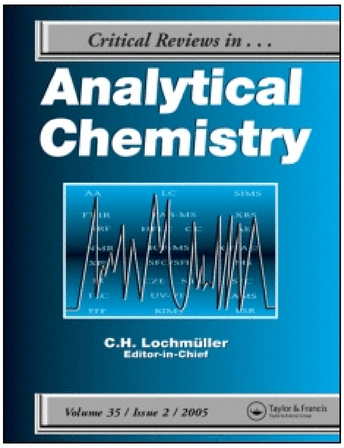

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Hudson, Robert J. M.(1998) 'MODELING THE FATE OF METALS IN AQUATIC SYSYEMS: THE MECHANISTIC BASIS OF PARTICLE-WATER PARTITIONING MODELS', Critical Reviews in Analytical Chemistry, 28: 2, 19 — 26

To link to this Article: DOI: 10.1080/10408349891194234

URL: http://dx.doi.org/10.1080/10408349891194234

Critical Reviews in Analytical Chemistry, 28(2):[SI]19–[SI]26 (1998)

MODELING THE FATE OF METALS IN AQUATIC SYSYEMS: THE MECHANISTIC BASIS OF PARTICLE-WATER PARTITIONING MODELS

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INTRODUCTION

Modeling plays a central role in applying chemical science to environmental problems. Models are used to investigate the fate of pollutants, compare the relative emissions of a substance from anthropogenic and natural sources, and predict the effects of pollutants on ecosystems and human health. Addressing questions such as these are essential when designing remediation strategies and formulating environmental regulations. While environmental models vary greatly in the degree of sophistication used to represent chemical reaction and physical transport processes, models of some kind, if only simple conceptual models or empirical correlations, are invariably applied in making important decisions regarding the environment.

Environmental chemists have played an active role in developing and applying the models needed to address environmental problems. Chemists contributions have been especially significant in the area of metal pollution of aquatic systems because of the complicated chemistry involved. Perhaps chemists' most fundamental contribution in this field has been the concept of chemical speciation [1]. Recognizing the fact that metals exist in the environment in different redox states and coordination complexes is essential because each different species may undergo different reactions, be transported by different mechanisms, or affect biota to different degrees.

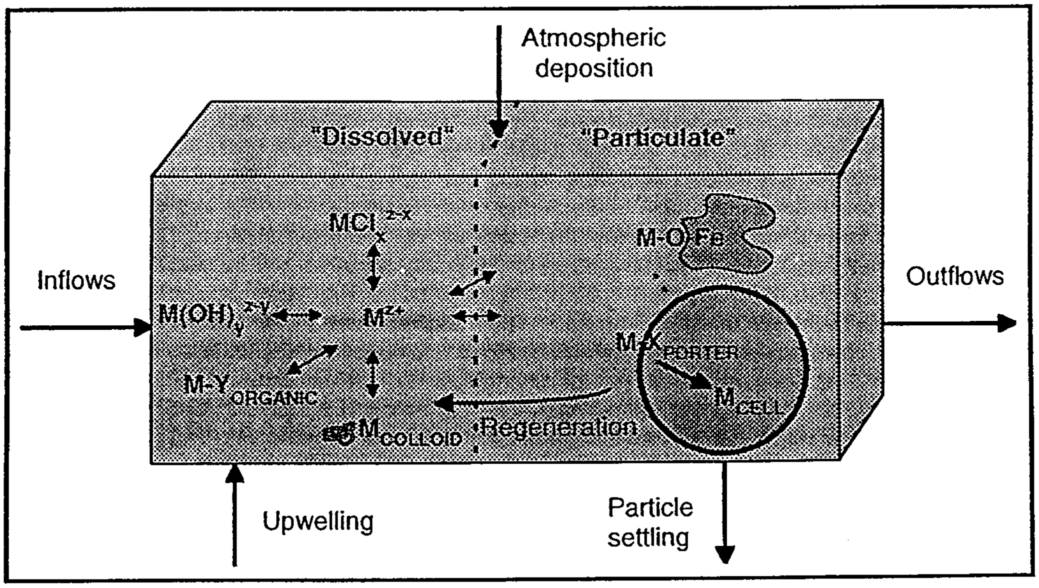

Figure 1. Interrelationship of the particle-water partitioning of a metal M^{z+} with the principal processes that affect its fate in surface waters. The separation obtained using typical filters with pore sizes of 0.45-1 μm is indicated by the dashed line. "Dissolved" species include various inorganic complexes as well as truly dissolved and colloidal organic complexes. "Particulate" species include living phytoplankton and metal oxide particles, as well other microbes and detritus which are not shown.

