

# Effect of oxygen on synergistic interactions between reductive and ligand-promoted Fe mobilization

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Iron (Fe) is an essential micronutrient that limits primary productivity in vast areas in both marine and terrestrial environments. Plants and microorganisms employ strategies for Fe acquisition based on exudation of ligands and reductants. Recently, it was demonstrated that the combined reactivity of ligands and reductants can synergistically enhance Fe mobilization from soil with low Fe bioavailability<sup>1</sup>. Such synergistic effects can be caused by Fe(II) catalyzing ligand-controlled dissolution of Fe(hydr)oxide minerals<sup>2</sup>. Such synergistic interactions may play a crucial role in the persistence of species in ecosystems with low Fe bioavailability.

The conditions under which synergistic Fe mobilization in soil was experimentally established differ considerably from those in environmental systems such as the rhizosphere, for instance with respect to oxygen partial pressure ( $pO_2$ ). To identify how synergistic Fe mobilization is affected by the  $pO_2$ , and to establish how synergistic Fe mobilization is constrained by the geochemistry of soils under natural conditions, a series of kinetic batch experiments was performed.

The plant siderophore 2'-deoxymugineic acid (DMA) and ascorbate, both found in root exudates, were used as model ligand and reductant, respectively. They were applied to a Spanish calcareous clay soil with low Fe bioavailability, both in separate and combined treatments. Experiments were performed in ambient air (oxic conditions) and under a  $N_2$  atmosphere (anoxic conditions).

Synergistic Fe mobilization was observed both under oxic and anoxic conditions. Surprisingly, the synergistic effect proved larger under oxic conditions. This suggests that either synergistic Fe mobilization from soil is not based on catalysis by Fe(II), or the residence time of Fe(II) in soil suspension is not substantially enhanced under anoxic conditions. The adverse effect of anaerobic conditions on Fe mobilization was attributed to enhanced mobilization of metals competing for complexation by DMA, particularly of cobalt and nickel. These findings indicate that a low  $pO_2$  in the rhizosphere compared to ambient atmosphere is not needed for accommodating synergistic Fe mobilization and that the process could likely be important under (typically) oxic rhizosphere conditions.

<sup>1</sup> Schenkeveld et al.,(2016) *Environ. Sci. Technol.* 2016, 50, 12, 6381–6388

<sup>2</sup> Kang et al.,(2018) *Environ. Sci. Technol.* 2019, 53, 1, 98–107