Metal speciation in LOIS rivers and estuaries

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Several LOIS projects are concerned with concentrations and fluxes of metals, with interest in rivers, estuaries and the sea, sediments and surface waters. Interpretation and prediction of metal behaviour, including bioavailability, require understanding of the chemical forms of the metals. Chemical modelling is a necessary part of this effort. The purpose of this contribution is to describe the modelling approach that we are developing, in collaboration with our colleagues at the University of Plymouth, under Special Topic RACS (R/C) 279.

For complexation and adsorption reactions, metals can be considered to exist in the following forms;

dissolved: free aquo ion (M^{z+}); inorganic complexes; organic complexes
colloidal: M adsorbed to small mineral particles or complexed by macromolecules
particulate: M adsorbed to larger mineral particles, to particulate organic matter or to biota

Equilibria involving the above chemical forms can be written, in general;

$$M + X = MX$$
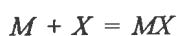
In natural systems there are many such reactions occurring simultaneously, and the X component can be highly complex and heterogeneous. The required calculations are therefore extensive and uncertain. For some time it has been possible to calculate the extents of inorganic complexation reactions using codes such as MINEQL, PHREEQE, WATEQ etc. More recently, codes for complexation by humic matter have been developed, including our on WHAM model. Metal interactions with colloidal and particulate matter are often described with the coefficient K_D, which is defined by;

$$K_D = \frac{[particulate\ metal]\ /\ [particulates}{[dissolved\ metal]}$$

The advantages of K_D are its simplicity, the fact that it is directly measurable, and the ease of its incorporation into larger models such as QUESTOR and ECoS. Its principle disadvantage is that it is not a constant, depending upon the solution speciation and the composition of the particulate matter. One of the main aims of our Special Topic project is to produce a more general model for adsorption by suspended particulates (SCAMP), in which equilibrium constants are used to describe the reactions. In principle, this model will be applicable to sediments as well, and also to soils.

The Surface Chemical Assemblage Model for Particles (SCAMP) treats natural particulate matter as an assemblage of different phases, for each of which there is a sub-model to describe adsorption. The phases considered so far are oxides of Al, Si, Mn and Fe, a mineral cation-exchanger, humic and fulvic acids. Data from published laboratory studies have been used to parameterise the sub-models. In combination with WHAM, SCAMP allows the complete speciation of a metal to be computed, given total concentrations of reactants, and their redox states. Competition and the effects of ionic strength are taken into account. Predictions using WHAM-SCAMP give encouraging results when applied to our measurements of solid-solution partitioning of metals in suspensions of riverine and estuarine particles (see abstract by Lawlor, Lofts, Tipping & Ferreira). SCAMP is applicable to both colloids and larger particles.

Computing demands may make it difficult to embed WHAM-SCAMP into larger models like QUESTOR and ECoS. If so, then the chemical speciation calculations could be performed independently and the outputs used as inputs, in the form of K_D values, to the larger models.

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