One of the most basic species distinctions is physical, i.e., between particulate and dissolved species of metals (Fig. 1). Metals associated with particulate matter can be either swept from the water column as the particles settle to sediments or regenerated as solution species by grazing planktonic animals, while dissolved metal species typically are transported only by molecular diffusion and water motion. In general, these processes have a dominant influence on metal concentrations in surface waters. Just as importantly, particulate metal species exert direct toxic effects only on biota that ingest them, while dissolved species can affect nearly all organisms in contact with the water mass they are dissolved in. For these reasons, the separation of particulate and dissolved species by filtration (typically 0.45 µm pore size) is the most common speciation measurement made for metals in aquatic systems. Since the partitioning of a metal between the particulate and dissolved states can vary widely between systems, accounting for the differences between water bodies is an important, basic problem in environmental modeling.

This paper will briefly review several important aspects of the environmental chemistry of metals that influence their particle-water partitioning. Primary attention will be paid to the organic complexation of dissolved metals and their uptake by aquatic microorganisms. The adsorption of metals onto abiotic particles, which is dominant in some systems, will be covered only briefly. (Redox reactions will not be considered. I assume that only a single redox state of a metal is under consideration at a time.) Particular attention will be paid to the ability of mechanistic models to accurately represent field data – the ultimate test of environmental simulation models.

FIELD DATA

Modeling of metal dynamics in aquatic systems depends on obtaining reliable measurements of their dissolved and particulate concentrations. Measuring the low concentrations of metals present in aquatic environments – typically ~1 pM for monomethylmercury to ~100 nM for transition metals in lakes and streams – requires great care. Small amounts of contamination from dust, analytical reagents, or sample containers can easily surpass the lower environmental metal levels. If sample contamination is not rigorously excluded, pollution problems can be partly or completely obscured, as was the case for lead pollution before the advent of clean techniques. For this reason, the development of ultraclean sampling protocols and sensitive analytical techniques for metals has been critical to progress in this field and has lead directly to major insights into the environmental behavior of metals.

Second, modeling of aqueous speciation requires that both the organic complexation of metals be characterized in addition to the more routine determination of the concentrations of significant inorganic ligands. Over the last decade, significant advances have been made in coupling electrochemical techniques with clean sample handling for quantifying organic ligands present in natural waters at levels as low as ~0.1 nM [2]. Because a significant fraction of dissolved organic matter is colloidal in nature, physical separation techniques, dialysis and ultrafiltration for example, have also been used successfully to characterize the organic complexation of metals. Truly dissolved, low molecular weight ligands will not be detected by physical means, however. Using these methods, analytical chemists can determine the degree to which an metal is complexed *in situ* and quantify the concentration and binding strength of organic ligands present in an environmental water sample (Fig. 2). These measurements of complexation in "whole water" samples (often filtered), although not as widely available as partitioning data, provide an extremely useful database for environmental modeling. It should be remembered that these analyses only quantify the strength and amounts of the organic chelators, not the chemical moieties responsible for binding the metals.

Thirdly, the chemical composition and nature of the particulate phases present in a natural water need to be considered. Commonly available data include total particle mass, the concentrations of particulate metals, organic matter content, and sometimes the chlorophyll content of the filterable particulate fraction. These measurements allow estimates to be made of the levels of metal oxides, clays, and living cells. They do not permit a detailed identification of the inorganic phases or species of phytoplankton and bacteria present in the particles, although these properties may be determined in some studies. These limitations are very important to keep in mind as models are developed.

