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Modelling the effects of copper on soil organisms and processes using the free ion approach: Towards a multi-species toxicity model

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ABSTRACT

The free ion approach has been previously used to calculate critical limit concentrations for soil metals based on point estimates of toxicity. Here, the approach was applied to dose–response data for copper effects on seven biological endpoints in each of 19 European soils. The approach was applied using the concept of an effective dose, comprising a function of the concentrations of free copper and 'protective' major cations, including H^+. A significant influence of H^+ on the toxicity of Cu^{2+} was found, while the effects of other cations were inconsistent. The model could be generalised by forcing the effect of H^+ and the slope of the dose–response relationship to be equal for all endpoints. This suggests the possibility of a general bioavailability model for copper effects on organisms. Furthermore, the possibility of such a model could be explored for other cationic metals such as nickel, zinc, cadmium and lead.

1. Introduction

Copper is a natural constituent of all soils, and in small quantities is an essential element for all plants and animals. Elevated concentrations of copper in soils can however lead to toxic effects on plants and soil-dwelling animals and hence on ecosystems as a whole (Flemming and Trevors, 1989). For this reason, ecological risk assessment of copper is an important aspect of the management of concentrations of the metal in soils.

Along with other cationic metals such as zinc and cadmium, the influence of soil chemistry on the bioaccumulation and toxicity of copper is well attested (Lexmond, 1980; Cheng and Allen, 2001). There is thus a need to develop approaches to quantify the influence of soil chemical properties on metal toxicity, in order to improve their ecological risk assessment. To date, approaches taken have been both empirical and mechanistic. In the former, endpoints from a single toxicity test, carried out in a variety of soils, are regressed against one or more soil properties believed to impact bioavailability. Such properties include soil solution pH, soil organic matter (OM) content and cation exchange capacity (CEC), and contents of mineral oxides of elements such as Fe and Mn. This type of work has been done for a number of soil organisms including barley and tomato (Rooney et al., 2006), wheat (Warne et al., 2008) and microbial processes (Oorts et al., 2006; Broos et al., 2007) for copper. The mechanistic approach centres on the Biotic Ligand Model (Paquin et al., 2002) which postulates that toxicity results from binding of specific metal species (usually the free metal ion) to a receptor on the organism (the Biotic Ligand), in competition with other solution cations such as H^+, Na^+ and Ca^{2+}. The concentration of metal bound to the biotic ligand, rather than a measurable or calculable pool of metal in the soil or soil solution, is assumed to correlate with the toxic response. The BLM was originally developed to describe the acute toxic effects of metal accumulation at the gill of fish, but has been applied to toxicity data for a number of other aquatic organisms. Some progress has been made in applying the principles of the BLM to soil-dwelling organisms: acute BLMs have been developed for soil organisms such as the earthworm *Aporrectodea caliginosa* (Steenbergen et al., 2005) and the enchytraeid *Enchytraeus albidus* (Lock et al., 2006), and the model has been applied to describe the effects of metals on plants in solution

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(Lock et al., 2007). Thakali et al. (2006a, b) have developed BLMs to predict the effects of copper on plants, invertebrates and microbial processes, based on testing using a set of European soils of contrasting soil chemistries (Rooney et al., 2006; Oorts et al., 2006; Criel et al., 2008).

An alternative approach to considering bioavailability effects has been taken by Lofts et al. (Lofts et al., 2004; De Vries et al., 2007). Termed the free ion approach, this method considers the toxic effect to depend upon the free metal ion in soil solution, and also on the amounts of other solution cations that 'protect' the organism against metal toxicity. The variables considered are thus the same as would be considered by the BLM, but the expression describing the loading of the biotic ligand with toxic metal is replaced with an empirical function, and the 'biotic ligand' is not explicitly considered. The free ion approach was used to derive functions giving critical limits (risk threshold concentrations) for copper and other metals in soils directly from existing literature (Lofts et al., 2004; De Vries et al., 2007). Because of the limited nature of the available data, a number of key assumptions were made in the derivation of the critical limit functions. Such assumptions require investigation, either to confirm that they are reasonable, or to allow further refinement of the methodology. In the case of copper, datasets now exist (Rooney et al., 2006; Oorts et al., 2006; Criel et al., 2008) that are suitable for such a purpose. These datasets comprise seven toxicity tests covering a range of species and microbial processes, each carried out in the same set of soils. The soils were chosen to cover a range of key soil properties, thus making the datasets ideal for investigating metal bioavailability effects. The subset of toxicity data from the non-calcareous soils has been previously used to develop terrestrial BLMs (Thakali et al., 2006a,b). The purpose of the work presented here is to extend the free ion approach to these data and to test, for copper, the assumptions previously made in applying the approach.

