Metal Speciation in Aquatic Systems

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The accumulation of toxic metals in the biosphere will continue to be a serious environmental problem, even if the immediate sources of pollution will be removed in the near future. Thus leachates from waste deposits, transfers from contaminated sediments to the water column and releases due to ground and surface water acidification will cause continuing problems.

To present suitable steps for lowering the concentrations of toxic metals circulating in biota, it has become of urgent importance to understand the conversion, transport and bio-uptake of these metals. These processes are often closely related to the speciation of the elements, i.e., a characterization of the individual physico-chemical forms of the element that together make up its total concentration. It is now well established that a knowledge of the speciation of a metal is a necessity to be able to understand its toxicity as well as its transport in natural waters. It has been shown that biological availability of dissolved trace metals often can be correlated through the activity of the free metal ion. Investigations of biological availability of trace metals therefore require means of determining the activities (or concentrations) of free metal ions, and of other relevant chemical species in case the free metal ion activity concept is not valid.

The speciation of a metal in natural aquatic environments is affected by a large number of different, simultaneously occurring processes. This web of processes comprises various complexation reactions in the aqueous phase, precipitation and dissolution reactions, sorption at surfaces of particulate matter and so on.

Trace metal speciation in natural waters has been based on the use of two different techniques: experimental measurements and computer chemical modelling. The first approach is still limited by the lack of experimental techniques sufficiently sensitive and selective to detect individual species at the concentrations normally found in natural systems.

The computer modelling approach to trace metal speciation in waters involves the use of thermodynamic data, together with known concentrations of reacting components, to compute the equilibrium concentrations (or activities) of the various species. The validity of the assumption that the system being modelled at equilibrium depends on the processes included in the model. Inorganic complexation reactions usually equilibrate quickly, whereas organic complexation reactions are slower, especially when natural organic substances are involved. Precipitation/dissolution processes are also slow, and frequently accompanied with time dependent phase transformations. Many adsorption reactions of trace metals onto particles are accompanied by slow incorporation of the adsorbed metal into the solid matrix so that no true equilibrium is obtained.

The validity of the equilibrium assumption should be considered carefully in speciation modelling exercises. A comparison of results from the model with data for the real system will help to identify gaps in our information and to reveal limitations in applying equilibrium model.
Besides scrutinizing the equilibrium concept, we have to face other limitations when applying an equilibrium model:

i) Important chemical equilibria with pertinent thermodynamic data have not been considered in formulating the model. The naturally occurring solid phases are very seldom pure substances but rather solid solutions. At the present time, reliable thermodynamic data for most of these solid solutions are lacking (especially at low temperatures). Instead idealized end-members of the different solid-solution series have been used as approximations. Furthermore, the chemical nature of naturally occurring organic substances are difficult to characterize. This is also the case thinking of particle surfaces in terms of functional groups and binding site concentrations.

ii) Available thermodynamic data are not always as accurate as one would wish. Temperature, pressure and medium dependences of formation constants may require refinements.

As a concluding remark, it should be stressed that a presented equilibrium model is to be regarded as a working hypothesis of how a real system may function chemically. It is inevitable that some results will be subject to revision as more detailed information of the real system becomes available. Computer modelling has made an important contribution towards an understanding of speciation in natural waters, and will continue to be an important technique in the future.