Specific parameterization of WHAM improves the prediction of copper competitive binding on plant roots

Stéphanie Guigues[1,2], Matthieu N. Bravin[3], Cédric Garnier[4] and Emmanuel Doelsch[1]

[1] CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France
[2] ADEME, 20 avenue du Grésillé, BP-90406, Angers cedex 01, France
[3] CIRAD, UPR Recyclage et risque, F-97408 Saint-Denis, Réunion, France
[4] Université de Toulon, PROTEE, EA 3819, 83957 La Garde, France
E-mail contact: matthieu.bravin@cirad.fr

1. Introduction

Models designed to predict the ecotoxicity of metal cations at the organism level, such as the biotic ligand model, are based on the description of the competitive binding of metal cations and protons to biotic ligands borne by the outer surface of the organism such as plant roots [1]. The model's ability to accurately describe the binding of metal cations on roots is therefore a crucial issue.

The Windermere humic aqueous model (WHAM) initially designed to model metal cation binding on humic substances were applied in predictive ecotoxicology [2]. For terrestrial higher plants, a recent investigation showed that WHAM was able to satisfactorily model cadmium (Cd), nickel (Ni), and zinc (Zn) concentrations in pea (Pisum sativum L.) roots, but that it overestimated the Cu concentration in roots [3].

We recently showed that Cu binding on wheat and tomato roots was driven by two types of sites, i.e. low- and high-affinity sites corresponding respectively to carboxylic and nitrogen (N) functional groups, the reactivity if the latter differing substantially from the default reactivity defined in WHAM [4]. These suggested that specific parameterization of WHAM would be necessary for terrestrial higher plants.

We thus compared the ability of WHAM parameterized with default settings and WHAM specifically parameterized for terrestrial higher plants to model the competitive binding of Cu on wheat (*Triticum aestivum* L.) and tomato (*Solanum lycopersicum* L.) roots.

2. Experimental approach

Wheat (cv. Premio) and tomato (cv. Moneymaker) roots were excised from plant seedlings pre-grown in hydroponics for 3 weeks. Roots were treated to obtain a root material metabolically inactive that prevented the physiologically-driven absorption of Cu in root cells and that enabled us to study only Cu binding onto root surfaces.

Acidic properties of roots were investigated by titrated them from pH 2.5 to 11.5. Copper binding properties of roots were investigated by sorption experiments carried out under varying ionic strength and concentration of competitive cations (proton, calcium, and zinc) representative of the chemical composition of soil solutions.

3. Modelling approach

Experimental data were modelled using the humic ion-binding model included in WHAM VII, which was designed to simulate the cation binding properties of humic substances depicted as a regular array of two types of binding sites [5].

The model was either used with one (WHAM) or two humic acids (WHAM-2HA) parameterized with the default settings or specifically parameterized with two humic acids for terrestrial higher plants (WHAM-THP). The quality of the fits obtained with WHAM, WHAM-2HA, and WHAM-THP were determined by calculating the root mean square residual (RMSR) between experimental data and model outputs.

4. Results and discussion

WHAM failed to fit the titration data for wheat and tomato (*RMSR* = 9 and 14.4 $cmol_c.kg^{-1}$; Figure 1.A). WHAM overestimated the density of binding sites observed experimentally over the whole investigated pH range. In comparison with WHAM, WHAM-2HA improved the fit of the titration data for wheat and tomato (*RMSR* = 4.7 and 5.2 $cmol_c.kg^{-1}$). WHAM-2HA however satisfactorily fitted the experimental data only for tomato at pH ≤ 6. The default parameterization of WHAM and WHAM-2HA was thus inadequate for wheat

and tomato roots. By contrast with WHAM and WHAM-2HA, WHAM-THP accurately fitted the titration data for wheat and tomato (RMSR = 1 and 1.8 $cmol_c.kg^{-1}$).

