

---

## PHOSPHORUS AND IRON CYCLING IN UNIT-PROCESS TREATMENT WETLANDS

Jean-Paul Wallis, Rachel Scholes, Aidan Cecchetti, David Sedlak

NSF Engineering Research Center for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt) at University of California, Berkeley

### BACKGROUND

Unit-process wetlands are a proven and promising new technology for polishing wastewater effluent<sup>1,2</sup>. Open water and subsurface wetlands, modeled after natural ecosystems, are two types of unit-process wetlands that can inexpensively remove a suite of common contaminants from wastewater effluent while simultaneously creating wildlife habitat and aesthetic open spaces.

A pilot-scale site located at the Oro Loma Sanitary District wastewater treatment plant employs an open-water wetland followed by a planted subsurface wetland (*Figure 1*). The primary purpose of these two unit-process wetlands is to remove nutrients (nitrate and phosphorus) and trace organic contaminants from treated wastewater. The open water wetland allows for optimal sunlight penetration into the water column, while the twelve subsurface wetland cells were designed to test the impact of substrate and plant type on contaminant removal. The specific designs of these two unit-process wetlands enhance photochemical and biotransformation processes to treat wastewater effluent.

The primary objective of our research aims to investigate the removal of phosphorus through in-situ iron oxidation. Iron oxide minerals (e.g. FeOOH) present in wetland substrates have high surface areas with acute affinities for phosphate<sup>3,4</sup>. Consequently, subsurface iron could be harnessed to remove phosphorus. The biogeochemical cycling of phosphorus and iron suggest a combined study to better understand their co-influence in unit-process wetlands.

### HYPOTHESES

Nitrified wastewater effluent typically contains phosphorus and trace levels of iron, but based on preliminary data the subsurface wetland is expected to leach iron and phosphorus from the installed media due to reductive dissolution of Fe(III) minerals. Due to the high phosphate sorption capacity of iron minerals, immobilization of phosphorus and iron in the oxic portions of the wetland (such as the layer closest to the ground surface) is hypothesized. Meanwhile, release of phosphorus is expected in the deep subsurface where iron is biologically reduced.

### METHODS

Samples were collected in triplicate from the subsurface wetland at Oro Loma, filtered, and stored on ice while being transported back to UC Berkeley where they were refrigerated without additional preservation. Samples from the influent to the subsurface as well as the effluent of each cell were collected every two weeks. Periodically, additional samples were collected from intermediate wells or through a pore-water sampler.

Several methods were used to investigate the concentrations of phosphorus and iron species. Total phosphorus was measured colorimetrically on a UV-Vis spectrophotometer at 880 nm following acid persulfate digestion and the addition of an ascorbic acid combined reagent<sup>5</sup>. Total P concentrations in the influent, effluent, intermediate well, and pore-water samples were measured by persulfate digestion. Ion chromatography (IC) was used to measure dissolved orthophosphate concentrations. Samples were also analyzed through inductively coupled plasma mass spectrometry (ICP-MS) to quantify iron concentrations. ICP-MS samples

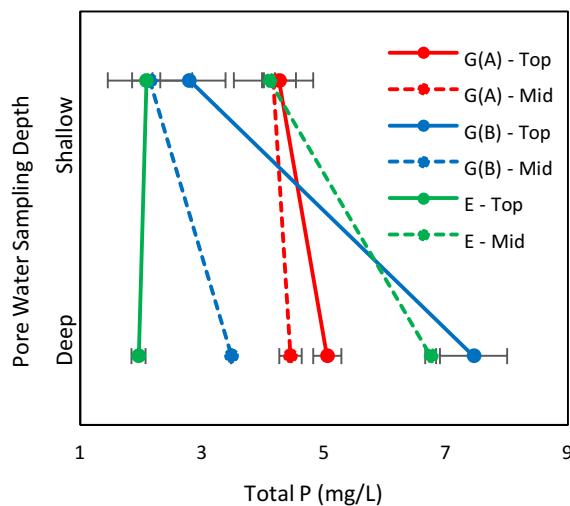


**Figure 1:** View of subsurface wetland cells at the Oro Loma Sanitary District.

were acidified either in the field or back at the laboratory. The effects of pH on iron and phosphorus dynamics were also investigated: wetland influent was spiked with 0.5 mM iron(II) or iron(III) followed by pH adjustment to pH 8 or 9 (similar to subsurface observations) using 1N sodium hydroxide. Phosphorus and iron concentrations were then measured over time using the total phosphorus protocol and ICP-MS.

