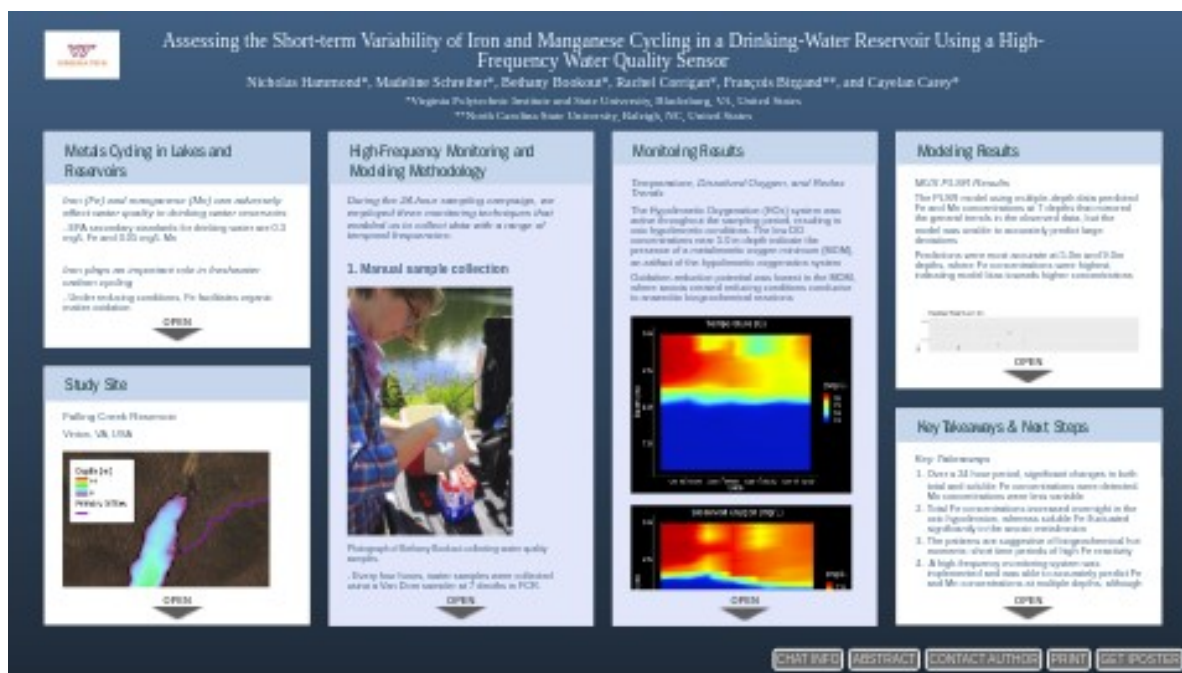# Assessing the Short-term Variability of Iron and Manganese Cycling in a Drinking-Water Reservoir Using a High-Frequency Water Quality Sensor

Nicholas Hammond*, Madeline Schreiber*, Bethany Bookout*, Rachel Corrigan*, François Birgand**, and Cayelan Carey*

*Virginia Polytechnic Institute and State University, Blacksburg, VA, United States
**North Carolina State University, Raleigh, NC, United States

PRESENTED AT:

METALS CYCLING IN LAKES AND RESERVOIRS

Iron (Fe) and manganese (Mn) can adversely affect water quality in drinking water reservoirs

- EPA secondary standards for drinking water are 0.3 mg/L Fe and 0.05 mg/L Mn

Iron plays an important role in freshwater carbon cycling

- Under reducing conditions, Fe facilitates organic matter oxidation

- Under oxidizing conditions, Fe promotes the immobilization of organic matter via complexation/adsorption processes

Therefore, understanding the dynamics of Fe and Mn in freshwater systems is important for properly managing drinking water sources, as well as understanding the vital role that these systems play in carbon cycling

