

Shallow, open water unit process wetlands for produced water treatment

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Motivation

- Unconventional oil and gas production, and specifically hydraulic fracturing, is becoming increasingly prominent to meet the world's growing demands for energy
- Unfortunately it produces large volumes of wastewater ranging from subsurface brines (i.e., produced water) to slurries of produced water mixed with chemical additives necessary for the fracturing process (i.e., flowback water)
- Produced and flowback water composition varies considerably from basin to basin, however salinity, organic constituents, excess nutrients, metals, and radionuclides are common concerns
- Treatment is challenged by salinity and organic loading, resulting in membrane fouling, high energy demand, and increased costs
- The incorporation of shallow, open water unit process wetlands in a produced water treatment scheme may lower costs and energy demands, decrease membrane fouling, and effectively remove excess nutrients, metals and radionuclides

Existing Case Study: Prado Wetlands, CA



- Shallow, open water wetlands have acted as a municipal wastewater polishing step for ~30 years in Orange County, CA
- Pilot scale unit process wetlands have demonstrated significant nitrate, trace organic, and pathogen removal via microbial and photolytic degradation processes [1, 2, 3]
- Diffuse, stratified biomats develop rapidly due to low flow rates (~0.06 cm s⁻¹), shallow depths (< 20 cm), and the absence of vegetation
- Photosynthetic diatoms produce diurnal oxygen and pH fluctuations in the water column
- Denitrifying and sulfate reducing conditions are present at depth within the biomat
- This redox stratification creates a unique environment for both aerobic (in the water column) and anaerobic (within the biomat) biological contaminant removal processes

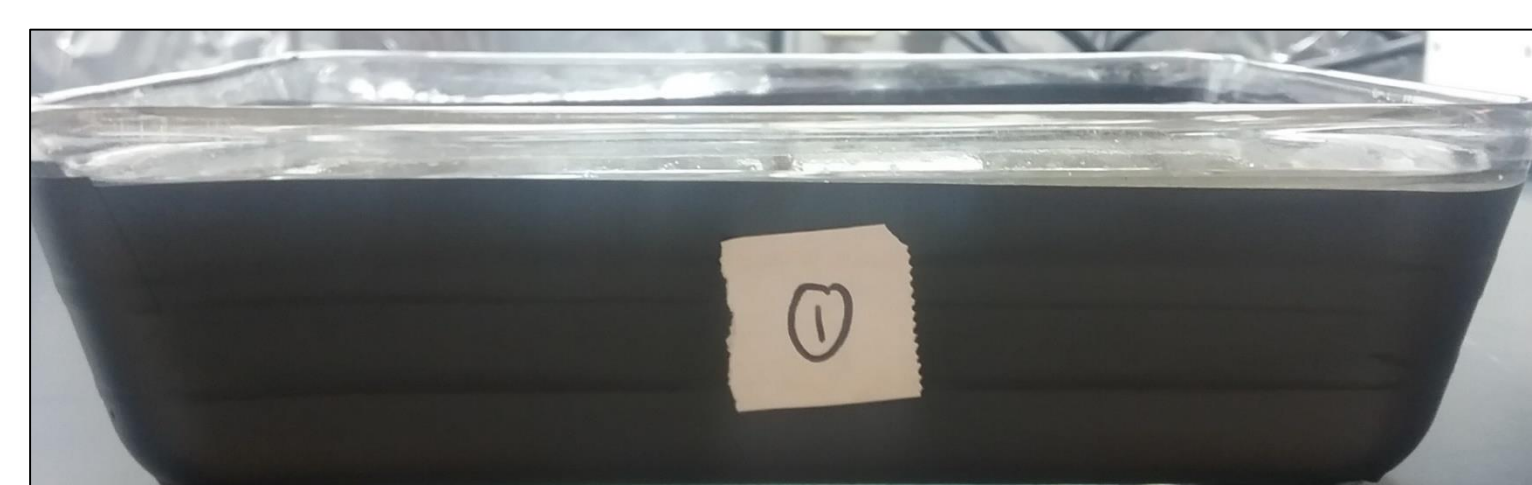
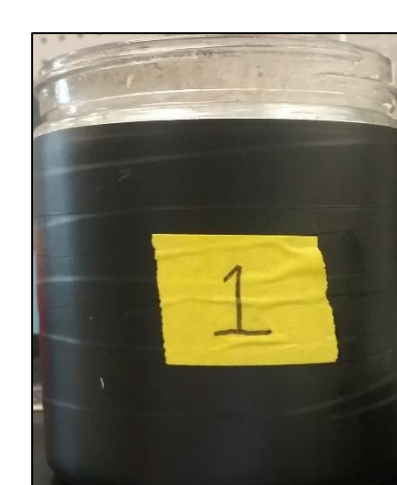
Project Objectives

