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Effect of major ions on the toxicity of copper to *Hyalella azteca* and implications for the biotic ligand model

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Abstract

The effect of major ions (Ca, Mg, Na, and K) and pH on Cu toxicity (LC50) to *Hyalella azteca* was determined in 1 week exposures. The simplest equation for describing Cu toxicity is a linear relationship between the total dissolved Cu LC50 and Ca and Na in water, ignoring pH. This equation would be useful in tier one of a two-tiered approach; if the measured dissolved Cu exceeds the value predicted from the equation, the sample should either be tested for toxicity, or a more detailed chemical speciation analysis can be conducted. The data were not consistent with a single-binding-site biotic ligand model, assuming that toxicity was due to the free Cu ion alone. However, toxicity could be predicted using a two-binding-site model. This requires separate coefficients to account for the effects of Ca and Na at low and high pH values (6.5–8.4), corresponding to the different binding sites (Mg and K did not affect toxicity). The single-binding-site BLM does not allow for this. Toxicity of Cu hydroxide or carbonate complexes does not need to be invoked, but cannot be excluded, and several models invoking the toxicity of these complexes can also explain the data. The free ion LC50 is strongly dependent on pH, but the LC50 for total dissolved Cu is almost pH independent. The effects of Ca and Na on the free ion LC50 are very different at high and low pH (contrary to single-site biotic ligand model predictions), but similar for total dissolved Cu. Published data suggest that the same model, with different coefficients, can also be applied to *Daphnia* and fish. A more critical evaluation of the effects of cations at both low and high pH for organisms other than *Hyalella* is needed to determine if the BLM needs to be adjusted to incorporate more than one binding site for other species as well. Hydrogen ions reduce the toxicity of free Cu ions to *Hyalella*, but Cu also reduces the toxicity of hydrogen ions. A mixture model accounting for the joint toxicity of Cu and pH, as well as their mutual antagonistic effects, is presented.

Keywords: *Hyalella*; Copper; Biotic ligand model; pH; Calcium; Sodium

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1. Introduction

It is well established that the toxicity of metals to aquatic biota is a function of water chemistry. For example, Ca, Mg, Na, pH, and dissolved organic carbon (DOC) have all been shown to affect the toxicity of copper (Niyogi and Wood, 2004 and references therein). This makes it difficult to determine when a metal is causing detrimental effects based on environmental metal concentrations alone. One way of circumventing this problem is to describe toxic effects relative to the amount of metal accumulated by the organism, rather than metal in water or sediment. For example, Cd, Ni, or Tl toxicity to the freshwater amphipod *Hyalella azteca* expressed on a lethal body concentration basis is much less variable than toxicity expressed relative to metal concentrations in water or sediment (Borgmann et al., 2004). This approach does not, however, work well with all metals or for all organisms. Concentrations of copper in *Hyalella* are physiologically regulated. They do not drop below about 1 μmol/g, even in the presence of strong chelating agents (Borgmann and Norwood, 1995) and, unlike other metals such as Cd, Co, and Ni, concentrations of Cu in *Hyalella* do not vary over a relatively wide range of Cu in the environment (Borgmann et al., 2001). This makes it necessary to describe the toxicity of Cu to *Hyalella* as a function of Cu concentrations in water, which requires an understanding of the effects of water chemistry on toxicity.

The purpose of this study was to determine the effect of major ions and pH on the toxicity of Cu to *Hyalella*. Since much of the research on metal toxicity, and the toxicity of Cu in particular, is now being interpreted using the biotic ligand model (BLM, Di Toro et al., 2001; Paquin et al., 2002), this was used as a starting point for modelling toxicity. Several versions of the BLM have been published, including a BLM for fish and several for *Daphnia*; the latter include models extrapolated from the BLM for fish and models developed using data exclusively from tests with *Daphnia* (see, Niyogi and Wood, 2004 for review). The BLM is currently being considered as a potential tool by regulatory agencies (Adams et al., 2002; USEPA, 2003), making it particularly relevant to determine if the BLM could be used to accurately predict Cu toxicity to *Hyalella*. We also test the utility of a multi-binding site model, where each site is treated similarly to the BLM, but with different coefficients for interactions between the various ions. Finally, because the low pH of some of the media used resulted in reduced survival, we also examine the interactive effects of Cu and pH toxicity.

2. Theory

2.1. Single-site biotic ligand model

As a first step (Eqs. (1)–(3)), the mathematical formulation for the traditional one-site BLM is presented. Although this appears complex when expressed in terms of stability constants and ligand concentrations (Eqs. (1) and (2)), the resultant formula for toxicity as a function of major ion concentrations is quite simple (Eq. (3)). In the BLM, originally applied only to acute toxicity (Di Toro et al., 2001), it is assumed that metal (M) binds to a ligand (L) somewhere on the surface of the organism. The total amount of metal bound to the ligand (ML) is given by:

$$[\mathrm{ML}] = \frac{K_{\mathrm{M}} \cdot [\mathrm{L_T}] \cdot [\mathrm{M}^{Z+}]}{1 + K_{\mathrm{M}} \cdot [\mathrm{M}^{Z+}] + K_{\mathrm{H}} \cdot [\mathrm{H}^{+}] + K_{\mathrm{H_2}} \cdot [\mathrm{H}^{+}]^2 + K_{\mathrm{Ca}} \cdot [\mathrm{Ca}^{2+}] + K_{\mathrm{Na}} \cdot [\mathrm{Na}^{+}] \ldots} \quad (1)$$

where $[\mathrm{L_T}]$ is the total (bound plus free) ligand ($[\mathrm{L_T}] = [\mathrm{L}] + [\mathrm{ML}] + [\mathrm{HL}] + [\mathrm{H_2L}] + [\mathrm{CaL}] + [\mathrm{NaL}] \ldots$) and K_{M} is the binding strength of the metal to L. K_{H}, $K_{\mathrm{H_2}}$, K_{Ca}, and K_{Na} are the binding strengths of competing ions for the same site, and $[\mathrm{M}^{Z+}]$, $[\mathrm{H}^{+}]$, $[\mathrm{Ca}^{2+}]$, and $[\mathrm{Na}^{+}]$ are the concentration of free metal, hydrogen, calcium, and sodium ions, respectively. Unlike most published versions of the BLM, two protonated forms of L are represented in Eq. (1), the more commonly identified HL complex and the double protonated $\mathrm{H_2L}$ complex. Other competing ions may also appear in the denominator (e.g., Mg^{2+} or K^{+}), and not all terms in the denominator will be important for all metals. The K values may represent true binding constants to external sites on the gill (e.g., Playle et al., 1993) or, when applied to chronic toxicity, they may represent composite terms, including initial binding to the external sites, rates of transport through the tissues, binding to the inside of the organism, and excretion.