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Improving and testing geochemical speciation predictions of metal ions in natural waters

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ABSTRACT

The ability of WHAM VII and NICA-Donnan models to predict free-ion activities of Cu in natural waters was examined from two perspectives, (i) the presence of EDTA and NTA contaminants, (ii) the need to improve estimates of HA and FA concentrations. Potentiometric responses of a Cu(II) ion-selective electrode were investigated in five assays containing dissolved organic matter (DOM) isolated from a series of polluted (urban) and relatively unpolluted (upland) streams in northern England. The [Cu]/[DOC] ratio in these assays spanned an environmentally realistic range of ~1–500 μmol/g. Reasonably good agreement between measured and predicted Cu^{2+} activities was obtained with both WHAM VII and NICA-Donnan models, assuming 65% of DOM as fulvic acid and including the measured EDTA and NTA concentrations, but generally the models overestimated the activities by a factor of ~2. In contrast, the models over-predicted the Cu^{2+} activities by up to 2 orders of magnitude at low [Cu]/[DOC] ratios in urban waters if anthropogenic ligands were not included in the model simulations. Three-dimensional fluorescence excitation –emission matrix (EEM) spectroscopy was used to measure the functional properties of the isolated DOM and to estimate the fractions of FA and HA present. Using these fractions in the models gave improvements in predictions compared to the 65% FA assumption, as shown by higher correlations, reduced error and reduced bias. These results highlight various issues with the use of the available speciation models for predicting free ion concentrations in natural waters, such as the use of the Biotic Ligand Model (BLM) for the derivation of environmental standards. It is clearly necessary to measure EDTA and NTA in waters with urban influences, while fluorescence measurements offer the possibility of appreciably improving the accuracy of predictions.

1. Introduction

Aquatic chemists have long recognised the importance of chemical speciation in elucidating elemental bioavailability and ecotoxicological significance. The early studies on metal uptake by biota gave rise to the free ion activity model (FIAM) (Morel, 1983; Campbell, 1995) and the biotic ligand model (BLM) (Playle, 1998). Both models considered free ions as the most important species because of their interactions with

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dissolved ligands and the membrane surfaces of biota. As metal bio-uptake, biological responses and toxicity are dependent on metal speciation, it is desirable to be able to measure and predict the free ion activity of a metal and all its 'labile' (or available) species in aquatic systems.

The concentrations of 'free' and labile metal species are regulated by a complex mixture of competition reactions between dissolved inorganic ligands, monomeric organic ligands, dissolved organic matter (DOM) and reactive colloidal and particulate surfaces. Metal complexation reactions at circumneutral to alkaline pH are dominated by the binding of metal ions to DOM. Aquatic DOM comprises complex, heterogeneous associations of organic compounds exhibiting different water solubilities and chemical reactivities (Tipping, 2002; Sutton and Sposito, 2005). The 'reactive' fraction of DOM consists of molecular components that carry a large number of complexing functional groups (such as phenols, carboxylates, thiols and amines). This 'reactive' DOM fraction is dominated by humic substances (HS), comprising humic and fulvic acids, and these play a major role in determining metal speciation in aquatic and terrestrial environments. Metal binding by HS occurs at high or low metal affinity sites, depending on the ambient metal:DOC ratio. High affinity sites are usually associated with phenolic groups whereas carboxylic groups host low affinity sites (de Wit et al., 1993; Kinniburgh et al., 1999; Benedetti et al., 1995). The total charge on the humic molecule and its sorptive properties are dependent on pH. At low pH, the functional groups are protonated and uncharged but as pH increases the molecule becomes more negatively charged. Charged humic molecules in solution develop a diffuse double layer, with the extent to which it screens the charge being dependent on ionic strength (Benedetti et al., 1996).

