Root-Induced Alterations of Copper Speciation in Solution in the Rhizosphere of Crop Species

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ABSTRACT: As a prerequisite to establish trace metal phytoavailability, it is essential to determine trace metal speciation in the solution of the rhizosphere, where substantial alterations of physical-chemical properties (e.g. pH, Eh, organic matters) are induced by root activities. Investigations in the past decades were mainly dedicated to studying illustrative cases of how each individual rhizosphere process is able to influence trace metal speciation in solution. On a more integrative perspective, the present study aimed at investigating (i) the diversity of chemical modifications occurring in the solution of the rhizosphere of crop species cultivated on soils exhibiting a very wide range of physical-chemical properties and (ii) their consequent impact on copper (Cu) speciation in solution.

Three plant species from three distinct botanical families, i.e. one graminaceous species, red fescue (*Festuca rubra*), two dicotyledonous species, tomato (*Lycopersicon esculentum*) and cabbage (*Brassica oleracea*), and 55 soils exhibiting a wide variety of physico-chemical properties (e.g. pH 4.4-8.2, 1-126 g Corg kg^{-1}, 6-1077 mg Cu_{total} kg^{-1}) were selected for this study. Plants were grown using the RHIZOtest experimental design. This biotest consists in growing plants for two weeks in hydroponics, then for 8 days in contact with soil. Soils harvested from planted and unplanted devices are considered to be representative of rhizosphere and bulk soil, respectively. The solution of each rhizosphere and bulk soil was extracted with an unbuffered salt solution, and pH, concentrations of major ions and trace elements, dissolved organic matter (DOM), as well as the free Cu^{2+} activity were measured. The reactivity of DOM towards Cu was also estimated by modeling of Cu speciation, using the Humic Ion-Binding Model VII.

Root activities induced variation in pH and in DOM concentration and its reactivity, thereby inducing substantial alterations of Cu speciation in solution. Fescue induced an overall alkalization of the rhizosphere that tended to be stronger as the bulk soil was more acidic. Conversely, tomato and cabbage induced an acidification or alkalisation of the rhizosphere depending on soil type. Surprisingly, the concentration of DOM tended to decrease in the rhizosphere, especially for soils initially exhibiting the highest DOM concentrations. This result could be explained by an increase in microbial activity in the rhizosphere leading to a higher rate of DOM mineralization. The reactivity of DOM varied in a complex pattern the rhizosphere , either increasing or decreasing compared to the bulk soil depending on soil properties and plant species. As a result of the drastic alteration of chemical properties in the solution of the rhizosphere and of Cu uptake by roots, the free Cu^{2+} activity was changed by up to three orders of magnitude in the rhizosphere compared to the bulk soil. Free Cu^{2+} activity tended to decrease in the rhizosphere for soil exhibiting the highest free Cu^{2+} activities in the bulk soil. Conversely, free Cu^{2+} activity increased up to 1 to 2 orders of magnitude in the rhizosphere for soil exhibiting the lowest free Cu^{2+} activities. In such soils, the decrease in DOM reactivity could explain the increase in free Cu^{2+} activity in the rhizosphere.

Our results show a consistent picture of how root activities can substantially alter trace metal speciation in the rhizosphere in a wide range of soils and plant species. Among the rhizosphere

properties relevant for trace metal biogeochemistry and phytoavailability, the characterization of DOM reactivity should deserve further attention