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Localized Flux Maxima of Arsenic, Lead, and Iron around Root Apices in Flooded Lowland Rice

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Supporting Information

ABSTRACT: In wetland-adapted plants, such as rice, it is typically root apexes, sites of rapid entry for water/nutrients, where radial oxygen losses (ROLs) are highest. Nutrient/toxic metal uptake therefore largely occurs through oxidized zones and pH microgradients. However, the processes controlling the acquisition of trace elements in rice have been difficult to explore experimentally because of a lack of techniques for simultaneously measuring labile trace elements and O2/pH. Here, we use new diffusive gradients in thin films (DGT)/planar optode sandwich sensors deployed in situ on rice roots to demonstrate a new geochemical niche of greatly enhanced As, Pb, and Fe(II) mobilization into solution immediately adjacent to the root tips characterized by O2 enrichment and low pH. Fe(II) flux to the DGT resin at the root apexes was 3-fold higher than the anaerobic bulk soil and 27 times greater than the aerobic rooting zone. These results provide new evidence for the importance of coupled diffusion and oxidation of Fe in modulating trace metal solubilization, dispersion, and plant uptake.

INTRODUCTION

Rice contains ~10 times more arsenic than other cereal staples and is the dominant food source of inorganic arsenic exposure to the world’s population. The prevalence of lead-enriched rice is less than that of arsenic but is a particular concern in regions where plastic waste recycling and base metal mining coexist with farming. Lead exposure is estimated to be responsible for 0.6% of the global burden of disease. When rice is consumed in quantity, representing the eating habits of many in southeast Asia, by children or expectant mothers, its contribution to critical exposure levels can be significant. Conversely, it is the sub-optimum concentrations of iron in polished rice that contribute to iron deficiency, the most common human micronutrient imbalance in the world. However, despite this, iron toxicity is one of the most devastating trace element disorders in lowland rice, inhibiting the uptake and use of essential nutrients. Plant uptake of arsenic, lead, and iron is influenced strongly by soil processes and root activities, but our understanding of related mobilization/immobilization of those elements in rice rhizospheres remains incomplete because of the lack of satisfactory biogeochemical in situ mapping technologies.

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Soil-grown rice plants have a heterogeneous distribution of iron "plaque" coatings on their roots. This discontinuous porous layer of amorphous oxyhydroxide minerals, believed to be composed of predominantly ferrihydrite, on the root surface possesses a high specific surface area laden with $-\text{OH}$ functional groups capable of reacting with metals, other cations, and anionic species. Studies have shown that root iron plaques inhibit Cu, Ni, Mn, and P uptake in plants, but given the right conditions, whereby Fe oxyhydroxide is reduced and recycled back into solution, they can also act as a source of supply. The occurrence of iron plaques is more common around mature roots away from root tips. As redox potentials decrease with rooting depth, this is matched by a decline in iron plaque formation. The sampling approach, advanced as it was at the time, could only partially validate the Fe(II) solubility phenomena, because the Fe(II) maxima could not be directly observed because the measurements were not obtained in situ. Furthermore, these studies were unable to observe the accompanying mobilization of other elements, such as arsenic and lead. Methodologies that can simultaneously capture these changes to decipher the underlying geochemical processes around rice roots have until now not been available. However, recent developments in chemical imaging techniques have enabled this study to report the first direct measurement of O$_2$ and H$^+$ concentrations along with the mobilization of Fe(II) and other trace metals, at a two-dimensional planar interface in rice rhizospheres.

The overall aim of the work was to determine whether metal mobilization is a common feature of rice rhizospheres and to establish the key processes controlling element release. To achieve this, we used new sandwich sensor technologies, consisting of planar optodes using O$_2$ and pH-sensitive luminophores, overlain by an ultrathin layer for measuring metals.