Numerous models have been developed to describe the electrostatic and specific interactions between the charged HS and ions. Among the most reliable and well-tested models that describe ion binding to humic substances are WHAM (V–VII) (Tipping et al., 2011; Tipping and Hurley, 1992; Tipping, 1994, 1998) and NICA-Donnan (Kinniburgh et al., 1999; Koopal et al., 2005; Kinniburgh et al., 1996). Both models are equilibrium-based and have been shown to provide adequate description of metal binding to DOM in various natural environments. The two models contain a large number of parameters to account for electrostatic interactions, competition, heterogeneity and variable reaction stoichiometry and have been calibrated using similar sets of published metal-binding data (Milne et al., 2001; Koopal et al., 2005). While both models adopt the Donnan volume concept, they differ slightly in its implementation. The WHAM model assumes a Donnan phase surrounding the charged humic macromolecule and containing only positively charged counterions. The electrostatic effect on ion binding is calculated using an empirical Boltzmann factor (Tipping and Hurley, 1992; Christensen et al., 1998; Benedetti et al., 1995). The NICA-Donnan model assumes an electrically neutral humic particle and uses an empirical relationship relating Donnan volume and ionic strength (Benedetti et al., 1995; Koopal et al., 2005; Kinniburgh et al., 1996). The two models employ different approaches in dealing with chemical heterogeneity and variable stoichiometry. Whereas the distribution of the affinity of the carboxylic and phenolic sites is treated as a discrete distribution in the WHAM model, the NICA-Donnan describes ion affinity using a continuous distribution following a Sips-type function.

Although the WHAM and NICA-Donnan models have been shown to successfully predict proton and metal binding to purified HS isolated in the laboratory, the situation is less clear with natural aquatic and terrestrial systems (Groenenberg et al., 2010; Doig and Liber, 2007; Baken et al., 2011). Agreement between in situ measurements and model predictions of free-ion concentrations is currently only within an order of magnitude for Al, Co, Zn, and Cd, and two orders of magnitude for Cu and Pb (Lofts and Tipping, 2011). Hamilton-Taylor et al. (2011) identified a number of uncertainties and various factors that may contribute to these discrepancies, including both modelling and analytical issues. One of the key uncertainties identified was whether isolated humic fractions, used to calibrate the models, are truly representative of freshwater DOM, since it has been suggested that the harsh pH conditions used during the isolation process may alter the metal binding properties of the DOM (Tipping, 2002). However, Ahmed et al. (2013) recently developed a protocol that combined a mild DOM isolation procedure with laboratory measurements of free-ion activity, using a well-proven and reliable analytical method (ion selective electrode). The protocol was applied to a series of humic-dominated headwater streams at environmentally realistic metal:DOM ratios. The results showed excellent agreement between speciation measurements and modelling, thus excluding the possibility that the harsh DOM-isolation conditions yield unrepresentative material for model calibration. Another important factor identified by Hamilton-Taylor et al. (2011) is the potential effect of unspecified ligands, particularly anthropogenic ligands in contaminated waters. The main aim of the present work therefore was to use the protocol developed by Ahmed et al. (2013) to assess the fidelity of model predictions in a range of water-types, including lowland waters impacted by agricultural, urban and industrial inputs.

A further modelling uncertainty is due to the usually unknown fraction of DOM comprising humic substances. In the absence of specific measures of humic concentrations, assumptions are made about their fractional contents. A standard assumption is that DOM comprises 65% fulvic acid and 35% inert HS material (Bryan et al., 2002; Lofts et al., 2008). The current availability of spectrofluorometric tools such as fluorescence spectroscopy allows for rapid characterisation of DOM and yields direct insights into DOM quality and composition (McKnight et al., 2001; Weishaar et al., 2003; Fellman et al., 2009). With Excitation–Emission Matrix (EEM) spectroscopy, DOM composition can be analysed by measuring the fluorescence emission over a range of excitation wavelengths. Each EEM dataset can be reduced into a number of building blocks reflecting the various DOM components. Thus, the second aim of this study was to determine whether WHAM and NICA-Donnan model predictions could be improved by incorporating fluorescence-spectroscopy measurements of DOM quality. Mueller et al. (2012) have recently provided direct evidence that fluorescence measurements have the potential to be used for this purpose.