- Determine how biomass collected from Prado wetlands acclimates and responds to a saline produced water environment.
- Preliminarily estimate nutrient and metal removal efficiencies and kinetics.
- Highlight the role of photosynthetic diatom communities in the oxidation and subsequent removal of ammonia.

Approach

The first phase of this project aims to understand the efficacy for wetlands to treat excess nutrients and trace metals in the presence of salinity, but absence of organics. Hence, all produced water utilized to date has been pre-treated by a biologically active filtration system to reduce organic loading.

Biomass from Prado wetlands was inoculated in flow through and batch systems to understand how diatom and bacterial periphyton communities function in a saline produced water environment. Preliminary examination of nutrient and metal removal efficiencies were performed.



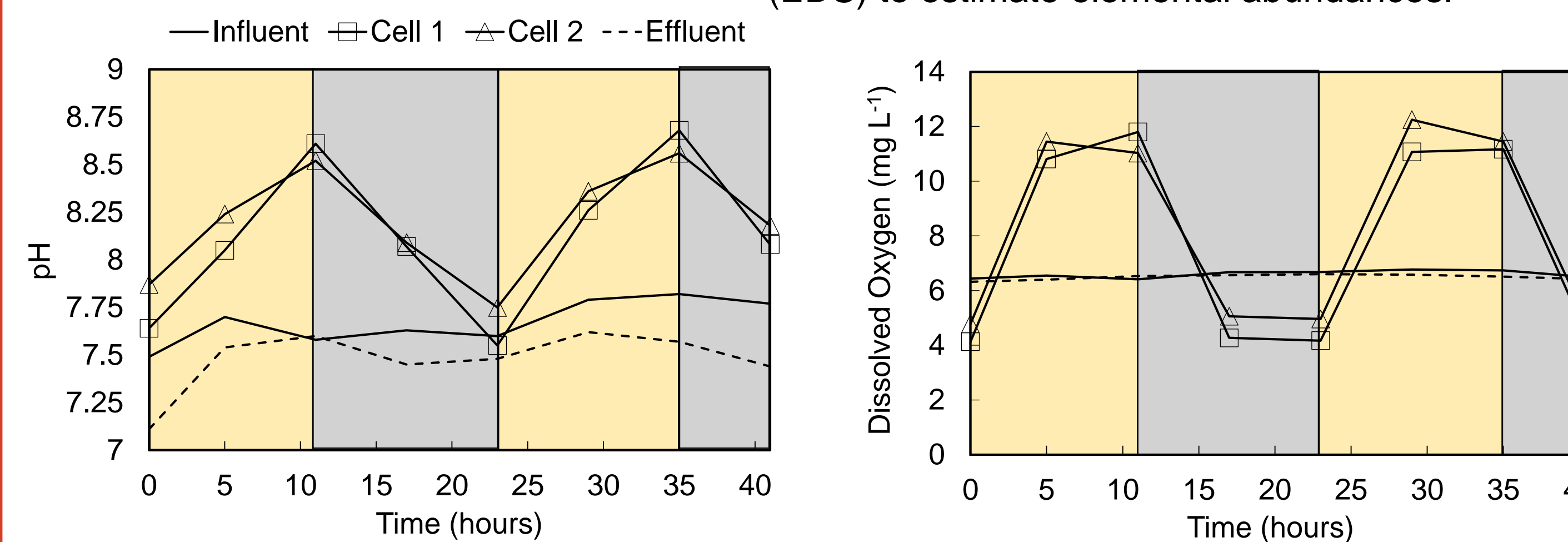
Preliminary Results

Bench Scale Flow Through System

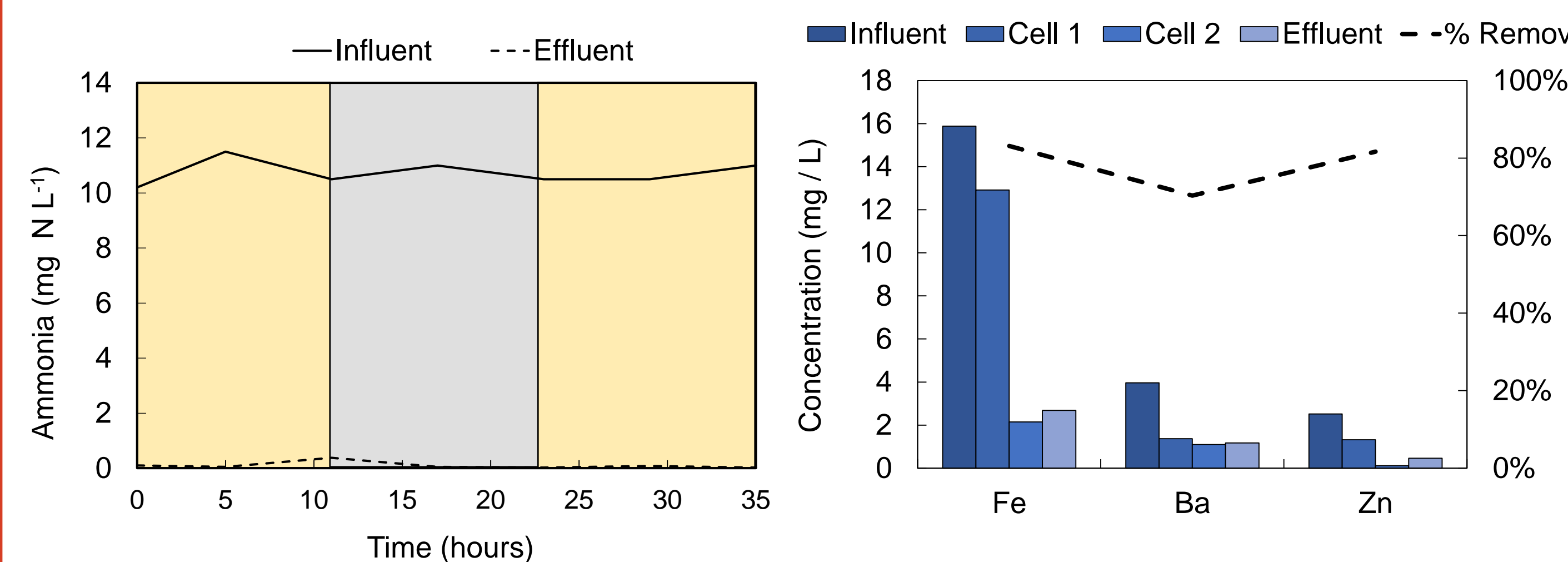
Design. Two rectangular Pyrex cells (~1.5 L) were inoculated with biomass from an active shallow, open water treatment wetland in California (Prado) with a solid to liquid ratio of ~ 1:3. Cells were assembled in series and fed with a produced water solution (~ 10 g L⁻¹ salinity) with a hydraulic residence time of ~ 3.8 days, and within a light chamber that operates on ~ twelve hour on / off cycles to simulate diurnal light cycling.



