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Review

The relationship between metal toxicity and biotic ligand binding affinities in aquatic and soil organisms: A review

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ABSTRACT

The biotic ligand model (BLM) is a theoretical, potentially mechanistic approach to assess metal bioavailability in soil and aquatic systems. In a BLM, toxicity is linked to the fraction of biotic ligand occupied, which in turn, depends on the various components of the solution, including activity of the metal. Bioavailability is a key factor in determining toxicity and uptake of metals in organisms. In this study, the present status of BLM development for soil and aquatic organisms is summarized. For all species and all metals, toxicity was correlated with the conditional biotic ligand binding constants. For almost all organisms, values for Ag, Cu, and Cd were higher than those for Zn and Ni. The constants derived for aquatic systems seem to be equally valid for soil organisms, but in the case of soils, bioavailability from the soil solution is greatly influenced by the presence of the soil solid phase.

1. Introduction

Zitko et al. (1973) and Zitko (1976) were the first to emphasize the importance of dissolved organic matter in mitigating the toxicity of metals to fish, and the effect of water hardness (Ca and Mg) to compete with the free metal ions for binding to the biotic ligand (BL) sites of the organism. Later, a chemical equilibrium-based model (FIAM, see below) was applied to explain the effect of water chemistries on the activity of free metal ions in the medium (Pagenkopf et al., 1974). These studies emphasized the importance of the free metal ion, thereby constructing the basic concept of the relationship between water chemistries and metal speciation for explaining metal toxicity to aquatic organisms. According to the free ion activity model (FIAM), toxicity is related to the concentration of metal present in the medium as a free metal ion species (Me^{n+}) (Morel, 1983; Campbell, 1995). Other cations such as Mg^{2+}, K^{+}, Ca^{2+}, Na^{+}, and H^{+} can compete with free metal ions to bind to the BL sites and thus decrease toxicity (e.g., Santore et al., 2001).

The gill surface interaction model (GSIM) was developed to assess toxicity of metals at the gill surface. The gills were assumed to represent the BL site of action in freshwater fish (Pagenkopf, 1983). This chemical equilibrium-based model considered both complexation of inorganic ligands with free metal ions and competition of other cations with free metal ions at the fish gill surface. In this model, toxicity of single and metal mixtures was considered. Playle et al. (1992, 1993a, b) used this model to explain the difference in gill metal accumulation over a range of water chemistries. Their results showed that cations in the solution compete for a limited number of binding sites at the gill surface, thereby affecting the degree of metal accumulation. They also evaluated binding site density of the gill and estimated the conditional binding constants for metal binding to the BL sites, which were then incorporated in chemical equilibrium-based models (Playle et al., 1992; Playle, 1998).

Campbell et al. (2002) revised the FIAM description to the point that “according to FIAM and its derivative BLM (see below), the biological response elicited by the metal will be proportional to M-X-Cell”. In this framework M-X-Cell is the complex of a metal with the biotic ligand. Chemical equilibrium-based biotic ligand models have been developed as a useful tool for predicting the effects of water chemistries on the bioavailability and speciation of metals in aquatic systems (Di Toro et al., 2001; Santore et al., 2001). Acute toxicity is the function of both metal affinity for the BL and the number of ligand sites on the organism's membrane occupied by the metal (Di Toro et al., 2001; Niyogi and Wood, 2004). BLMs explicitly consider metal speciation and competitive binding of protective cations to the BL sites (Di Toro et al., 2001; Niyogi and Wood, 2004).

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BLMs provide a quantitative framework for assessing metal toxicity over a range of hardness, pH and dissolved organic carbon (DOC) levels (Paquin et al., 2000). They predict metal accumulation and toxicity based on metal concentrations, competition, and complexation processes in solution. BLMs show how metal toxicity is mitigated by competition of the free metal ion with other cations for binding to the BL sites (Schroeder et al., 2010) and complexation of the free metal ion with organic and inorganic phases (Pagenkopf, 1983; Playle, 1998; Paquin et al., 1999; McGeer et al., 2000; Santore et al., 2001; De Schamphelaere and Janssen, 2002; De Schamphelaere and Janssen, 2004b; Gillis et al., 2010).

Regarding the main concept of the BLM and the site of action of metals (e.g., fish gill), the interaction of metals and other cations at the BL surface is very important for better understanding of metal toxicity in aquatic organisms. For this reason, Paquin et al. (2002b) developed a physiologically-based BLM to consider the effects of water chemistry factors not only on bioavailability and toxicity of metals to aquatic organisms, but also on the physiological status of the organism. The main BLM does not explicitly predict the physiological effects of metals on aquatic organisms and does not consider direct effects of water chemistry factors on their physiology. In the physiologically-based models, BL sites on the gill membrane (surface), having negatively charged proteins, are assumed the same targets as the other dissolved ligands (such as dissolved organic carbon) in solution for positive ions. These positive ions are the free metal ions and other cations. Moreover, electrical potential at the gill plasma membrane influences the activity of the free metal ion as well as its transport across the membrane of the organism, on which biotic ligands are available (Kinraide, 2006; Wang et al., 2011).

