Variability in the binding capacity of dissolved organic matters toward trace metals in soil: impact on predictive ecotoxicology

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1. Introduction

Predictive ecotoxicology is gaining a large audience in the scientific community as a powerful approach to sustain risk assessment of contaminated soils. Regarding the issue of trace metals, this approach is based on the development of semi-mechanistic models such as the free ion effective dose (FRIED) model [1]. These models notably require characterising the exposure of soil organism to trace metals in soil.

The exposure module is based on the characterisation of the chemical bioavailability, through the critical determination of trace metal speciation in the soil solution. As it is tedious and time-consuming to determine trace metal speciation analytically, most authors used advanced geochemical codes to calculate free metal concentration in soil solution. These codes notably requires a detailed description of the binding capacity of humic substances as a surrogate of dissolved organic matters (DOM) in soil [2]. The binding capacity of DOM is then deduced as a percentage of the total DOM that reacts as a fulvic acid. This percentage of reactivity is usually fixed at a given value, i.e. between 50 to 70 %. However, experimental evidences supporting this hypothesis are rather few in comparison with its very wide use in predictive ecotoxicology.

Consequently, the present study aims at exploring the variability of this percentage of DOM reactivity in soils and evaluating the impact of a large variability of this parameter on the toxic effect of trace metals on soil organisms as predicted with a multi-species toxicity model recently developped. This work was focused on the behaviour of copper (Cu).

2. Materials and methods

Fifty five soil samples coming from the temperate (n = 46) and tropical (n = 9) areas in France were collected for this experiment. These soil samples exhibited a very broad range of physical-chemical properties, with a large variability in the origin and the concentration of trace metals (*Tab 1*). Each soil was firstly incubated for 2 weeks at 70 % of its water holding capacity (WHC), then further incubated for 8 days at 100 %WHC.

n = 55	Corg	CEC	Total Cu	pH_{ss}	$p\{Cu^{2+}\}$	% DOM
	g kg^{-1}	$cmol_+$ kg^{-1}	mg kg^{-1}			
Minimum	0.1	0.1	6	5.4	5.8	5
Quartile 1	1.3	5.1	21	6.4	9.0	13
Median	2.1	10.4	30	6.7	9.7	30
Mean	2.6	13.3	107	6.7	9.4	46
Quartile 3	3.4	18.9	100	7.1	10.1	70
Maximum	12.6	73.8	1070	7.6	11.1	200

Table 1: Distribution patterns of organic C (Corg), cation exchange capacity (CEC), total Cu concentration (Total Cu), soil solution pH (pH_{ss}), free Cu activity (p{Cu2+}) and DOM binding capacity (% DOM) for the 55 soil samples tested. All parameters were determined analytically, except DOM binding capacity that was fitted as a percentage of the total DOM concentration.

At the end of the two-step incubation, soil solution was extracted with an unbuffered saline solution (i.e. $Ca(NO_3)_2$ 2 mM, KNO_3 2 mM and $MgSO_4$ 1 mM) at a soil:solution ratio of 1:10. Soil solutions were analysed for pH, total organic carbon concentration and the concentration of major cations/anions and trace metals. Free Cu activity was determined with an ion selective electrode calibrated in the range 13.2-5.4 $p\{Cu^{2+}\}$.

Free Cu activity was further calculated using the Model VII and considering that a given percentage of DOM react as the default fulvic acid [2]. On one hand, the percentage of DOM reactivity was fixed for all soil solutions at 65 %, which corresponds to the usual parameterisation used in ecotoxicological models. On the other hand, the percentage of DOM reactivity was fitted individually for each soil solution to simulate accurately the free Cu activity measured.

Each of the two sets of free Cu activity calculated using Model VII, with fixed or fitted percentages of DOM reactivity, was used to estimate the theoretical toxic effect of Cu on soil organisms in the 55 soils by applying the FRIED model [1].

3. Results and discussion

Free Cu activity calculated with Model VII using a unique percentage of DOM reactivity fixed at 65 % was weakly correlated to free Cu activity determined analytically (R^2 = 0.51; results not shown). This set of calculations mostly underestimated free Cu activity up to 2 p{Cu^{2+}} unit. This shows that fixing the percentrage of DOM reactivity at unique value does not enable an accurate estimation of free Cu acitvity in soils exhibiting a broad range of physical-chemical properties.

Consequently, free Cu activity was further calculated with Model VII by fitting the percentage of DOM reactivity in each solution to recover accurately free Cu activity determined analytically. The resulting percentage of DOM reactivity consequently ranged between 5 to 200 % (*Tab 1*), which far exceeded the range of 40 to 91 % estimated in 15 samples of fresh waters [3].

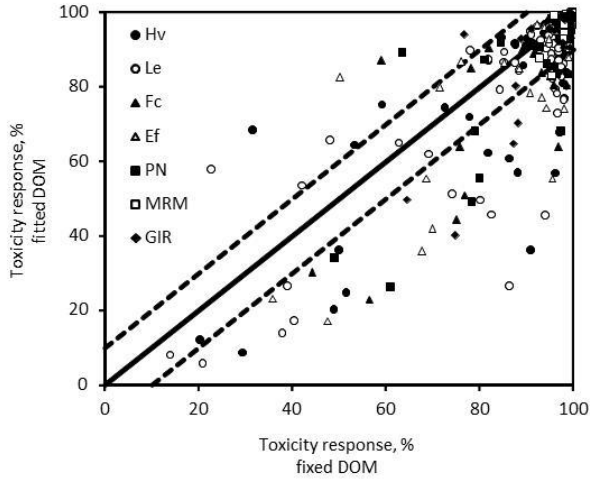

Figure 1: Comparison of the toxic response (% of the control) simulated with the FRIED model using a fixed (x-axis) or fitted (y-axis) percentage of DOM reactivity. Soil organisms and endpoints were H. vulgare (Hv), L. esculentum (Le), F. candida (Fc), E. fetida (Ef), potential nitrification (PN), maize residue mineralisation (MRM) and glucose-induced respiration (GIR).

Finally, the comparison of the toxic effect of Cu on soil organisms predicted by the FRIED model was alternatively over-estimated up to 37 % or under-estimated up to 60 % when using free Cu activities calculated with the fixed percentage of DOM reactivity (*Fig 1*). The extent of this deviation depended on the soil organisms considered and the level of toxicity predicted.

4. Conclusions

This study suggests that the variability in the binding capacity of DOM towards trace metals could be much greater than previously expected, therefore involving a substantial inaccuracy in predicting metal speciation in soil solution when applying a unique percentage of reactivity for DOM. This inaccuracy in metal speciation could further alter the predictive power of ecotoxicological models based on trace metal speciation.

5. References

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