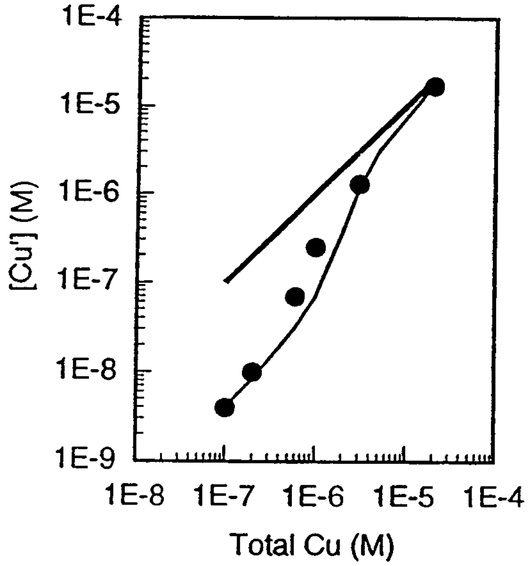

Figure 2. Complexometric titration of DOM in a river with copper(II) [3]. [Cu'] denotes total inorganic copper concentration. Data points (●) for a Blackstone River sample taken on 12/28/93; expected [Cu'] in the absence of organic complexation (straight line); the curved line is calculated for a single ligand with stability constant (K $=10^{7.1}$ M^{-1}) and concentration ($[Y_{organic}] = 2$ μM) adjusted to fit the observations at both high and low Cu(II) additions. The poor fit in the intermediate range is indicative of a range of ligands with different binding strengths being present.

SPECIATION MODELING

From the brief consideration of the types of data that are to be modeled, it should be apparent that the particle-water partitioning of metals potentially is very complicated. First, the low concentrations at which metals are present mean that modelers must consider how their behavior might be influenced by a wide variety of ligands that are quantitatively minor solutes in natural waters. Not only are the ligands and particles heterogeneous and/or poorly characterized, but competitive interactions with numerous metals need to be considered for ligands present at levels comparable to those of the metals themselves. For these reasons, speciation in the environment is difficult to rigorously define and some degree of empiricism is often necessary.

Scientists working in this area may be categorized according to the degree to which their approach is either empirical or mechanistic (physico-chemical). Progress in this field has depended upon using both approaches. For example, an empirical partition coefficient (K_P) is defined from an equilibrium mass law equation that uses only the most basic observational data:

$$K_P = \frac{[M_{Particulate}]}{[M_{Dissolved}][Particles]} \tag{1}$$

A mechanistic approach would involve identifying the key reactions involved in the association of the metal with particles. For example, the equilibrium association of metals with the particulate binding sites of type X_j might be defined by:

$$K_{MX_j} = \frac{[MX_j]}{[M^{z+}][X_j]} \tag{2}$$

where M^{z+} is the free metal ion. For biotic particles, a steady-state approximation equating uptake rates to dilution by growth and other losses is typically applied and different metal species may control the uptake rate. The overall partition coefficient would be derived by summing the various modeled particulate metal species.

Ultimately, mechanistic modelers attempt to explain empirical observations, while empiricists make measurements that are shaped by mechanistic concepts and models. Modelers might hope to identify quantities of sufficient generality and importance that empiricists will routinely measure them. In the remainder of this section, I will discuss some mechanistic approaches that are currently being applied in the study of chemical speciation and particle-water partitioning. In the following section, their application to field data is considered.

Aqueous speciation. The aqueous species of a metal ion potentially include important inorganic and organic complexes. Typically, equilibrium modeling of the inorganic speciation is fairly straightforward since most inorganic ligands in the environment need to be present at readily measurable levels in order to significantly influence metal speciation. A very important exception is hydrogen sulfide, which can be present at nanomolar levels in oxic waters [4]. A number of equilibrium models and databases exist from which relatively consistent predictions of inorganic complexation of metals can be made. One well documented and widely-used model and database is MINTEQA2 [5], which is available over the World Wide Web.