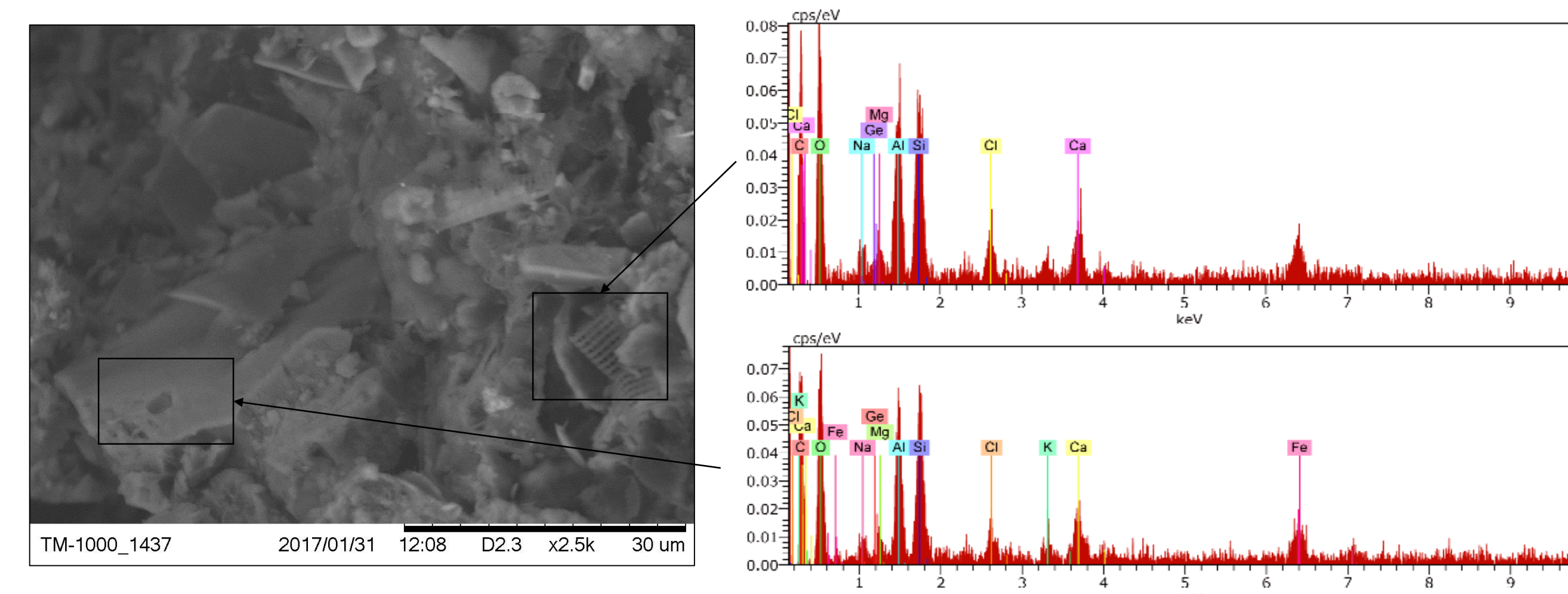
Monitoring. pH, dissolved oxygen, conductivity, temperature, and water level were measured in the morning and evening of each cell, as well as the influent and effluent reservoirs. After three weeks of acclimation (i.e., once the system had stabilized), a 40-hour removal experiment was conducted to quantify ammonia removal and metal immobilization. Biomass was examined under a scanning electron microscope (SEM) equipped with electron dispersive spectroscopy (EDS) to estimate elemental abundances.



Periods exposed to light (shaded yellow) demonstrated increasing pH and dissolved oxygen values, suggesting photosynthesis, whereas dark periods (shaded gray) demonstrated decreases in these parameters, suggesting respiration. Such diurnal fluctuations are comparable to trends observed in full and pilot scale open water unit process wetlands.



Ammonia removal efficiency of 99% (~ 10 mg N / L) was achieved, with approximate removal rates of 3 mg NH₃-N day⁻¹. Metals commonly found in produced water precipitated out within cells yielding removal efficiencies between ~ 70 and 83 %.