Originally, the BLM concept was developed to model acute toxicity of metals to aquatic organisms (McGeer et al., 2000; Di Toro et al., 2001; Santore et al., 2001; De Schamphelaere and Janssen, 2002; Paquin et al., 2002a; Heijerick et al., 2002a; Santore et al., 2002). In these studies, toxicity of different metals to fish and daphnid species and the influence of different water chemistries on metal toxicity was investigated. Acute BLMs were also developed for other organisms such as euryhaline crustaceans and green algae (Bianchini et al., 2004; Heijerick et al., 2002b). Hatano and Shoji (2010) emphasized that metal toxicity is strongly dependent on exposure time, which therefore should be considered in developing a BLM. Thus, chronic BLM models have been developed for predicting metal toxicity to aquatic organisms (Bianchini and Wood, 2002; McGeer et al., 2002; Brauner and Wood, 2002; Ward and Kramer, 2002). But, so far, chronic BLMs are not completely validated as a routine tool for predicting metal accumulation and toxicity (Schroeder et al., 2010).

A number of studies in the literature applied BLMs relating metal toxicity to accumulation in entire organisms or for instance, a specific organ (fish gill) as the site of metal accumulation. In the latter studies, toxicity is related to the metal accumulation in specific site of action of the organism. Few studies focused on metal accumulation at cellular levels and tried to link toxicity to the metal accumulation in cells. For instance, these studies considered application of BLMs to algae (e.g., Bell et al., 2002; Heijerick et al., 2002b; Campbell et al., 2002). Some studies have obtained indications that there may be different types of biotic ligands, e.g. high and low-affinity ligands, which may have different contributions to metal uptake and possibly also to metal toxicity (e.g., Niyogi et al., 2008). These findings do need further investigation, for different organisms and also for different metals.

In addition to BLMs applied for aquatic organisms, BLMs have been developed to predict metal toxicity to organisms living in sediment and soil. For sediment, few BLMs are reported in the literature (e.g., Ankley et al., 1996). For soil, already several terrestrial BLMs (t-BLMs) have been developed for predicting toxicity of metals (e.g., Steenbergen et al., 2005; Antunes et al., 2006; Thakali et al., 2006a, b; Lock et al., 2007a–c; Li et al., 2008, 2009a, b). Fig. 1 gives a schematic overview of a t-BLM for soil-living organisms.

The t-BLMs are mainly based on the soil porewater hypothesis or equilibrium partitioning concept, which assumes that metal concentration in the soil pore water (aqueous fraction of soil) is determining the effect on soil organisms (Van Gestel et al., 1995; Van Gestel, 1997). This hypothesis assumes that the main uptake route for soil organisms is from soil pore water. Toxicity of metals to soil organisms such as collembolans and earthworms is related to the free metal ion activity in soil solution, which in turn is influenced by soil characteristics (e.g., Lanno et al., 2004). For instance, pH (protons) affect(s) metal toxicity (e.g., Erickson et al., 1996; Meyer et al., 1999; Thakali et al., 2006a, b). However, no effect of pH was reported in other studies (De Schamphelaere and Janssen, 2002; Markich et al., 2003; Lock et al., 2007b; Wang et al., 2009; Li et al., 2009a). This suggests that the effects of soil properties and water chemistries can be metal-specific, and the relationships between toxicity and soil properties or soil solution composition greatly depend on experimental conditions.

Regarding the effect of physical–chemical parameters, soil is a complex system with factors such as organic matter content and clay particles influencing free metal ion activities. Better prediction of metal toxicity in t-BLMs for soil organisms may be possible using an aqueous solution, simulating soil pore water (see e.g., Steenbergen et al., 2005; Lock et al., 2006; Li et al., 2008; Ardestani and van Gestel, 2013c; Ardestani et al., 2013a, b; Ardestani and van Gestel, 2014; Ardestani et al., 2014a). A number of studies have been reported in the literature using a BLM approach for predicting metal toxicity to plants (Lock et al., 2007a–c; Antunes et al., 2007; Luo et al., 2008; Antunes and Kreager, 2009; Wang et al., 2010a; Wu and Hendershot, 2010a–c). In all of these studies, the developed BLMs aim at describing the effect of soil porewater composition or soil properties on metal toxicity.

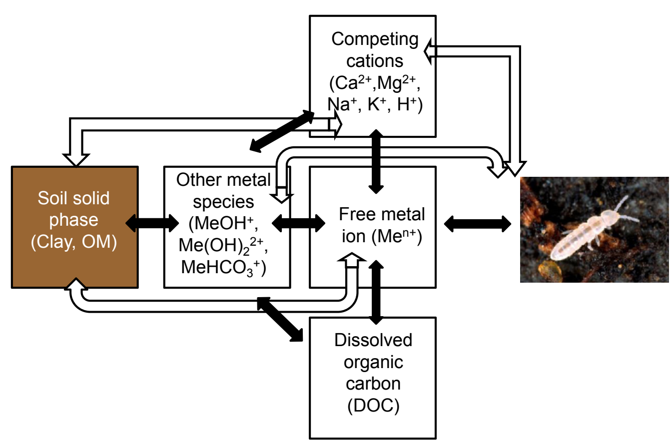

Fig. 1. Schematic pattern of a terrestrial biotic ligand model (t-BLM) for predicting toxicity of metals to soil invertebrates, here represented by the springtail *Folsomia candida*. The free metal ion may be bound to the biotic ligand, and its activity is influenced by other factors in the soil solution (pore water). These factors are classified in two groups: competition and complexation factors. Competition factors such as different cations compete with the free metal ions to bind to the biotic ligand sites of the organism. Complexation factors such as dissolved organic carbon (DOC) and other metal species (and may be anions) present in pore water bind to the free metal ions, thereby reducing their availability in the system. Also, the soil solid phase should be taken into account when studying bioavailability of metals. Negatively charged particles such as clay will have a high tendency to bind to cations in the soil solution including the free metal ion.