Complexation by natural dissolved organic matter (DOM) is a much more complicated problem. Natural DOM is formed through the decomposition of plant matter. But because DOM consists of a large number of poorly-characterized ligands, data from whole-water analyses for metal complexation typically are not described well by a single-ligand model (Fig. 2). To describe this behavior, a wide variety of models have been developed, as described in the recent review by Westall et al. [6]. Some models simply provide an empirical description of the data, while others attempt to provide a mechanistic basis for predicting the metal complexation properties of DOM. The basic approaches adopted in models of humic complexation differ in: 1) the number of metal binding sites (from a few to a continuous distribution), 2) the use of model ligands to predict pKa's or the relative affinities for different metals of the binding sites (carboxylic, catecholic, and picolinic moieties have been used), and 3) the inclusion of an electrostatic binding term (which may assume a particular geometry, a Donnan phase, or not be used at all). All have been applied with some success for different purposes, but the more empirical multiple-ligand approaches are more often used in modeling environmental systems because of their simplicity and ability to fit a wide range of data.

In some water bodies, synthetic ligands are present at high enough levels to influence metal speciation. One synthetic ligand, EDTA (ethylenediaminetetraacetic acid) is widely used in industry and consumer products to control metal speciation and has been found at concentrations in excess of 10 μM in municipal sewage effluent [3]. Because its microbial degradation in the environment is slow, rivers receiving EDTA-containing effluent have been observed to contain EDTA at 0.2 to 0.6 μM levels. Since its concentrations exceed those of some metals and because it has such a high affinity for many metals, EDTA should significantly influence metal speciation in these systems.

Finally, aquatic microorganisms are known to produce strong organic chelators for iron (siderophores) as well as copper. Microbial iron chelators are well studied in experimental systems, but there is little direct evidence of their presence in surface waters. However, it is quite likely that microbes produce the strongest iron-binding ligands observed in marine systems [7]. Recent experimental work has also shown that marine cyanobacteria produce copper-chelating ligands in direct proportion to the amount of copper added to their growth medium [8]. Freshwater cyanobacteria are also known to produce Cu chelators [9]. These findings suggests that these organisms are able to regulate the ambient speciation of iron and copper to some degree, which as we discuss next, influences both the nutrition and the toxicity of metals to the organisms.

Sorption by Abiotic Particles. Metals' interactions with abiotic particles can be an important, often dominant, component of particle-water partitioning. Adsorption onto inorganic particles is generally modeled using some kind of surface complexation model [10], which represent the adsorption of metals as having both an electrostatic and coordinative component. Dzombak and Morel's [11] application of this approach to adsorption on ferric oxide particles is notable for its consistent analysis of a wide set of experimental data. Adsorption onto detrital organic matter is also of great importance in surface waters. Most approaches to modeling their metal binding properties are analogous to those used for dissolved organic matter. In one recent study, the surface complexation model was successfully used to represent adsorption onto river sediments that included diverse organic and mineral components [12].

Interactions with Aquatic Microorganisms. Metals dissolved in natural waters become associated with aquatic microorganisms (usually phytoplankton predominate quantitatively) via adsorption onto surfaces and intracellular uptake. Adsorption occurs via coordination of the metal ion by sites on the cell surface, which can be reasonably represented as an equilibrium reaction. Intracellular uptake generally occurs via facilitated transport (Fig. 3), which requires coordination by a cellular transport ligand either in solution (siderophores) or in a membrane-bound porter. In a few cases, uptake can involve passive diffusion of neutral metal complexes through membranes. In all of these processes, the speciation of the metal is critical in determining the rate of uptake and the ultimate metal content of the organisms.