## RESULTS

Some of the key findings from our research are shown in *Figures 2-3*. Total P concentrations were greater than orthophosphate for the same sample sites at Oro Loma indicates the presence of organic or adsorbed phosphorus up to seven times the phosphorus measured by IC (e.g. 14.5 vs. 1.8 mg/L, data not shown). These forms of phosphorus were expected at the site but were not measured by previous monitoring. Investigating the pore water in the subsurface cells revealed a depth gradient of phosphorus (*Figure 2*), with on average 52% higher concentrations of total P in deep pore water versus near-surface samples. Key parameters that change with depth include oxygen and pH. Higher P concentrations seen at lower depths are likely due to release of adsorbed P during iron (III) reduction. Therefore, we designed an experiment to replicate iron oxidation at relevant pH conditions and measured

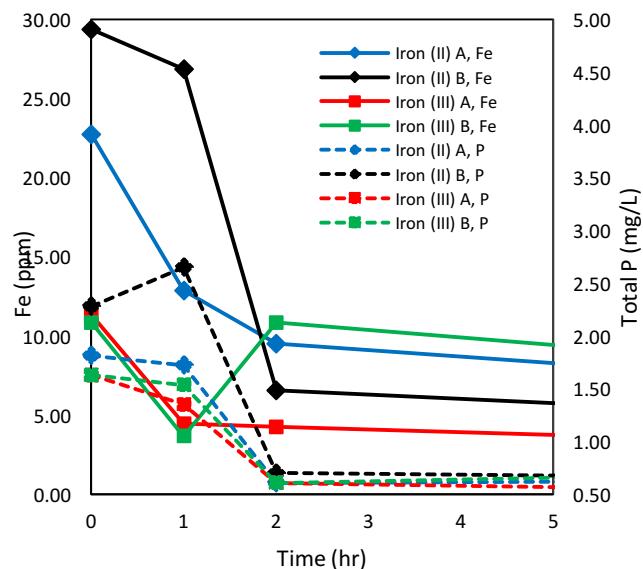


**Figure 3:** Depth profiles of total phosphorus concentration for the top and middle sections of subsurface cells G and E

total P and dissolved iron over time (*Figure 3*). We found that a 0.5 mM concentration of iron (II) or iron (III) led to >50% total P removal via observable iron flocculation within two hours. Reductive dissolution of iron (III) is expected to lead to the observed leaching of phosphorus from the subsurface cells (orthophosphate concentrations increased from influent to effluent of every subsurface cell by 48-266%, avg. 108%, data not shown).

## DISCUSSION

To reduce leaching and develop a phosphorus removal process, the Oro Loma wetland system could cycle the influent between anoxic and oxic conditions. An alternative is to involve a post-subsurface oxidation pond or ditch that allows for flocculation and removal of the phosphate-rich iron oxide precipitates. The unit-process wetlands approach is essential to this system due to the necessarily sequential oxic and anoxic treatment requirements. Although iron and phosphorus cycling warrants further study, this investigation encourages unit-process wetlands as a viable tool for controlling phosphorus emissions in wastewater effluent.



**Figure 2:** Phosphorus and iron concentration over time in sample wastewater spiked with 0.5 mM iron (II) and (III).

---

## **ACKNOWLEDGEMENTS**

The main author of this extended abstract would like to thank the Sedlak lab group for their continued support, Angela Perantoni for her help in the field, Dr. Pam McLeod, ReNUWIt, and the National Science Foundation.

## **REFERENCES**

- (1) Jasper, J. T., Jones, Z. L., Sharp, J. O., & Sedlak, D. L. (2014). Nitrate removal in shallow, open-water treatment wetlands. *Environmental science & technology*, 48(19), 11512-11520.
  - (2) Jasper, J. T., Jones, Z. L., Sharp, J. O., & Sedlak, D. L. (2014). Biotransformation of trace organic contaminants in open-water unit process treatment wetlands. *Environmental science & technology*, 48(9), 5136-5144.
  - (3) Chacon, N., Silver, W. L., Dubinsky, E. A., & Cusack, D. F. (2006). Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound. *Biogeochemistry*, 78(1), 67-84.
  - (4) Burgin, A. J., Yang, W. H., Hamilton, S. K., & Silver, W. L. (2011). Beyond carbon and nitrogen: how the microbial energy economy couples elemental cycles in diverse ecosystems. *Frontiers in Ecology and the Environment*, 9(1), 44-52.
  - (5) Dayton, E. A., Whitacre, S., & Holloman, C. (2017). Comparison of three persulfate digestion methods for total phosphorus analysis and estimation of suspended sediments. *Applied Geochemistry*, 78, 357-362.
-