**Figure 1.** Scheme of the experimental design. Illustrated within the diagram is the rhizotron (RH), planar optode (PO), ultrathin resin gel and filter layer (GFL), aquarium (AQ), rice plant (RP), camera (Cam.), trigger box (Tri.), light-emitting diode (LED), and computer (Comp.). The water level in both the rhizotron and aquarium is denoted by WL. The diagram is not to scale.
Method Summary. An ultrathin DGT layer is exposed to the soil and backed by a planar optode. It accumulates metals on a small particle size (0.2 μm) chelating resin and records directly the locally induced flux of trace metals during the entire deployment.28–30 The planar optode resolves the O₂ concentrations or pH dynamics in near real time at a temporal resolution of 30 min.27 For the same locations, two-dimensional images of metals, analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) after laser ablation, and either O₂ or pH could be resolved with a spatial resolution of ~100 μm. Both Fe(II) and Fe(III) are accumulated, but calculations using the speciation code WHAM indicated that Fe(III) would be negligible at the applied conditions, because of the low solubility of Fe(OH)₃. Arsenic binds quantitatively to iminodiacetic chelating resins in the presence of iron. For the ratio of accumulated As and Fe(II) observed in this work, the accumulation of As is unaffected by the amount of accumulated iron.32

The sensors were deployed in purpose-built rice rhizotrons designed to simulate natural anaerobic conditions encountered in the field. The rhizotron was transferred into an aquarium, and the front window of the rhizotron was removed to enable contact of the combined sensor with a Nucleopore membrane (0.2 μm pore size and ~10 μm thickness) support that overlaid the root and soil surface. Ingress of O₂ into the anaerobic soils was minimal because this operation was performed in aquarium water that had previously been deoxygenated with nitrogen. The planar optode foil was attached with tape (Scotch super 33+) to the support membrane and, subsequently, was overlain by the ultrathin resin gel and filter layer (GFL), which was also fixed with tape (Figure 1).

Seed Germination. Rice seeds (RIL 46) were sterilized in 0.5% NaOCl for 10 min and rinsed 3 times with deionized water. Seeds were soaked in deionized water overnight and then germinated at 25 °C for 2 days. Seedlings were transferred to a nylon net floating on 1/2 strength Hoagland’s solution, in a greenhouse (12 h photoperiod with a light intensity of 379 ± 89 W m⁻², day/night temperatures of 26.5 ± 2.4 and 20.2 ± 1.5 °C, respectively, CO₂ concentration of 743 ± 31 mg/m³, and relative humidity of >70%). The experimental campaign consisted of four components: Experiments 1 and 2 targeted the rhizospheres of rice seedlings. The first partnered oxygen with metal measurements, and the latter partnered pH and metals. Experiment 3 was conducted without a plant, to ascertain the heterogeneity of the soil. In experiment 4, abiotic conditions of the rhizosphere were simulated with an artificial root. In the oxygen optode experiments (experiment 1), the rice was grown hydroponically for 2 weeks prior to transplanting into the rhizotrons for a further 2 weeks. Transfer of rice into the rhizotron soil was performed after 5 days in the pH study (experiment 2), and the plants left to grow for 3 weeks before sensor deployment.

Preparation of Rhizotrons. Perspex rhizotrons with detachable front plates (inner dimensions of H x W x D = 40 x 10 x 15 cm) were filled with pre-moistened (~10%, wt/ wt), sieved (<2 mm) A-horizon Cambisol with a pH₄Cl₅ of 5.4, and fine loam texture (1.7% Fe, 20 mg of Pb kg⁻¹ from aqua regia digestion, and <2 mg of As kg⁻¹ measured by X-ray fluorescence (XRF)), which was tamped in layers to achieve a homogeneous soil structure with a consistent bulk density of 1.3 kg L⁻¹. Soils were saturated evenly using a water feed system, to enable the placement of Nucleopore membranes (0.2 μm pore size and ~10 μm thickness). The membrane ensures that soil uniformity was maintained during sandwich sensor deployment and avoided disturbance to roots and soil when the perpex covering window was removed. Seedlings (RIL 46) were transplanted in close proximity to the front plate of the rhizotron. Roots were encouraged to develop alongside the membrane by setting the rhizotrons at an inclination of 30–45°. In each case, the rooting/soil zones were kept in darkness to avoid exposing the roots and associated soil to light, which could affect the root development and induce microphytic growth. Control (unplanted) systems accompanied planted experimental setups.