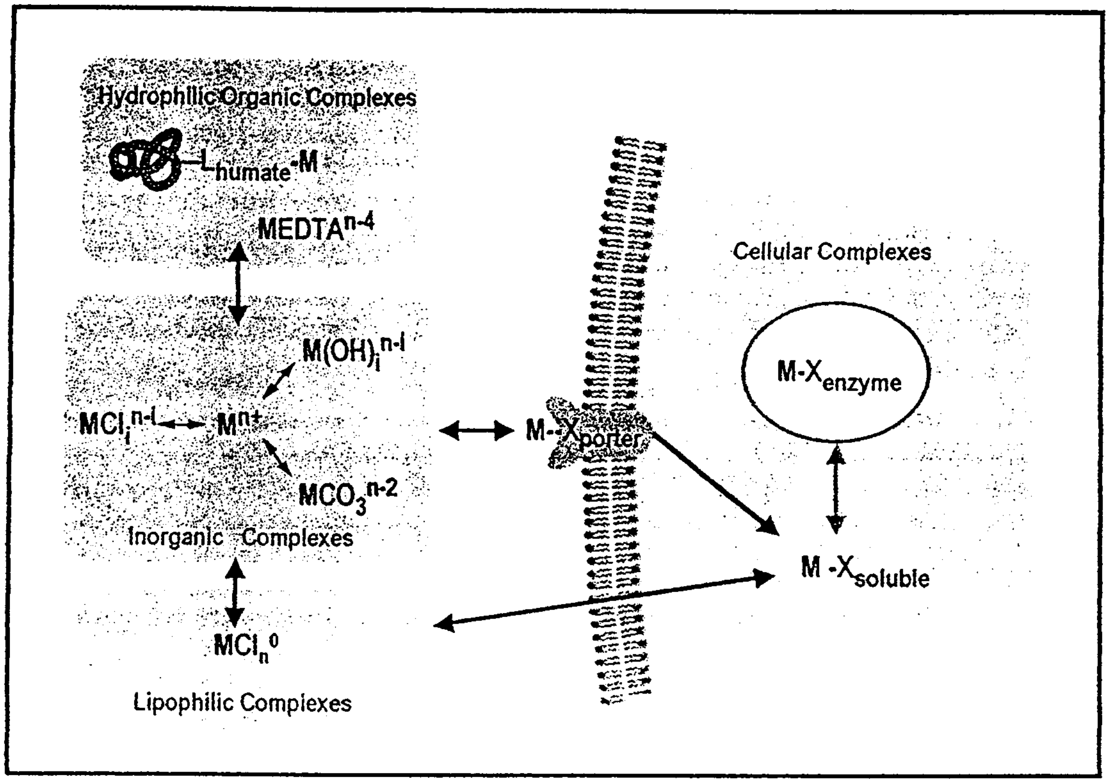

Figure 3. Schematic diagram illustrating the dependence of metal uptake by aquatic organisms on metal speciation. Lipophilic complexes can diffuse directly through membranes. Common inorganic species react at rapid rates with porter sites (X_{porter}), while organic chelates typically react slowly.

The dominant conceptual model that has been applied to the study of metal uptake by aquatic microorganisms is often referred to as the "free ion model" [1]. According to this model, dissolved metals in solution are at equilibrium with porter sites in the cell membranes of aquatic organisms. At equilibrium, the fraction of porter sites that are bound to metals is controlled by the free metal ion concentration. It follows, then, that the rate of metal uptake would exhibit a Michelis-Menten type dependence on free metal ion concentrations. This model has been widely applied to model the influence of organic complexation on metal uptake observed in experimental studies. It has also been used to explain toxic metal effects, including the competitive inhibition of essential metal uptake and/or utilization by toxic metals. The number of natural systems to which it has been applied is rather limited. For example, Sunda [13] has shown that natural DOM can modulate Cu^{2+} toxicity. However, Parent et al. [14] found that Al complexation by natural DOM did not have the expected effects on phytoplankton growth due to the natural DOM's ability to act as an additional P source.

Other complications to the free ion model include the finding that reaction kinetics rather than equilibria can control uptake rates. This was observed to occur when the turnover of iron bound to porter sites was fast enough that equilibrium was not attained with respect to iron species in solution

[15]. An additional complication of the free ion model has been posed by recent work showing that phytoplankton are capable of reducing chelated Fe [16]. Finally, if transport rates to microorganisms approach the physical limits posed by diffusion, the apparent controlling species can differ from the species that actually control binding at the transport sites. These complications of the free ion model suggest that the mechanistic approach to modeling metal uptake needs to be carefully applied on a case by case basis.

MODELING FIELD DATA

In this final section, several cases where mechanistic concepts or models have been applied to the analysis of field data are examined. Although they differ considerably, in each the aqueous speciation of metals was considered explicitly. Together, they illustrate how speciation modeling can succeed for the purpose of making predictions that are not otherwise possible with empirical models.

