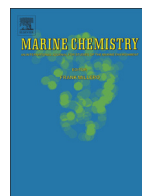




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The effect of natural organic ligands on trace metal speciation in San Francisco Bay: Implications for water quality criteria

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ABSTRACT

Speciation affects bioavailability, the latter of which is a prerequisite for toxic effects. At present, a recognized shortcoming in some speciation models is inadequacies in the specification of interactions between trace metals and natural organic matter in some environmental settings. In particular, naturally occurring organic ligands, which are referred to as strong metal-binding ligands, are often neglected in speciation calculations. This work utilizes a recently developed approach to the determination of ligand concentrations and conditional stability constants for strong metal-binding ligands to characterize strong copper (Cu)-binding ligands in San Francisco Bay, a complex multi-reach estuary with site-specific environmental variability. We find that increased precision in ligand concentrations and conditional stability constant parameters enables the differentiation of ligand signatures, and multivariate analysis shows that ligand signatures vary consistently with expectations from seasonal and geographical changes within the bay. We also use the parameters in speciation calculations to assess what effect site-specific characterization of organic matter might have. While all speciation calculations indicate that the majority of Cu is bound to organic matter, when strong metal-binding ligands are included, for all sites the majority of Cu is bound to strong Cu-binding ligands. This shift in speciation has important implications for bioavailability and toxicity, which we address with the biotic ligand model (BLM), a U.S. EPA speciation-based mechanistic model to develop water quality criteria that is not yet fully extensible to estuarine and marine environments. We find that the toxicity predicted to *Mytilus* sp. in the presence of strong Cu-binding ligands is significantly less than in BLM default calculations, consistent with a BLM bias previously reported for San Francisco Bay. The approach taken here is generalizable to many metals and natural aqueous systems, most speciation models, and, with respect to the BLM, any biological species for which the model is used.

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1. Introduction

Bioavailability is strongly mediated by geochemical conditions and has been increasingly recognized as important for understanding the ecological impacts of trace metals (Hill, 1997; Morel and Price, 2003; Worms et al., 2006). Metals such as Cu and Fe are essential micronutrients to marine phytoplankton and hence affect primary productivity in many open ocean regions, which in turn affects the global carbon cycle (Fennel et al., 2003; Sunda, 2012). Conversely, metals such as Cu and Pb can be toxic and are increasingly the subject of contaminated site investigation and remediation (Fairbrother et al., 2007; He et al., 2005; Hill, 1997). Some trace metals potentially serve as either nutrient or toxicant, the gap between which can be narrow,

and elevated metal concentrations impact intolerant species, thus consequently the diversity and trophic structure of biological communities (Nadella et al., 2009, and references therein). In this context, bioavailability is a function of chemical speciation and can be thought of as a key intermediate controlling the relationship between concentration and biological effects, including toxicity.

It is well known that both inorganic and organic constituents of environmental samples can strongly affect the speciation, and thus bioavailability, of metals (Morel and Hering, 1993; Schwarzenbach et al., 2002; Turner et al., 1981). For aqueous environments most inorganic substances of importance are known, have a specific chemical structure, are readily analyzed, and have metal binding affinities that have been characterized (Morel and Hering, 1993; Turner et al. 1981). In contrast, organic substances are often generically grouped under the heading of dissolved organic carbon (DOC). In aqueous environmental settings, DOC occurs as a spectrum of different species, many of which may not have a specific chemical formula (Schwarzenbach et al., 2002). As such, the metal binding capacity of different DOC fractions is highly variable in the environment (Town and Filella, 2000) and, unlike inorganic substances, is often not well characterized. Important components of DOC

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are humic and fulvic acids (humic substances), and two commonly used models to describe metal complexation by humic substances are the Windermere Humic Aqueous Model (WHAM, Tipping, 1994) and the Stockholm Humic Model (SHM, Gustafsson, 2001). These models do not inherently account for the so-called organic strong metal-binding ligands, denoted as L_i , and the addition of site-specific parameters that describe such ligands would thus augment the WHAM and SHM approaches to describe metal binding with DOC.

The research community has recently refocused on the determination of metal–ligand binding parameters as part of international programs such as GEOTRACES (www.geotraces.org) and the Scientific Committee on Oceanic Research Working Group 139 (Sander et al., 2012). As a consequence, several new or revised approaches to calculate the binding parameters of metals in fresh and seawater have been published and/or made open accessible (Gerringa et al., 2014; Hudson, 2014; Omanovic (in this issue); Sander et al., 2011; Wells et al., 2013). We have recently made advances in estimating the metal complexation parameters of L_i , wherein competitive ligand exchange/adsorptive cathodic stripping voltammetry (CLE/AdCSV) data was used in conjunction with an automated numerical optimization process (Sander et al., 2011; Pižeta et al., this issue). Parameters obtained include conditional stability constants, K'_i , and total ligand concentrations, $[L_{iT}]$, for each ligand class, i (where i is operationally defined according to binding strength). This approach, referred to as the Sander–Wells method (Sander et al., 2011; Wells et al., 2013), in comparison to others in common use (outlined in Wells et al., 2013) is automated, obviates systematic user bias (e.g. subjective assessment of outliers), provides substantial improvements in accuracy and precision, is capable of describing any number of discrete naturally-occurring ligand classes, simultaneously generates site-specific parameters needed to enhance modeling of metal–DOC interactions, and can be used at environmentally relevant concentrations, unlike some approaches (see Sánchez-Marín et al., 2010). Of specific interest here, parameters obtained from the Sander–Wells (S–W) method enable inclusion of calculations for metal– L_i complexation in speciation models. By including L_i s in speciation calculations, we can test the hypothesis that the presence of L_i s in natural aqueous samples substantially affects the overall distribution of metal speciation.