Optode Sensor Fabrication. The oxygen quenchable luminophore platinum(II)-5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)-porphyrin (PtTFPP, http://www.frontiersci.com/) was chosen as an oxygen indicator.33 PtTFPP and an antenna dye (coumarin CS45, https://www.sigmaaldrich.com/) were mixed in a 1:2% (w/w) ratio, respectively, and dissolved in 4% (w/w) polyoxymethylene dichloromethane as the solvent. For the pH-sensitive optode, the lipophillic 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium (HPTS) indicator was chosen.27,34 HPTS and an antenna dye (Macrolow yellow coumarin, http://www.simon-und-werner.de/) were mixed in a 1.5:1.5% (w/w) ratio, respectively, and dissolved in 10% (w/w) polyurethane hydrogel (Hydromed D4) in a 9:1 (v/v) ethanol/water mixture.35 For both the O₂ and pH sensor, the coumarin antenna dye was added to increase the brightness of the respective indicator.

The respective sensing cocktails were coated onto a 125 μm thick transparent polyester foil (http://www.goodfellow.com/) using a homemade knife-coating device. The final dry thickness of the sensing layers was ~5 and ~20 μm for the oxygen and pH sensor, respectively. The cured sensing layers were additionally coated with a translucent thick carbon powder containing a silicone or hydrogel layer for the O₂ and pH optode, respectively. The carbon-containing layer was added to avoid wavelength-dependent scattering from roots and soil.27 DGT. The DGT resin gel used in the sensors was a suspended particulate reagent—iminodiacetate (SPR–IDA).36 The SPR–IDA resin was supplied pre-cleaned as a 1 g suspension. A total of 10 mL of acrylamide (40%, BDH Electran) and 2.5 mL of DGT cross-linker (DGT Research, Ltd.) were mixed together. A total of 1 mL of this mixture was then added to 1 mL of SPR–IDA, which forms a 5% SPR–IDA gel resin solution. To this solution, 14 μL of ammonium persulfate (BDH) and 4 μL of N,N,N,N-tetramethylethlenediamine (TEMED, BDH Electran) were added. The gel solution was then immediately pipetted between two glass plates, where a 0.05 mm spacer was used to ensure that the solution polymerized into a gel with the desired thickness.30 The glass plate assembly was then placed in a 45 °C oven for 1 h, after which the glass plates were separated and the resin gel was placed into 0.5 L of ultrapure water (filtered by Millipore, 18.2 MΩ) and allowed to fully hydrate for a minimum of 24 h. Prior to deployment, the resin gel was sandwiched between two acid-washed polycarbonate filter membranes (Nucleopore, Whatman, 0.4 μm pore size and 10 μm thickness). The combined thickness of the hydrated resin gel and filter membranes was 0.07 mm. The polycarbonate filter membranes served as a diffusion layer for the resin gel and protected it from direct contact with the sediment. To minimize contamination, all preparation and processing of gels was carried out in a laminar...
flow class-100 clean bench within a clean room using ultraclean trace metal techniques.

**Planar Optode Imaging.** Two planar optode systems were applied in this study. They were previously described in detail27,37,38 and will only be described briefly. O2 images were recorded with a fast gateable 12-bit camera through a 590 nm long-pass filter. Excitation light was delivered from four high-power light-emitting diodes (LEDs; λ peak = 445 nm; LXHLLR3C, Luxeon) equipped with a 470 nm short-pass filter. Recorded images were calibrated using the phosphorescent lifetime of known O2 concentrations (saturation in the overlying water and 0% air saturation in anoxic soil), using a modified Stern–Volmer equation.39

The pH images were recorded using a standard digital single-lens reflex camera equipped with a 450 nm long-pass filter. Excitation light was delivered from five high-power ultraviolet (UV) LEDs (λ peak = 405 nm; LZ1-10UA05, LedEngin) equipped with a 405 nm short-pass filter. Recorded images were calibrated using the intensity ratio of the blue and red images recorded simultaneously by the camera, for known pH concentrations using a four parameter sigmoidal curve.27