Organic Complexation: An elegant effort to test their ability to isolate and model the key components responsible for organically-chelating metals was conducted by Breault et al. [3]. They compared the copper speciation measured from titrations of whole water samples (Fig. 2) to model results based on measurements of Cu-binding by the humic acid fraction of DOM (extracted at low pH using a hydrophobic resin), of EDTA concentrations, and of the concentrations of competing metals (Fig. 4). The comparison is remarkably good and what discrepancies there are may largely result from not accounting for the slow kinetics of EDTA metal-exchange reactions needed to fully reach equilibrium. The results are encouraging for further efforts to model the speciation of metals in natural waters in a mechanistic fashion.

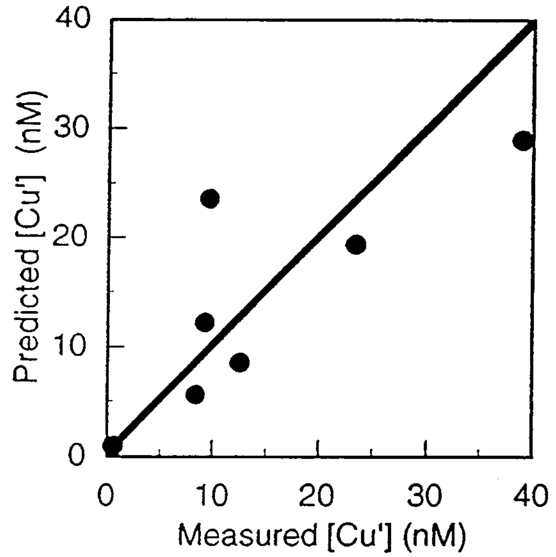

Figure 4. Comparison of observed and modeled inorganic Cu concentrations, [Cu'], for northeastern United States rivers containing natural DOM and EDTA. [3]

Metal Cycling in the Ocean: Oceanography has been in the forefront of the recent advances in clean sampling protocols and sensitive analytical techniques for trace metals. The profiles of metal concentrations in the oceanic water column record an integrated history of the biologically-mediated uptake and regeneration cycle of metals and the mixing processes that transport them. Coupled with recent data on the organic complexation of metals in the ocean, Sunda and Huntsman have shown that the Zn [17] and Cu [18] content of oceanic phytoplankton measured both directly and implied from metal to phosphate ratios in oceanic concentration profiles are consistent with laboratory studies of the metal contents of phytoplankton only when organic complexation of these metals is taken into account in both the laboratory and natural marine systems. These results suggest that metal uptake and regeneration by phytoplankton is the primary process controlling metal concentrations in the upper water column of the open ocean. This fact is consistent with phytoplankton growth being the major source of particulate matter in these waters.

Monomethylmercury Uptake by Freshwater Plankton: The level to which mercury accumulates in fish varies greatly, even among lakes receiving similar input fluxes. In some otherwise pristine systems, mercury levels exceed health standards while in others they are quite safe. Although several factors contribute to these differences, one of them certainly is the partitioning of mercury into the microorganisms at the lowest level of the food web, since this is where the initial transfer from the aqueous phase occurs. pH and DOM concentrations have been correlated with fish mercury, but the causal linkages have not been established.

Since in excess of 95 percent of the mercury in fish is monomethylmercury, it is the bioaccumulation of this compound (CH_3Hg^+) that is of greatest concern. Although it is well established that methylmercury can be taken up via passive diffusion of neutral CH_3HgCl^0 (and CH_3HgOH^0 to a lesser extent), it is not known whether other mechanisms of uptake are involved. Using the mechanistic principles outlined above, a set of high quality field data from several lakes were analyzed [19]. Significant organic complexation of CH_3Hg^+ was suggested by the inverse relationship of methylmercury bioconcentration factors for fish and DOM (Fig. 5). But the expected dependence was not observed in particle-water partition coefficients for CH_3Hg^+, where the effect should be most direct.

