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Co-localized arsenic speciation and cycling in the rhizosphere of hyperaccumulating ferns

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Compared to other plants, ferns from the Pteris genus are unique in their ability to take up and translocate high amounts of arsenic (As) from soil to above ground tissues and are thus studied intensively since their first discovery. Recently, it was demonstrated in hydroponic conditions that the As-hyperaccumulator fern Pteris vittata may excrete relatively high amounts of As(III) via its roots when exposed to high external As(V) concentrations. Moreover it was shown that translocated As may be stored also exocellularely in its fronds. Both of these observations contributed to changing the current view on its tolerance mechanism to As.
Yet, it is still unclear if soil-grown hyperaccumulator ferns also release As(III) from their roots and where such As(III) efflux might by localised in the root system. Here we applied a two-dimensional, passive solute sampling technique for the in situ speciation of As(III), As(V) and other associated solutes around P. vittata and P. quadriaurita roots grown on As rich soil.
Solute mapping revealed areas of labile As(V) depletion in the rhizosphere of individual P. vittata roots confining zones of labile As(III) and As(V) enrichment. Areas of enrichment spatially match with elevated levels of labile manganese (Mn^{2+}) indicating redox mediated speciation changes. Contrarily, no As(III) was found in the rhizosphere of P. quadriaurita, strongly indicating differential plant physiological rhizosphere management of As.
We conclude that highly dynamic redox transformations in the direct vicinity of fern roots may trigger the localized presence of labile As(III) and As(V) and their rapid transformation along with other elements involved in the redox chemistry of As. The observed increase in labile Mn may be attributed to the chemical re-oxidation of released As(III) by electron transfer to Mn (III, IV) oxides.
Our findings demonstrate the complexity of biogeochemical interactions in the rhizosphere of As-hyperaccumulator ferns and indicate that part of the As taken up by ferns may cycle between roots and the associated rhizosphere soil solution.
To the best of our knowledge, it was shown for the first time that both As(III) and As(V) are present co-localized at the immediate location of the P. vittata roots. Thus, internal and external As(III)/As(V) redox transformation in the rhizosphere and in the P. vittata root cells appear to control resupply and detoxification concurrently.