

## Iron Plaque on Rice Roots – A Sink or Source for Arsenic?

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Rice, as one of the Earth's oldest cultivars, is the major food source for more than half of the world's population. Traditionally grown on water-logged soils, the plant is regulating the uptake of dissolved iron(II) (Fe(II)) by the release of oxygen from the roots – so called radial oxygen loss (ROL). ROL typically leads to an oxidation of Fe(II) and forms Fe(III) plaque precipitates on the root surface which serve as a sorption template for nutrients and contaminants such as arsenic (As). Iron plaques therefore might function as a quasi-biotechnological adsorption surface, with a high potential to immobilize As in the rhizosphere and to prevent its distribution in the soil. The goal of this study is to quantify the As (im)mobilization potential of iron plaque. We focus on the capability of naturally abundant Fe(III)-reducing bacteria to remobilize As during reduction of As-loaded iron plaque.

In transparent soil replacements, we quantitatively followed iron plaque formation on the roots, as well as the establishment of geochemical gradients of O<sub>2</sub> and Fe<sup>2+</sup> (on a high temporal and spatial resolution) as a function of the vegetative stages of rice plants. We could show that the mineralogy of iron plaque varied dynamically within the rhizosphere. Using Mössbauer spectroscopy, we identified poorly crystalline ferrihydrite on root tips, while higher crystalline goethite was detected at the older root parts. The spatial arsenic distribution within the rhizosphere was determined using a biosensor (ARSOLux), and consecutively correlated with the iron minerals. Additionally, in microcosm setups, we spiked iron plaque covered roots with As and subsequently incubated them with Fe(III)-reducing bacteria that were isolated from a native rice paddy field. During Fe(III) reduction, we observed the mobilization of Fe(II) and As and a re-precipitation of Fe(II)-bearing minerals which we identified as siderite and vivianite as resulting Fe(II) plaque transformation products. Synchrotron mapping highlighted the speciation of Fe(II)/(III) in these (trans)formed iron plaque minerals and indicated local hot spots for elemental adsorption processes that potentially serve as As binding sites during microbial Fe(III) reduction. Combining these findings, we were able to demonstrate that plant-induced iron plaque formation can sequester toxic metals such as As, while microbial Fe(III) reduction can re-mobilize the As into the rhizosphere.