Fe and Mn have predictable seasonal trends in lakes and reservoirs, which are dictated by the presence and magnitude of thermal stratification in the summer...
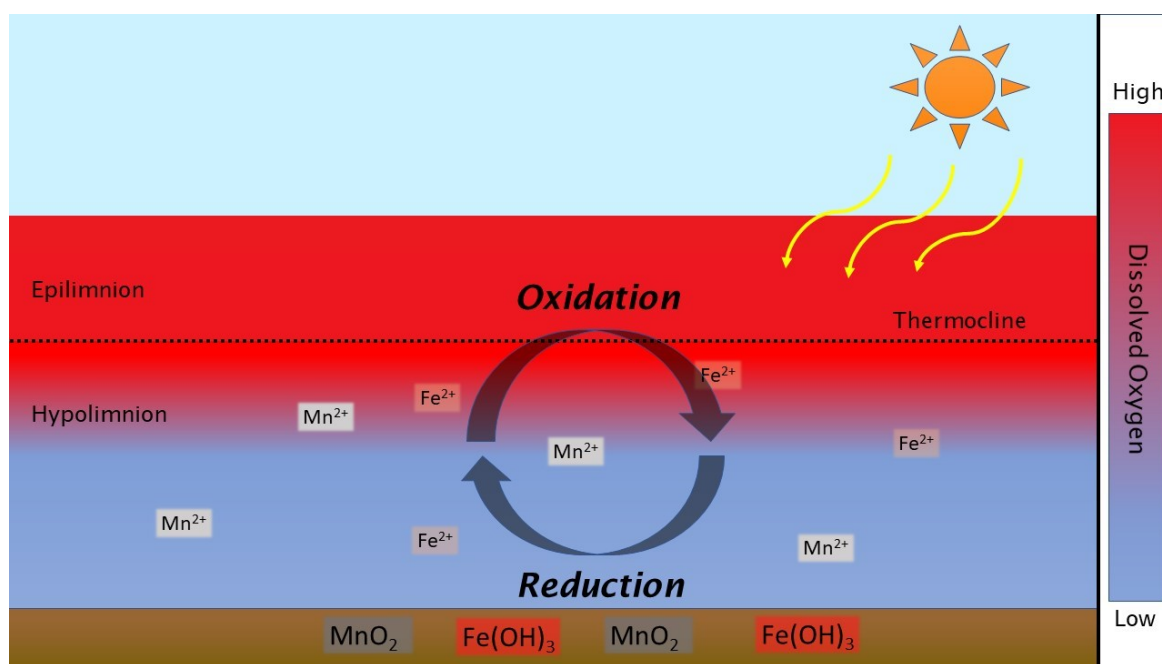

Figure 1: Iron and manganese chemistry in lakes and reservoirs is largely governed by redox potential, and therefore tightly linked to dissolved oxygen (DO) concentrations.

...but little is know about the short-term (hourly to daily) dynamics of Fe and Mn

Traditional sampling methods limit the temporal resolution of data collection, since they require manual sample collection and laboratory analysis

In this study, our objectives were to:

1. Assess the short-term variability of Fe and Mn concentrations throughout the water column of a eutrophic drinking water reservoir

2. Test the appicability of a novel, in-situ monitoring system for collecting high-frequency water quality data

To address our objectives, we conducted a 24 hour overnight sampling and data collection campaign beginning at 13:00 on October 16th, 2020 and ending at 13:00 on October 17th, 2020 at Falling Creek Reservoir (FCR)

STUDY SITE

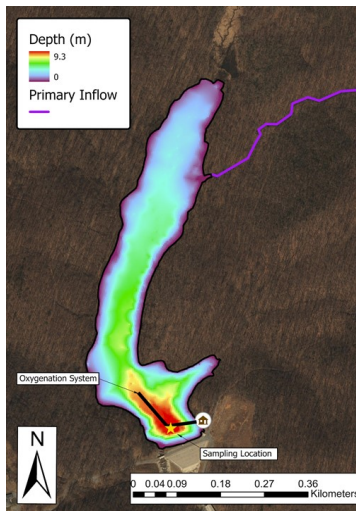Falling Creek Reservoir

Vinton, VA, USA

Figure 2: Bathymetric map of FCR. All data for this study was collected at the sampling location near the deepest part of the reservoir.