At the time of the study, complexation of methylmercury by DOM had not been quantified. However, because of the direct influence of organic complexation on partitioning, it was possible to calculate the strength of organic ligands needed to obtain a good fit to the empirical partitioning data given an assumption of the mechanism and controlling species for biotic uptake and/or adsorption on detritus. Adsorption onto iron oxides was not a significant. Models of partitioning that did not account for uptake by microorganisms did not fit the data well either. The best overall fit to the data was obtained with by assuming that organic complexation of CH_3Hg^+ was moderately strong (72-97 % compelxed) and that a combination of facilitated and passive uptake caused a much greater accumulation in living plankton relative to detritus. The lack of relationship between K_P and [DOM] resulted from a negative correlation of living plankton biomass and [DOM]. Subsequent reports of CH_3Hg^+ complexation by weak binding sites in DOM agree reasonably well at pH 6.5 [20]. While this approach cannot prove, what the operative mechanisms for methylmercury uptake are, it does illustrate how modeling can be used to test our experimental knowledge and point towards improvements.

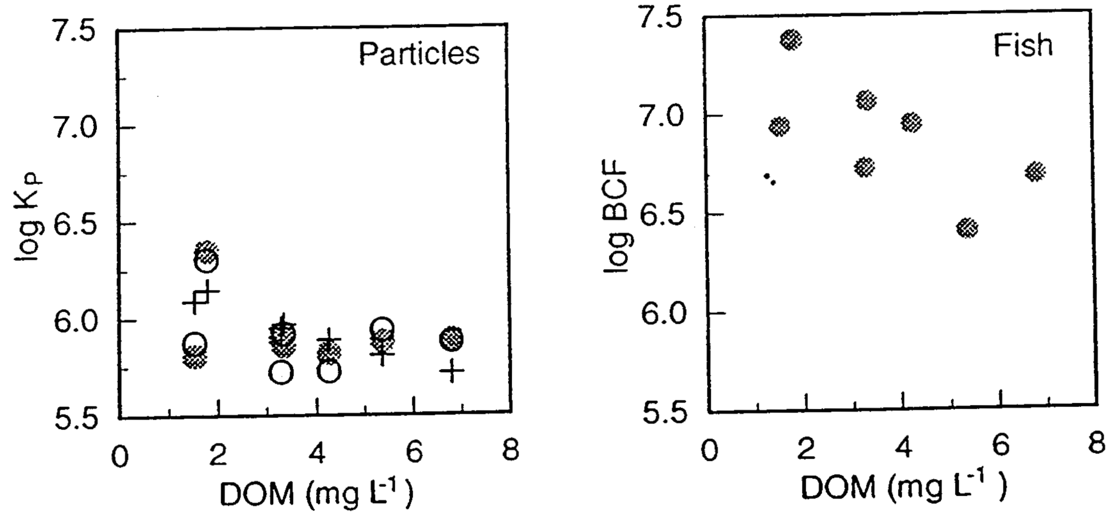

Figure 5. Influence of natural dissolved organic matter (DOM) on monomethylmercury bioaccumulation in 7 Wisconsin, USA seepage lakes. K_P is defined in equation 1 and BCF is the ratio of MMHg concentrations in fish (dry wt.) to that in water. Both have units of L kg^{-1} . Symbols are: field data (●), modeled values with live phytoplankton+detritus (O), and modeled values with detritus

only (+). DOM derived from 2 × [DOC].

CONCLUSIONS

Much progress has been made in developing a theoretical and experimental basis for fully mechanistic models of the particle-water partitioning of metals in aquatic systems. In addition, environmental analytical chemists are now able to accurately quantify low natural metal concentrations and their complexation by natural dissolved organic matter. We have seen that some recent studies have demonstrated a good agreement between the mechanistic models and environmental data. However, significant challenges to mechanistic modelers remain in the large number of unknowns and the degree of variability in aquatic systems. These challenges mean that a significant amount of site-specific data are still required and that partially empirical approaches remain necessary. It is my hope to that this brief review stimulates further advances by environmental chemists on these scientifically interesting problems and inspires further application of basic chemical insights in environmental models used for solving problems of practical importance.

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