Goldschmidt2019 Abstract

Fe acquisition by coumarins; an interplay between ligand-controlled and reductive dissolution

WALTER D.C. SCHENKEVELD[1*], KYOUNGLIM KANG[2], STEPHAN M. KRAEMER [2]

[1] Environmental Sciences, Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, Netherlands
[2] Environmental Geosciences, University of Vienna, Althanstrasse 14 UZAII 1090 Vienna, Austria
(*correspondence: w.d.c.schenkeveld@uu.nl)

Recently it was established that plants employing Strategy I Fe acquisition (all plants except for grasses) strongly upregulate the exudation of coumarin compounds under conditions of low Fe availability. This suggests that coumarins, which have reducing and ligating properties, may enhance the Fe concentration in soil solution. The mechanism by which these compounds enhance Fe availability, as well as how their effectiveness is affected by environmental parameters (pH, P_{O2}) had however remained unexplored. These issues have been addressed in the current work.

A series of kinetic batch dissolution experiments were carried out in which several coumarins (esculetin, scopoletin and fraxetin) interacted with Fe(hydr)oxide minerals (lepidocrocite, goethite and ferrihydrite), under oxic and anoxic conditions, in presence and absence of the Fe(II) scavenger Ferrozine and over a wide environmentally relevant pH range (4 – 8.5). Fe(II) and Fe(III) solution concentrations were measured over time and the corresponding dissolution rates were determined.

At low pH values, exclusively Fe(II) was mobilized through reductive dissolution. At circumneutral pH, both Fe(II) and Fe(III) were mobilized, indicating the formation of stable, soluble Fe-coumarin complexes for both Fe redox species. Counterintuitively, under oxic conditions, and in the presence of Ferrozine, the Fe(III) mobilization rate decreased. This suggests Fe mobilization by coumarins at circumneutral pH is autocatalyzed: the Fe(II) generated by surface Fe reduction catalyzes the ligand-promoted dissolution of Fe(III); removal of this Fe(II) from the mineral surface, either through oxidation or through Fe(II) scavenging, eliminated the catalysis. Our findings indicate an intricate interaction between reductive and ligand-controlled dissolution in the mechanisms by which coumarins enhance the bioavailability of Fe to plants.