Modifications of chemical properties and copper speciation in the solution of field-collected rhizosphere

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ABSTRACT: Among the potential soil drivers of trace element phytoavailability, the ability of plant roots to alter the chemical properties and consequently trace element speciation in the solution of their rhizosphere remained comparatively poorly addressed. Ex situ investigations based on rhizobox experimental set-up already showed how substantial this rhizosphere effect can be. However, the relevance of this rhizosphere effect remains very barely evidenced at field scale. Consequently, we tackled this issue by investigating the modifications of chemical properties and copper (Cu) speciation in the solution of field-collected rhizosphere.

Our investigation was conducted on a long-term field trial implemented in two stages. Five market-gardened crops were grown for 14 cropping cycles (i.e. 7 y), then tomato (*Lycopersicon esculentum* L.) and fescue (*Festuca arundinacea* L.) were grown for the last three cropping cycles. Soil was fertilized at each cropping cycle either with a mineral fertilizer, a pig slurry compost or a poultry litter compost. At the end of the last cropping cycle, the rhizosphere was collected by gently brushing the roots of tomato and fescue, while the bulk-soil was collected with an auger. The solution of the rhizosphere and the bulk-soil of each plot was then extracted (1:5 dry soil to solution ratio) on fresh samples with an unbuffered ionic solution mimicking the average composition of the soil solution in this field trial. After filtration (0.22 µm), pH, free Cu^{2+} activity, total concentration of dissolved organic matters (DOM), DOM fluorescence and DOM acidic properties were measured.

Ranging between 10.5 and 12, pCu^{2+} in the rhizosphere solution was 0.5 to 2 pCu^{2+} units lower than the pCu^{2+} of their respective bulk-soil whatever the plant species and the type of fertilizer applied. With a similar trend, pH in the rhizosphere solution which ranged between 7 and 8.2 was 0.1 to 1 pH unit lower than the pH of their respective bulk-soil. However, pH changes between rhizosphere and bulk-soil only explained half of the variance observed for pCu^{2+}. Concomitantly, total DOM concentration was higher in the rhizosphere than in the bulk-soil up to 30 mg l^{-1}. Preliminary investigations further showed that the density of carboxylic-like sites ($pKa < 7$) and the fluorescence of DOM respectively decreased and increased in the rhizosphere of both species compared to their respective bulk-soil. These quantitative and qualitative changes in DOM were even more marked when organic fertilizers were applied to soil. Consequently, these results suggest that the quantitative and qualitative modifications of DOM also impact substantially Cu speciation in the rhizosphere solution of both species.

Overall, this investigation of field-collected rhizosphere showed that plant roots are able to induce substantial modifications of the chemical properties that govern trace element speciation in solution. The current in-depth examination of the qualitative changes of DOM in the rhizosphere should enable us to parameterize an advanced geochemical code (e.g. WHAM) for predicting Cu speciation in the rhizosphere solution.