Root-induced alterations of copper speciation in solution in the rhizosphere of crop species

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ABSTRACT: As a prerequisite to 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 study 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 fescue (*Festuca rubra*) and 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 in planted and unplanted devices are considered to be representative of the rhizosphere and the bulk soil, respectively. The solution of each rhizosphere and bulk soil was extracted with an unbuffered salt solution and pH, concentrations of major ions, dissolved organic matters (DOM) and trace elements as well as free Cu^{2+} activity were measured. The reactivity of DOM towards Cu was also estimated by the modeling of Cu speciation using the Humic Ion-Binding Model VII.

Root activities induced variation in pH and in DOM concentration and 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. The concentration of DOM tended surprisingly to decrease in the rhizosphere and especially for soil exhibiting initialy the highest DOM concentrations in the bulk soil. 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 also varied in the rhizosphere with a complex pattern, 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, 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 soil, the decrease in DOM reactivity could explain the increase in free Cu^{2+} activity in the rhizosphere.

Our results introduce a consistent picture of how root activities can substantially alter trace metal speciation in the rhizosphere in a wide range of both soils and plant species. Among important rhizosphere properties as regard to trace metals, the characterization of DOM reactivity should deserve further attention for a more thorough understanding of trace metal biogeochemistry in the rhizosphere and phytoavailability.