A speciation model that includes expressions to describe metal complexation with critical biological ligands is the Biotic Ligand Model (BLM). A biological or biotic ligand is a specific receptor within an organism for which complexation by a metal can lead to acute toxicity (Di Toro et al., 2001). Since the total concentration of biotic ligands in the water column is vanishingly small, compared to many other constituents, most speciation models neglect biotic ligands. In BLM calculations, all species concentrations for a metal of interest are determined, including metal–biotic ligand complexes. The BLM was developed as an efficient computational alternative to conducting toxicity tests (Di Toro et al., 2001; U.S. EPA, 2003a and 2003b), and obtaining the concentration of metal–biotic ligand complexes allows a more explicit way to understand biological effects. Many studies have demonstrated that there is a direct relationship between the metal–biotic ligand complex and toxic response (DiToro et al., 2001; Paquin et al., 2002); as a result, the BLM is now calibrated for different metals and biological species (Niyogi and Wood, 2004; Slaveykova and Wilkinson, 2005). In many cases the BLM predicts toxicity sufficiently well that BLM-based water quality criteria (WQC) are in common use (US EPA, 2007 and 2003a). Software used for performing BLM calculations includes HydroQual's BLM Windows Interface and Visual MINTEQ (Gustafsson, 2010; HydroQual, 2014). Both may be used to calculate the total metal concentration that will result in an effect, such as EC_{50} , for a given water composition.

A metal may be prevented from binding with a biotic ligand by the presence of inorganic and organic ligands that themselves complex with the metal of interest. Such competing complexation changes the metal speciation, and may serve to reduce metal bioavailability and

hence toxicity. As noted above, metal complexation with inorganic constituents in the water column is relatively well understood. To account for the complexation of trace metals with natural organic matter, either the WHAM or SHM are typically employed in BLM calculations. Both models use a single set of parameters to universally describe metal–DOC interactions, which the USEPA (USEPA, 2003b) has specified as a default approach to BLM calculations. It is widely recognized that for trace metals the “important need at present is to derive adjustment factors for the very different protective abilities of different types of DOM [dissolved organic matter]” (Niyogi and Wood, 2004). As an example, in a study of Cu toxicity to *Mytilus* sp., Arnold et al. (2005) have documented a DOC-dependent systematic bias between observed and BLM-predicted toxicity for estuarine and coastal waters, and they conclude that “the difference is likely due to errors in the BLM treatment of DOC”. Since the BLM is essentially a variation on speciation calculation, this implies errors in the fundamental calculation that determines how much, and how strongly metals bind to DOC (Arnold et al., 2009 and 2005; Niyogi and Wood; and references therein).

At least three approaches relevant to the present work, and to the BLM, for refinement of metal–DOC binding in speciation calculations have thus far been described. One approach uses an analytical expression, with fitted parameters from actual toxicity observations, to empirically correct for the bias (Arnold et al., 2009 and 2005). This approach is entirely empirical and makes no assumptions regarding the underlying causative factors. A second approach is another empirical work that proposed alteration of a scaling term in the SHM to increase high affinity metal binding sites based on fitting of voltammetric data (Ndung'u, 2012). As with the first approach, this implicitly addresses the potential inadequacy of using one set of default settings to describe metal binding with humic substances, when the characteristics of the latter vary in natural environments. However, all variability in DOC is fundamentally inferred, with no delineation of different DOC fractions or their contributions to speciation. Demonstrating a third approach, Sánchez-Marín et al. (2010) used anodic stripping voltammetry to obtain K'_i and $[L_{iT}]$, parameters that are required by the BLM. The approach in this third work acknowledges that the ab initio decision to develop the BLM was based on the idea that mechanistic approaches, once appropriately formulated, hold greater promise than empirical approaches for use as fully generalizable models. Though L_i are typically a small part of DOC, the work of Sánchez-Marín et al. (2010) suggests that they are nonetheless important, as their concentrations correlated very well with measured toxicity. These authors noted that future efforts would benefit from use of environmentally relevant concentrations.

Here, we use the S–W method to determine a set of parameters that describe metal complexation with L_i for a series of environmental samples from San Francisco Bay. The area is a polluted estuarine environment having sufficient geochemical variability between sample sites to manifest variability in the characteristics of the L_i present (Buck and Bruland, 2005; Wells et al., 2013). Such variability is useful to test the potential importance of site specificity in speciation. The resulting parameters are first evaluated with respect to solution quality, which is important in assessing the feasibility of developing ligand signatures. Next, the influence of geochemical setting on site-to-site variability is discussed, followed by an examination of how ligand signatures vary with geochemical setting in a site-specific way. Subsequently, we incorporate ligand parameters in speciation models and examine how this affects metal speciation. Lastly, we explore how the effect of L_i s on speciation propagates to BLM predicted toxicity for the case of Cu toxicity to *Mytilus* sp. *Mytilus* sp. is a commercially important organism (Arnold et al., 2009) that is one of the most sensitive marine species to Cu (Grosell et al., 2007), and Cu is a marine contaminant of increasing prevalence and regulation (State of California, 2010). Using Cu as test case here is further useful since Cu was the metal that was used in initial development of the BLM (U.S. EPA, 2007; 2003a and 2003b), and hence biotic ligand parameters for Cu have been developed and are available (particulars are given below). Also, most of Arnold et al.'s prior work

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