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PARAMETERIZING THE BINDING PROPERTIES OF DISSOLVED ORGANIC MATTER WITH DEFAULT VALUES SKEWS THE PREDICTION OF COPPER SOLUTION SPECIATION AND ECOTOXICITY IN SOIL

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Abstract: Parameterizing speciation models by setting the percentage of dissolved organic matter (DOM) that is reactive (% r-DOM) toward metal cations at a single 65% default value is very common in predictive ecotoxicology. The authors tested this practice by comparing the free copper activity ($pCu^{2+} = -\log_{10}[Cu^{2+}]$) measured in 55 soil sample solutions with pCu^{2+} predicted with the Windermere humic aqueous model (WHAM) parameterized by default. Predictions of Cu toxicity to soil organisms based on measured or predicted pCu^{2+} were also compared. Default WHAM parameterization substantially skewed the prediction of measured pCu^{2+} by up to 2.7 pCu^{2+} units (root mean square residual = 0.75–1.3) and subsequently the prediction of Cu toxicity for microbial functions, invertebrates, and plants by up to 36%, 45%, and 59% (root mean square residuals $\leq$9 %, 11%, and 17%), respectively. Reparametrizing WHAM by optimizing the 2 DOM binding properties (i.e., % r-DOM and the Cu complexation constant) within a physically realistic value range much improved the prediction of measured pCu^{2+} (root mean square residual = 0.14–0.25). Accordingly, this WHAM parameterization successfully predicted Cu toxicity for microbial functions, invertebrates, and plants (root mean square residual $\leq$3.4%, 4.4%, and 5.8%, respectively). Thus, it is essential to account for the real heterogeneity in DOM binding properties for relatively accurate prediction of Cu speciation in soil solution and Cu toxic effects on soil organisms. *Environ Toxicol Chem* 2016;9999:1–8.

Keywords: Trace elements Dose–response modeling Complexation Fulvic acid Windermere humic aqueous model (WHAM)

INTRODUCTION

Speciation in solution is unequivocally considered to be an effective way to estimate the bioavailability and toxicity of metal cations to soil organisms. Among metal species in solution, free metal cations are considered to be the main bioavailable and toxic species for soil organisms [1,2]. Accordingly, determination of the activity of free metal cations in soil solution is critical for most recently developed ecotoxicological models [3–5].

The most direct approach to estimate the activity of free metal cations in soil solution is to determine it analytically. Many analytical techniques, such as the Donnan membrane technique and electrochemical methods based on voltammetry or potentiometry, are still used to measure the activity of metal cations in soil solution [6]. All of these techniques have, however, specific analytical drawbacks, such as being time-consuming, not directly related to the free metal form, and not sensitive enough to deal with the full range of the environmentally relevant activities of free metal cations usually found in real soil solutions.

The activity of free metal cations in soil solution may also be estimated by modeling. Speciation models work with 1) input parameters that can be measured routinely in soil solutions, such as pH and total metal cation and dissolved organic matter (DOM) concentrations, and 2) databases describing metal cation binding with inorganic ligands and DOM. Because of the high affinity of DOM for metal cations and the heterogeneity and complexity of the molecular structure of DOM, the modeling of metal cation binding with DOM is highly challenging [7].

The humic ion-binding model included in the Windermere humic aqueous model (WHAM) [8] and the nonideal competitive adsorption (NICA)-Donnan model [9,10] are currently the 2 models most widely used for simulating metal cation binding with DOM and consequently for estimating free metal cation activity. Because fulvic acids are among the most abundant DOM components in soil and particularly reactive toward metal cations [11–13], these 2 models similarly describe the binding properties of DOM as those of a reference fulvic acid parameterized specifically in each model. Beyond the analytically determined input parameters (e.g., pH, metal cation, and DOM concentrations), the activity of free metal cations is thus estimated in WHAM and the NICA–Donnan model by theoretically adjusting the percentage of DOM reactive toward metal cations (hereafter referred to as % r-DOM), corresponding to the fraction of DOM assumed to have the same reactivity toward metal cations as the defined reference fulvic acid, with the remaining DOM being considered inert. The free metal cation activity could also be successfully predicted by optimizing the binding constant of metal cations of the reference fulvic acid. However, model optimization by adjusting the % r-DOM is a more generic and practical approach [14–17].

Early studies focused on reactive DOM in natural waters revealed that the % r-DOM ranged from 30% to 120% but that the bulk of it was within the 40% to 80% range [14,15].

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