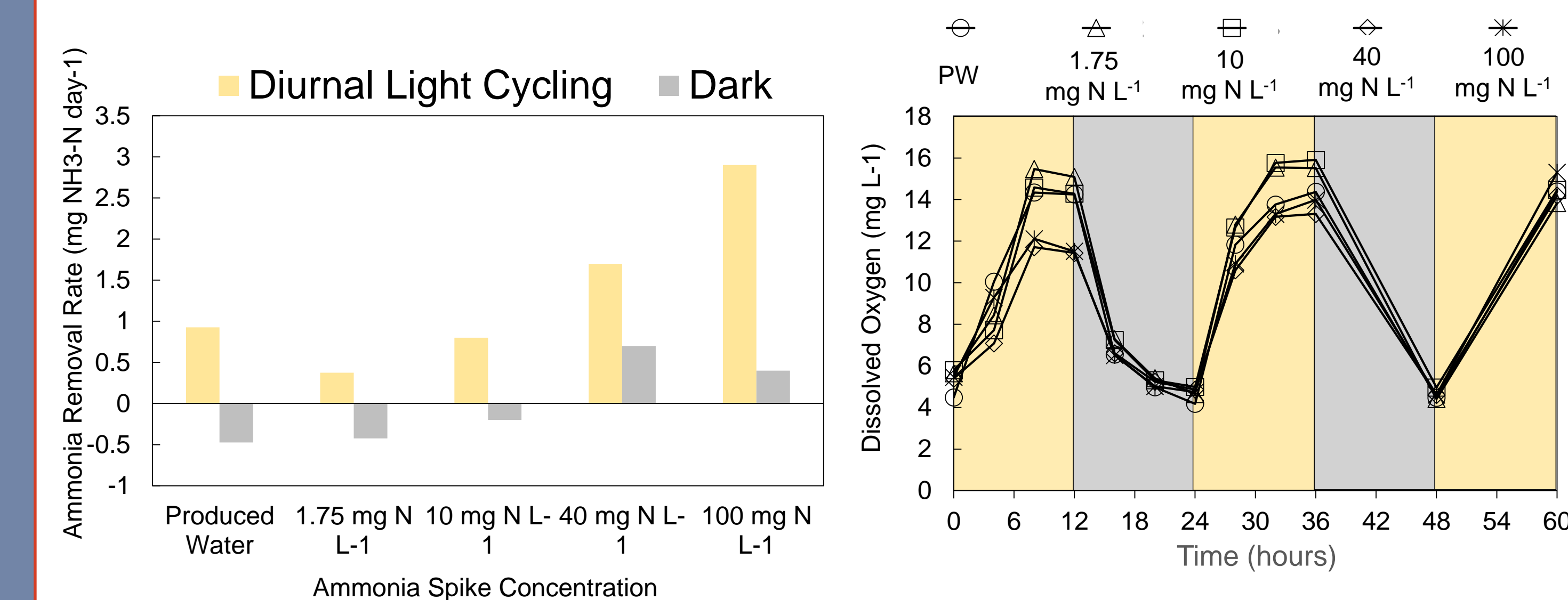


SEM images of wetland biomass acclimated in biologically active filtered produced water show the presence of photosynthetic diatoms and platey mineral phases. EDS data highlights silicon and oxygen abundance associated with diatom cell membranes and detectable aluminum and iron signatures associated with mineral phases, which may act to adsorb trace metals.