**Combination of Sensors.** The planar optode foil was attached with tape (Scotch super 33+) to the inside of a transparent rhizotron and, subsequently, overlain by the ultrathin resin gel and filter layer (GFL). The backing membrane that facilitated transport was left on. The GFL was fixed on the top of the planar optode with tape (Scotch super 33+). After deployment, the GFL was rinsed with MQ water and removed from the planar optode, using a Teflon-coated razor blade and plastic forceps. It was placed immediately in a pre-cleaned sealable polythene bag, double-bagged, and stored flat at 4 °C until analysis. Before laser ablation, the GFL was mounted on a 0.04 cm thick hydrogel layer backed by a hydrated polysulphone filter membrane. The stack was left to partially air dry in a class-100 clean bench for 1 h before being placed on thick blotting paper and covered with acid and MQ-washed plastic film. Light pressure was then applied to the stack for 12 h to enable further removal of water from the gels. Finally, the gels were transferred to a gel drier (Bio-Rad model S43) at 50 °C for 8 h. When completely dry, the gel was mounted onto glass panes (6 × 5 × 0.4 cm) with double-sided adhesive tape while maintaining the original area dimensions.28

**Laser Ablation–ICP–MS.** Thermo X series 2 ICP–MS was operated with an Xs high-sensitivity interface and Pt-tipped sampler and microkammer cones. Calibration and detector performance were optimized prior to commencing dry plasma tuning. A Nd:YAG laser (New Wave, Cambridge, U.K.), with wavelength quadrupoled to 215 mm, was equipped with a large format ablation cell (W × L × L = 15.24 × 15.24 × 2.54 cm). Line scans of the gels were conducted at a scanning speed of 100 μm s−1, an interline spacing of 400 μm, a beam diameter of 100 μm, and a repetition rate of 20 Hz.40 The ablation intensity was set at 50%, which equated to a fluence of 0.012 J cm−2. During all runs, laser intensity and fluences were automatically logged to monitor laser stability. ICP–MS was tuned on m/z 7, 29, 59, 89, 115, 175, and 238 by the continuous ablation of a certified reference material, National Institute of Standards and Technology (NIST) 612 glass wafer (https://www-s.nist.gov/srmors/view_detail.cfm?srm=612). In addition, oxide formation (m/z 254/238), ArOH (m/z 57), ArAr (m/z 79), and backgrounds (m/z 5 and 220) were monitored. ICP–MS was used to record 54Cu, 66Zn, 79As, 77Se, 83Kr, 111Cd, and 115In signals; the readout time for a single reading was 0.266 s. See the Supporting Information for a summary of the element-specific limits of detection (LODs). Carbon (m/z 13) was used as an internal standard to cancel out variations in ablation, transport, and ionization efficiency. Data processing was conducted in Excel40 and DGT and optode images were produced in ImageJ 1.46 [National Institutes of Health (NIH), Bethesda, MD].

**RESULTS**

A sensor assembly with an O2-sensitive optode was deployed with a DGT measurement window of 20 × 14 mm centered on a root tip below the soil/water interface and encompassing aerobic and anaerobic root zones (experiment 1 in Figure 2).

![Figure 2. Oxygen distributions, imaged by a planar optode sensor, within a rice seedling rhizosphere. The O2 level (percent air saturation) increased sequentially with the color scale shown from black to white. The outlined position of the DGT ultrathin GFL that is featured in Figure 3 is indicated by white dash markings. This image is part of 36 images recorded in series, with an interval time of 30 min.](image-url)
A pH-sensitive optode was partnered with DGT and deployed against a different set of rice roots (same cultivar, RIL 46) grown in the same soil (experiment 2). In contrast to the \( \text{O}_2 \) optode experiment, the rice grew for 3 weeks in the soil and, in that period, developed a deeper root system. The DGT/optode sensors were positioned 8 cm below the soil–water interface, and a similar suite of metals was measured. In agreement with the first experiment, Fe(II), As, and Pb mobilization at the rice root tips exceeded that of the bulk soil environment, while Co, Ni, and Cu were diminished (Figure 4). Planar optode measurements of \( \text{pH} \) demonstrated a localized acidification around roots of \( \sim \)0.5 pH units, consistent with one- and two-dimensional observations of root-associated \( \text{pH} \) changes,26,43,44 because metal cations are liberated from soil constituent surfaces as \( \text{pH} \) is lowered.45 \( \text{pH} \) changes appear to be at least partially responsible for the observed metal dynamics.

