

## Fe(II) oxidation kinetics and Fe hydroxyphosphate precipitation upon aeration of anaerobic (ground)water

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Exfiltration of anaerobic Fe-rich groundwater into surface water plays an important role in controlling the transport of phosphate (P) from agricultural areas to the sea. Previous laboratory and field studies showed that Fe(II) oxidation upon aeration leads to effective immobilization of dissolved P during the initial stage of the Fe(II) oxidation process resulting in P-depleted water before Fe(II) is completely consumed [1] [2]. Although the removal of P was attributed to the precipitation of Fe hydroxyphosphates, the relationship between the kinetics of the reaction and the composition of the solution and the produced solids is still unclear. From a series of batch experiments with synthetic water and groundwater, in which we continuously measured the H<sup>+</sup> production during the Fe(II) oxidation reaction, we gained new insights in Fe(II) oxidation kinetics and P/Fe stoichiometry of the Fe hydroxyphosphates as function of pH, the initial aqueous P/Fe ratio and reaction progress.

In the presence of dissolved P, oxidation of Fe(II) led to the formation of Fe hydroxyphosphates whose P/Fe ratios remained constant throughout the reaction despite the change in P/Fe ratio in the solution. However, the P/Fe ratio of the solids varied depending on initial P/Fe ratio and pH value.

Presence of dissolved P exerted influence on the rates of Fe(II) oxidation. In general, Fe(II) oxidation proceeded slower in the presence of dissolved P but consumption of P caused additional retardation. Although the dependency of the reaction rates on P concentration might be complicated, the progress of the reaction in our experiments could be described using a pseudo second-order rate law with first-order dependencies on P and Fe(II) concentrations.

After P depletion, Fe(II) oxidation followed pseudo first order kinetics, however, the first-order rate constants after P depletion were lower compared to Fe(II) oxidation in a P free solution. This implies that the initially formed Fe hydroxyphosphate affects the kinetics of continuing Fe(II) oxidation after PO<sub>4</sub> depletion.

[1] Voegelin et al. (2013) *GCA* **117**, 216-231. [2] Van der Grift et al. (2014) *HESS* **18**, 4687-4702