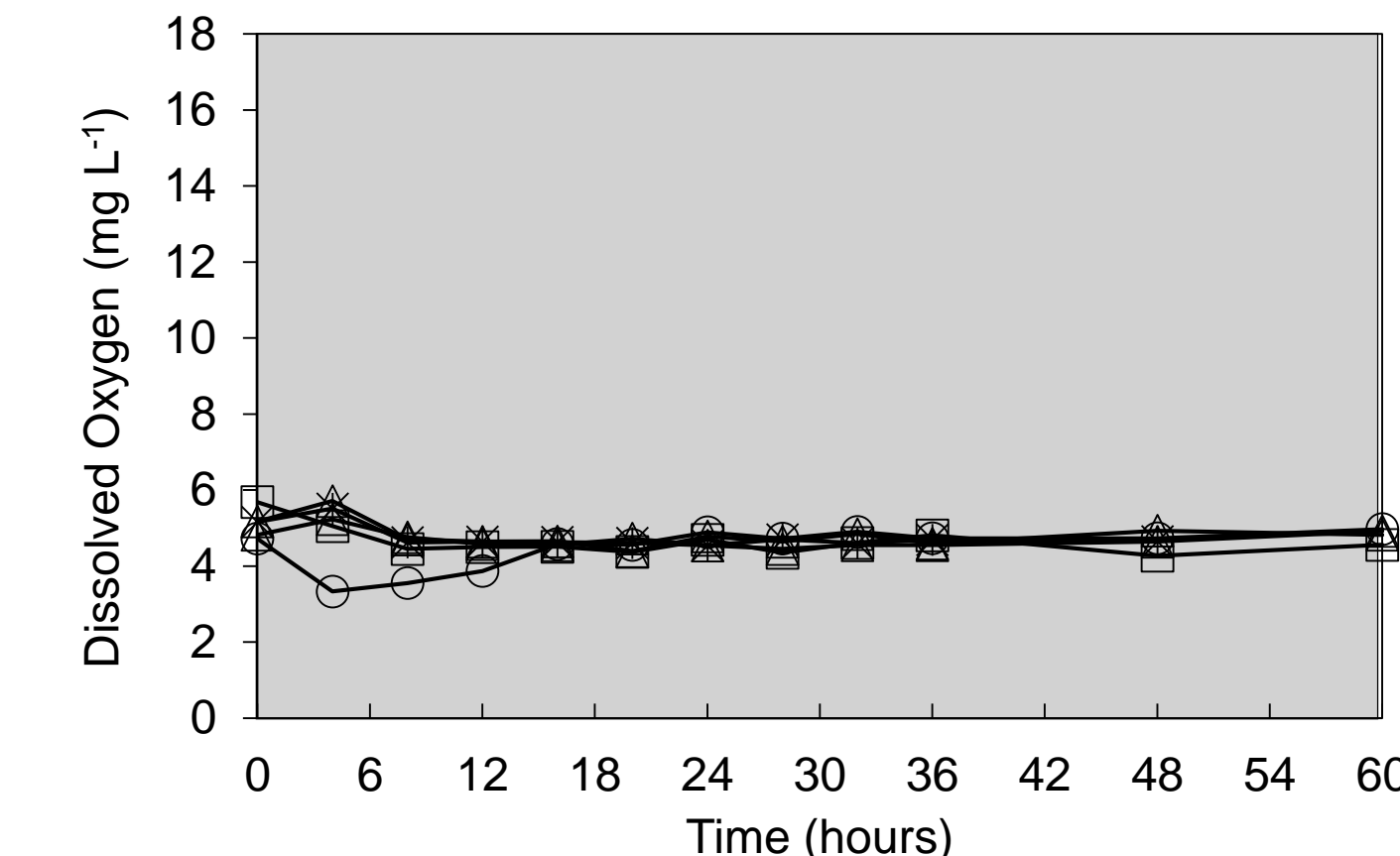
Preliminary Results (cont.)

Bench Scale Batch Systems

Design. Ten batch reactors (500 mL) were inoculated with biomass from Prado wetlands with a solid to liquid ratio of 1:3. Reactors were acclimated with produced water (~ 25 mg N L⁻¹, ~ 28 g L⁻¹ salinity) under diurnal light cycling conditions for 11 days by supplying ~ 1 mg N L⁻¹ day⁻¹ in order to offset evaporative losses and provide nutrients for cell growth. After stabilization, five reactors were placed in dark conditions while the remaining five stayed in the light chamber. Reactors in each condition were spiked with ammonia such that the concentration would increase by 1.75, 10, 40, and 100 mg N L⁻¹ to understand how removal varies across ammonia gradients and in the presence and absence of diurnal oxygen fluctuations. One permutation was spiked with produced water (~ 1.75 mg N L⁻¹ increase).



Diurnal dissolved oxygen fluctuations observed in the oscillating light condition were absent in the dark incubated condition. Further, ammonia removal rates were significantly higher under all ammonia spike permutations inside the light chamber, suggesting that the production of oxygen by photosynthetic diatoms promotes and enhances the oxidation and removal of ammonia from produced water.



Relevance & Future Work

Shallow, open water unit process wetlands may be a cost effective option for removing ammonia from produced water with pre-treatment to decrease organic loading. The natural production of oxygen by photosynthetic diatom communities appears to enhance ammonia removal, making this system unique relative to mainstream aeration operations, which are both cost and energy intensive. Furthermore, metal removal may decrease membrane fouling in downstream treatment operations.

Future work includes formally quantifying ammonia removal kinetics, delineating the role of ammonium oxidizing bacteria through the use of 16S rRNA sequencing and the identification of ammonium oxidizing genes, exploring the potential syntrophic interactions between photosynthetic diatom communities and ammonium oxidizing bacteria, and testing results across salinity gradients.

References

- Jasper et al. (2013). Environ. Eng. Sci. 30(8), 421 – 436.
- Jasper et al. (2014a). Environ. Sci. Tech. 48(9), 5136 – 5144.
- Jasper et al. (2014b). Environ. Sci. Tech. 48(19), 11512 – 11520.

Acknowledgements

