METAL-ORGANIC BINDING: A COMPARISON OF MODELS
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1. INTRODUCTION

A model for metal-DOM speciation in oceans and other environments must reflect the complex nature of DOM. The simplest possible model assumes a single binding site, 1:1 stoichiometry and no interactions between sites but is inappropriate for most samples of DOM (Gamble, et al., 1980; Perdue and Lytle, 1983a). More complex models proposed for metal-DOM binding include assumptions of electrostatic interactions between sites (Wilson and Kinney, 1977), variable stoichiometry (Buffle, et al., 1977), a continuous, Gaussian distribution of binding constants among sites (Perdue and Lytle, 1983a) and a continuous distribution of binding constants of unknown form (Gamble, et al., 1980; Shuman, et al., 1983). Data analysis methods proposed for other binding systems (Scatchard, 1949; Gordon, 1979) can also be used to analyze metal-DOM equilibria.

The complexity of the DOM and its low concentration lead to analytical and theoretical problems. A model may fit very well a wide range of experimental data, but unless it fits well at environmental conditions, which are usually those of low \( \bar{\nu} \) (bound metal concentration/total ligand concentration) it is of questionable use for metal-DOM speciation. Extrapolations from high \( \bar{\nu} \) to low \( \bar{\nu} \) are unreliable (Saar and Weber, 1979; Gamble, et al., 1980); thus, the availability of good experimental binding data at environmental levels and below is extremely important. Even a model which fits low \( \bar{\nu} \) data well, though useful, will not substitute for sensitive analytical techniques.

The most general, rigorous model of metal-DOM binding is

conceptually straightforward, but very complex in practice. Each different binding site requires a set of acidity constants, a series of complex formation constants, $\beta_j$, and terms correcting them for interactions between sites. Each possible grouping of sites which could bind to a single metal ion requires a mixed-ligand stability constant. The number of parameters necessary to describe a five or six component system is quite large (Byrne, 1983), and greatly exceeds the number of data points in typical titrations (15-40). Clearly this type of model is unsuitable for data analysis.

Models in current use represent a compromise between rigor and practicality. Proton competition terms are unnecessary if measurements at constant pH are used to obtain conditional constants. Although not rigorously correct, certain assumptions about stoichiometry, interactions and the number of sites simplify the data analysis considerably. Models using some of these assumptions with three or more parameters often fit the data much better than the simple single-site model. This improved fit has been cited as supporting evidence for these models (Buffle, et al., 1977; Wilson and Kinney, 1977).

Goodness-of-fit criteria alone cannot justify these assumptions, however; several models with contradictory assumptions can curve-fit metal-DOM binding data (see below).

Any comparison of models must include the following important considerations:

1. Chemical correctness - What are the assumptions and are they reasonable? Can the model be used to think intuitively about metal-DOM chemistry?

2. Accuracy - Does the model fit the data within experimental error? Are the important data points at low saturation well described?

3. Simplicity - Is the data analysis readily reproducible by other workers? Are the resulting parameters useable with equilibrium speciation programs, e.g. REDEQL, MINEQL, etc.?

The purpose of this paper is to review critically the models that are presently used with metal-DOM binding data and to