

## Iron oxidation kinetics and phosphorus immobilization at the groundwater-surface water interface

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Eutrophication of freshwater environments following diffuse nutrient loads is a widely recognized water quality problem in catchments. Fluxes of non-point P sources to surface waters originate from surface runoff and flow from soil water and groundwater into surface water. The availability of P in surface waters is controlled strongly by biogeochemical nutrient cycling processes at the soil-water interface. The mechanisms and rates of the iron oxidation process with associated binding of phosphate during exfiltration of anaerobic Fe(II) bearing groundwater are among the key unknowns in P retention processes in surface waters in delta areas where the shallow groundwater is typically pH-neutral to slightly acid, anoxic, iron-rich.

We developed an experimental field set-up to study the dynamics in Fe(II) oxidation and mechanisms of P immobilization at the groundwater-surface water interface in an agricultural experimental catchment of a small lowland river. We physically separated tube drain effluent from groundwater discharge before it entered a ditch in an agricultural field. The exfiltrating groundwater was captured in in-stream reservoirs constructed in the ditch. Through continuous discharge measurements and weekly water quality sampling of groundwater, tube drain water, exfiltrated groundwater, and ditch water, we quantified Fe(II) oxidation kinetics and P immobilization processes across the seasons.

This study showed that seasonal changes in climatic conditions affect the Fe(II) oxidation process. In winter time the dissolved iron concentrations in the in-stream reservoirs reached the levels of the anaerobic groundwater. In summer time, the dissolved iron concentrations of the water in the reservoirs are low, indicating that dissolved Fe(II) is completely oxidized prior to inflow into the reservoirs. Higher discharges, lower temperatures and lower pH of the exfiltrated groundwater in winter compared to summer shifts the location of the redox transition zone, with Fe(II) oxidation taking place in the soil surrounding the ditch during summer and in the surface water during winter. The dynamics in Fe(II) oxidation did not affect the dissolved P concentrations. The dissolved P concentrations of the in-stream reservoirs water were an order of magnitude lower than observed in the groundwater and have no seasonal trend. Our data showed preferential binding of P during initial stage of the Fe(II) oxidation process, indicating the formation of Fe(III)-phosphate precipitates. The formation of Fe(III)-phosphates at the groundwater-surface water interface is an important geochemical mechanism in the transformation of dissolved phosphate to particulate phosphate and therefore a major control on the P retention in natural waters that drain anaerobic aquifers.