Several other additional lines of evidence for root-intensified metal dynamics associated with local and \( \text{pH} \) minima \( \text{O}_2 \) leakage are available. The homogeneity of metal mobilization was interrogated on a flooded soil-packed rhizotron (experiment 3 in Figure 5). The key features of the soil system without the influence of the rice were uniform two-dimensional flux characteristics, with the overlying water reflecting higher concentrations of Pb, Zn, Cu, and Ni than in the anaerobic zone, which was typified by mobilization of Fe, As, and Co.

**Table 1. DGT Flux Measurements for Pb, Fe, As, Co, and Mn for Experiment 1**

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Fe</th>
<th>As</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>root tip</td>
<td>0.171 ± 0.002</td>
<td>1572 ± 766</td>
<td>0.38 ± 0.1</td>
<td>0.29 ± 0.02</td>
<td>28 ± 1</td>
</tr>
<tr>
<td>microniche</td>
<td>0.166 ± 0.001</td>
<td>730 ± 152</td>
<td>0.04 ± 0.0</td>
<td>0.49 ± 0.09</td>
<td>61 ± 16</td>
</tr>
<tr>
<td>anaerobic bulk soil</td>
<td>0.166 ± 0.000</td>
<td>578 ± 9</td>
<td>0.03 ± 0.0</td>
<td>0.33 ± 0.01</td>
<td>32 ± 1</td>
</tr>
<tr>
<td>aerobic rhizosphere</td>
<td>0.165 ± 0.000</td>
<td>58 ± 3</td>
<td>0.01 ± 0.0</td>
<td>0.24 ± 0.02</td>
<td>30 ± 1</td>
</tr>
</tbody>
</table>

Average ± standard deviation for 50 averaged measurements, each 0.24 mm².
phenomenon in submerged soils\textsuperscript{49} and fuel-localized, microbial-driven reductive mobilization of Fe, Mn, and associated trace metals.\textsuperscript{48} Such a feature was observed approximately 8 mm away from the root apex (Figure 3). Fluxes of Fe and Mn in the microniche were statistically different from either the bulk soil or root tip (Mann–Whitney test; $p < 0.0001$; $n = 50$; 0.24 mm$^2$ averaged measurements). However, the most prominent trends were the high fluxes observed in Pb, Zn, Cu, and Ni. The elemental ratios of mobilized metals and the morphological characteristics of this microniche were similar to those observed previously for microniches\textsuperscript{50} and distinctly different from those observed adjacent to the root, indicating their mechanistic separation (see Figure S2 of the Supporting Information).

\section*{DISCUSSION}

Our findings are consistent with a series of finely poised competitive processes. The two main mechanisms to be considered are the physicochemical process of Fe(II) diffusion and its chemical oxidation. As Fe(II) diffuses from the reduced zone of submerged soil to an adjacent oxidized zone, it accumulates as precipitated Fe(III) iron; this removal of Fe from solution by oxidation is clearly visualized for the first time (Figure 3) by simultaneous DGT and optode measurements. However, the most prominent trends were the high fluxes observed in Pb, Zn, Cu, and Ni. The elemental ratios of mobilized metals and the morphological characteristics of this microniche were similar to those observed previously for microniches\textsuperscript{50} and distinctly different from those observed adjacent to the root, indicating their mechanistic separation (see Figure S2 of the Supporting Information).

Acidification by H$^+$ release from roots, other efflux processes, and microbial metal release may further compound the process, but these mechanisms alone do not explain the tight association between O$_2$ diffusion and Fe mobility, with a similar mobility maxima being observed in the absence of a plant (see Figure S1 of the Supporting Information).

Diffusion gradients or a depletion of Fe(II) was not observed in the anaerobic bulk soil immediately adjacent to metal flux maxima (Figure 3). On the basis of models of Fe(II) diffusion toward the oxidation zone\textsuperscript{25} and considering the microscale resolution of the measurements, a decrease in Fe(II) would have been predicted. The oxidation rate and Fe(II) resupply from the bulk soil could partially account for this, because this

\begin{equation}
4\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} = 4\text{FeOOH} + 8\text{H}^+
\end{equation}
would impact the net rate of oxidation and the distribution of iron species in the soil. The slower the rate, the further the oxidation front would develop and the more effectively Fe(II) diffusion would be able to match Fe(II) consumption via oxidation. A faster rate would result in smaller depletion zones, less dispersion into the soil, and hence, greater iron accumulation near the root surface. Higher Fe concentrations would give rise to a larger net rate of oxidation.

