



## **Resolving the soil-root interface – Use of Cryo-XRF and TXM at the low and tender X-rays to determine C colocalization and P speciation at the microscale**

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The soil-root interface (rhizosphere) is a dynamic and heterogeneous region, where important changes in element speciation occur. This is especially true for P, an element with limited bioavailability in soils due to its strong interactions with the soil matrix components (iron oxides, carbonates, and clay minerals). Changes in P speciation at soil microsites and interfaces occur as if under an independent high throughput microchemical reactor, where changes of thermodynamical parameters influence the overall P micro-speciation. In this regard, the rhizosphere is specially characterized by a high input of plant and microbial C and solutes, thus creating a gradient of physical-chemical conditions that benefit unexpected P species. In this study we aimed to assess the changes in P speciation at the rhizosphere by using synchrotron spectromicroscopy. To this end plants of Norway spruce were grown in artificial soils of different mineralogy (Carbonate and Silicate derived) and initial P speciation (either organic or inorganic) and had its root-soil interface analyzed. To faithfully probe the interactions of C and P, without the introduction of analytical artefacts, we analyzed our samples using either synchrotron based cryo- $\mu$ XRF/ $\mu$ XANES at the Swiss Light Source (SLS) or fresh thin section combined with  $\mu$ -XRF/ $\mu$ -XANES at the Diamond Light Source. Elemental maps were obtained using  $\mu$ -XRF and the resulting maps were processed using an image segmentation superpixel algorithm, and P speciation was determined by linear combination fitting of  $\mu$ -XANES data. Overall, we have observed that P and C co-localization within the soil-root interface increases in comparison to control soils, at both soils, independent of initial P speciation. Specifically, in the control silicate derived soil, with inorganic P as initial species, P is spatially collocated with Fe > C > Al. Meanwhile in the same soil, but with organic P as initial species, P is spatially correlated with Al but not with Fe. At the root-soil interface inorganic P loses its correlation with Al and Fe and is highly correlated with C, this tendency is also followed at the root-soil interface of soils with initial organic P speciation. These findings concur with  $\mu$ -XANES speciation, of the same regions. In carbonate derived control soils with inorganic P as its starting point, P is spatially collocated with Ca > Mg > Al, while in the organic variant P is collocated with Al and Ca only. At the root interface of both carbonate derived soils an increase in P collocalization with C and the formation of Mg - P complexes was observed. Our results suggest that sharp changes in P speciation occur at the root-soil interface, leading to mainly organic P forms, different from what is expected from chemical extractions. Finally, the use of highend spectromicroscopy techniques such as synchrotron based  $\mu$ -XRF and  $\mu$ -XANES either under cryo-conditions or using fresh thin sections allowed not only the combined visualization of C - P interactions at the microscale but also a more confident quantification of organic P.