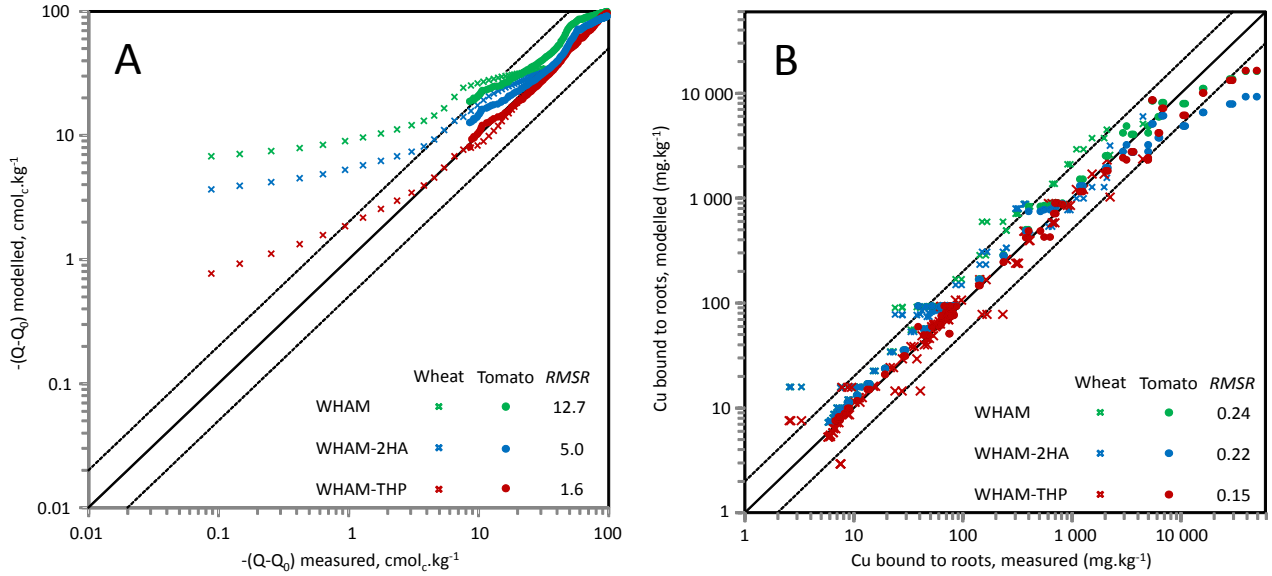

Figure 1: Measured versus modelled acidic properties (A; expressed in charge Q corrected by the initial charge Q_0) and copper (Cu) binding (B) on wheat (crosses) and tomato (circles) roots. Green, blue and red symbols correspond to data modelled with WHAM, WHAM-2HA, and WHAM-THP (see section 3 for rationale), respectively. The root mean square residuals (RMSR) pool data for wheat and tomato. The solid line refers to 1:1 line and dashed lines refer to a factor ± 2.

Overall, WHAM-THP better fitted the experimental data (*RMSR* = 0.15; Figure 1.B) than WHAM (*RMSR* = 0.24) and WHAM-2HA (*RMSR* = 0.22). The better fits obtained with WHAM-THP than with WHAM and WHAM-2HA could thus be attributed to the specific parameterization of Cu binding affinity of nitrogen (N) functional groups in WHAM-THP that substantially differ from the Cu binding affinity of phenolic groups defined by default in WHAM and WHAM-2HA [4].

WHAM-THP better fitted the experimental data for the two ionic strengths (*RMSR* = 0.11 and 0.21 for tomato and wheat, respectively) than WHAM and WHAM-2HA (*RMSR* = 0.18 and 0.39) and thus better accounted for the effect of the ionic strength on Cu binding on roots. Proton competition was the only effect for which WHAM-THP (*RMSR* = 0.31 and 0.17 for wheat and tomato, respectively) did not improve the fit of the experimental data obtained with WHAM (*RMSR* = 0.38 and 0.18) and WHAM-2HA (*RMSR* = 0.27 and 0.10). WHAM and WHAM-2HA modelled a very weak competitive effect of Ca and Zn and thus overestimated Cu binding on wheat and tomato roots (*RMSR* = 0.12-0.28). By contrast, WHAM-THP correctly fitted (*RMSR* = 0.03-0.04) the competitive effect of Ca and Zn on Cu binding on wheat and tomato roots.

5. Conclusions

The improvement in the goodness of fit obtained with WHAM-THP as compared with WHAM and WHAM-2HA supports the relevance of the specific parameterization of WHAM-THP. WHAM-THP was satisfactorily parameterized with a single set of parameters for wheat and tomato roots (except for the total density of binding sites). The pratical application of WHAM-THP to improve the prediction of the concentration in roots and the rhizotoxicity of metal cations should be tested.

6. References

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