2. Theory

The free ion approach is summarised in an empirical expression describing the variation of the effect concentration of a potentially toxic cationic metal in soil solution with the soil solution pH and concentrations of 'protective' cations. For copper:

$$\log\left[Cu^{2+}\right]_{effect} = \alpha\cdot pH_{ss} + \sum_{1}^{n}\eta_n\cdot\left[pC^{z+}\right] + \gamma_{effect} \quad (1)$$

Here pH_{ss} is the soil solution pH, $[C^{z+}]$ is the free concentration of a 'protective' cation, α, η and γ_{effect} are constants, and $[Cu^{2+}]_{effect}$ is the 'effect' concentration of the free copper ion. The subscript 'effect' refers to a constant level of toxic effect, which can be for a single species or microbial process (e.g. a no-observed effect concentration or $L(E)C_x$) or for multi-species endpoint data (e.g. a given percentile of a sensitivity distribution of species endpoints). The subscript 'effect' associated with the term γ indicates that although this term is constant at a given effect level, it will vary according to the level of effect being described. The terms α and η are assumed to be independent of effect level.

In the initial application of the theory by Lofts et al. (2004), two key assumptions were made. Firstly, the free concentrations of protective cations (e.g. Na^+, Mg^{2+}, Ca^{2+}) were assumed to co-vary with pH. Thus, Eq. (1) was reduced to:

$$\log\left[Cu^{2+}\right]_{effect} = \alpha\cdot pH_{ss} + \gamma_{effect} \quad (2)$$

Previously employed literature data comprised chronic endpoints (no-observed effect concentrations, NOECs, and 10% effect concentrations, EC10s) for plants, soil invertebrates and microbial processes. The data were rather unsystematic with respect to combinations of soil chemistry and test species, i.e. only a few test results were available for the same species across different soil types. Because of this, the data for all species were used together in a single analysis to derive the pH dependence of free ion toxicity (the term α in Eq. (2)). Thus, the second assumption was that the pH dependence of free ion toxicity for all organisms and processes in the tests could be described by a single constant.

The dataset used in the present study is sufficiently comprehensive to allow the two key assumptions previously made to be tested. Firstly, concentrations of the cations Na^+, Mg^{2+}, K^+ and Ca^{2+} in soil solution can be calculated. Secondly, the pH dependence of free ion toxicity can be evaluated separately for each endpoint measured. Thus, we can formulate two central questions to be considered in the analysis of the new dataset:

1. Are the endpoint-specific dependencies of pH upon Cu^{2+} toxicity sufficiently similar to justify the use of a single, endpoint-independent value, i.e. is α similar for all endpoints?
2. Do the cations Na^+, Mg^{2+}, K^+ and Ca^{2+} exert significant protective effects against Cu^{2+} toxicity and are these all similar for all endpoints, i.e. is η_n significantly different from zero and similar for all endpoints?

2.1. The free ion effective dose model

In applying the free ion approach to these data, it would be possible to replicate in part the previous work by calculating individual toxic endpoints (e.g. EC10s or EC50s) for each test in each soil, this time expressed as free metal ion concentration, and considering how these varied with soil chemistry parameters (e.g. Oorts et al., 2006). However, a more powerful approach is to extend the free ion approach to consider the entire dose–response curve. If we rearrange Eq. (1) as follows:

$$\gamma_{effect} = \log\left[Cu^{2+}\right]_{effect} - \alpha\cdot pH_{ss} - \sum_{1}^{n}\eta_n\cdot\left[pC^{z+}\right] \quad (3)$$

it becomes clear that, since γ_{effect} is constant for a given effect level, the right hand side of the expression is also constant. Generalising to any response level, γ can be interpreted as an 'effective dose' that incorporates not only a concentration of the toxic substance, but also terms describing the effects of bioavailability. This expression can be substituted into a log–logistic dose–response equation, e.g.,

$$R = \frac{R_0}{1 + e^{\beta\left(D_{eff} - D_{eff,50}\right)}} \quad (4)$$

where R is the response, R_0 is the control response, β is the slope parameter, D_{eff} is the effective dose of toxicant and $D_{eff,\ 50}$ is the effective dose causing a 50% effect – equivalent to the ED50. If we simply substitute the effective dose term γ_{effect} in Eq. (3) for the term D_{eff} then the resulting expression can in principle be fitted to dose–response curves for the same toxicity test in different soils. Fitting parameters are the terms β and $D_{eff,\ 50}$ in Eq. (4) and the coefficients α and η_n in Eq. (3). This expression will be referred to as the FRIED (FRee Ion Effective Dose) model.

Although ion binding to the organism is not explicit in FRIED, the effective dose term can be related to bound metal. Mertens et al. (2007) showed that for the binding of a metal to an adsorbate in competition with H^+ and other cations, expressed by a competitive Freundlich isotherm, (Eq. (5)):