The rice rhizosphere is an element sink maintained by radial O$_2$ loss, while adjustments to the redox equilibrium can cause localized accretions to disperse. Such variations may provide a possible explanation of what is being observed at the root tips, namely, diffusion of Fe(II) to the surrounding anaerobic soil, as indicated in Figure 6. In contrast, Figure 6 shows that, in regions of the root zone aerobic/anaerobic interface, where the Fe(II) flux maxima was not observed, there is a diffusion gradient of Fe(II) from the bulk soil toward the redox interface. In a highly dynamic system, as evident around the root apexes (Figures 3 and 4), multiple diffusion—oxidation reactions would be overlaid, with the DGT measurement providing a summation of these processes.

Rice plants immobilize trace metals in the root zone, which ensures protection from toxicity, but at the same time must mine this elemental resource for essential nutrients. It is in this paradox that the functionality of the dynamic and heterogeneously distributed Fe plaques arises. The low Co, Ni, Cu, and Zn fluxes observed around the root tip might simply be due to competition from other sinks, i.e., plant or microbial uptake. However, given that this phenomenon only occurred specifically within the As, Pb, and Fe(II) mobilization maxima whether or not they formed in the presence of a plant, this suggests a geochemical process.

The sorption of trace metals to Fe oxides is pH-sensitive, but it is also well-established that elemental retention is in proportions that both reflect solution composition and element-specific binding properties. Freshly formed oxy-hydroxides act as highly reactive surfaces for rapid immobilization of trace metals by sorption, yet these most reactive phases are very amorphous and more susceptible to rapid dissolution. Pb has a particularly high affinity for Fe oxide, with binding constants at least an order of magnitude higher than Ni, Cu, Co, and Zn. We hypothesize that the localized mobilization of Pb in the root zone developed because the desorptive release of Pb was faster than its concomitant removal as fresh iron oxide forms. This proportionally higher release rate for Pb would be aided by the reservoir/pool of Fe-oxide-captured Pb being greater than that of the other metals. For the metals that do not partition so strongly, namely, Co, Ni, Cu, and Zn, their pH-mediated desorptive release did not outweigh their overall removal at any point in the concentration gradient.

The co-occurrence of As and Fe flux maxima is not unexpected. Arsenic is readily retained on Fe oxides, and their release often coincides. Meanwhile, with the redox threshold for the Fe(III)/Fe(II) transition lying close to the arsenate/arsenite boundary, the transformation to arsenite would favor a more rapid and extensive desorption. Other mechanisms also are viable. Acid-soluble phosphate pools can account for 90% of the phosphate taken up in the rhizospheres of lowland rice. This includes phosphates sorbed to ferrous carbonates and hydroxides and fractions that are immobilized by Fe(II)-bridging mechanisms to negatively charged surfaces. An analogous situation may also be occurring in the case of arsenic release here. Fe dissolution mechanisms could also play a role, but the time scale for this transformation would be greater. Natural organic matter (NOM) release in flooded soils can be substantial, occurring in less reducing conditions and faster than Fe(II) mobilization. NOM can promote desorption of metals and arsenic from solid phases by altering soil/solution equilibrium, both directly by binding elements via ligand-exchange reactions or mediating changes in redox conditions.

Root iron plaques are a ubiquitous feature of wetland systems, forming a discontinuous precipitate that encapsulates the roots of not only rice but also many other aquatic plants. It is perhaps surprising that rice exhibits such an inclination to accumulate As and Pb if root plaques functioned solely to block metal uptake. This demonstration of mobilization of metals within the plaque provides a new perspective in understanding the supply of micronutrients and contaminants in both rice cultivation and wetland soils more generally.

**ASSOCIATED CONTENT**

**Supporting Information**

Soil characterization (Table S1), LODs (Table S2), artificial root experiment (Figure S1), and comparison of geochemical trends in the root tip and microniche zones (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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