concentrations in soil solution or in surface water, and these can be combined with information on ecotoxicity to gauge toxic effects. Soil metal toxicity data have been analysed, using multiple regression equations describing free ion concentrations, to derive pH-dependent free ion Critical Limit Functions. These CLFs are used in a proposed method to determine steady-state Critical Loads for heavy metals in Europe. They can also be combined with CHUM-AM outputs to explore temporal variations in potential toxicity.

Metal binding to NOM from database to field systems

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In the past decade advances in modelling metal ion binding to natural organic matter have been made. In parallel an extensive data set has been produce to help to validate and calibrate the modelling effort. Today robust models are available to describe complex geochemical systems such as soils and rivers.

The validity of the model calculation is however strongly dependant on the reliability of the database used for calibration. This is the case for elements like Cu, Cd, Ca, Eu for which numerous experimentals data are available and can be compared to each other.

However for important elements like Al, Fe and in general tri and tetravalent elements the range covered by the available experiments is not sufficient for reliable model predictions.

In the present contribution I will report new data for trace elements interactions with various types of natural organic matter at different pH and metal to ligand ratios. The model parameters like affinity constants, heterogeneity and site densities derived within the NICA-Donan model framework are compared to existing values.

Based on those new parameters complex geochemical systems will be simulated. The case of iron in tropical rivers and trace elements in contaminated soil solutions will be discussed.