Key Characteristics:

- Small (~ 12 ha), shallow (9.3m max depth), eutrophic

- Dimictic - thermal stratification occurs April - October

- Managed by the Western Virginia Water Authority (WVWA) as a drinking water source

- Contains a hypolimnetic oxygenation (HOx) system (black line on map)

Photograph of Falling Creek Reservoir.

HIGH-FREQUENCY MONITORING AND MODELING METHODOLOGY

During the 24-hour sampling campaign, we employed three monitoring techniques that enabled us to collect data with a range of temporal frequencies:

1. Manual sample collection

Photograph of Bethany Bookout collecting water quality samples.

- Every four hours, water samples were collected using a Van Dorn sampler at 7 depths in FCR, ranging from 0.1m to 9.0m below the surface

 - Samples were analyzed for Fe and Mn concentrations using Inductively-Coupled Plasma Mass Spectroscopy

- Depth profiles of dissolved oxygen, temperature, and oxidation-reduction potential were also taken concurrent with sampling, using a SeaBird CTD

2. Multiplexor pumping system ('MUX' from MultiplexÔ) with in-situ spectrophotometric analysis
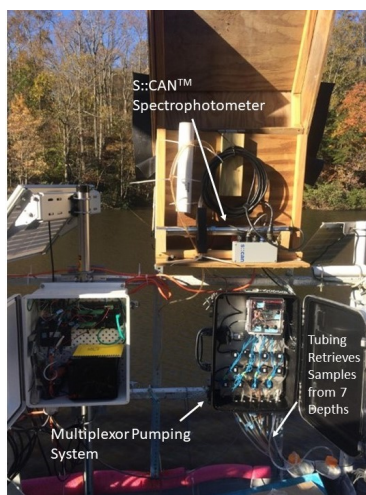
Photograph of the MUX from MultiplexÔ.

- The MUX system uses a microcontroller to operate a peristaltic pump and a series of solenoid valves that can retrieve water samples from tubing placed at multiple locations in the water column:

A.) The microcontroller cycles through a program that retrieves samples from seven depths every 78 minutes
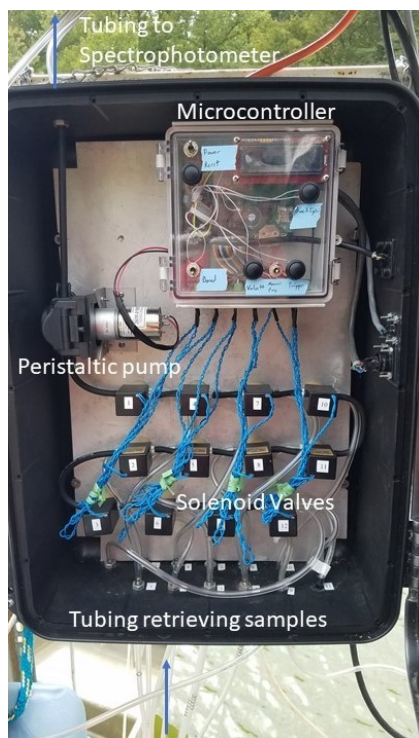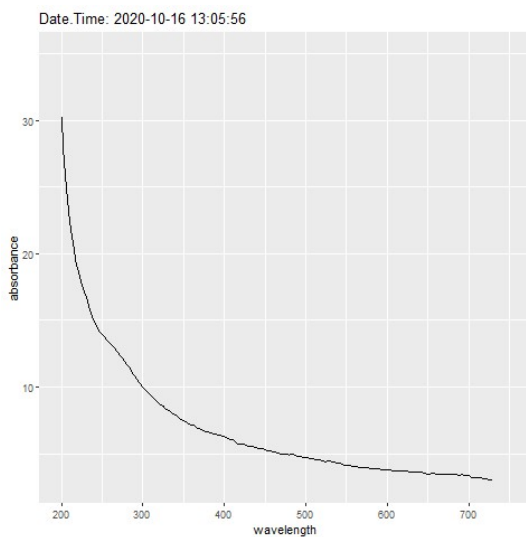

Close-up photograph of the MUX.

B.) The water is pumped into a flow-through cuvette attached to a field spectrophotometer, the Spectro::lyser^{TM}(S::CAN^{TM}, Vienna, Austria)
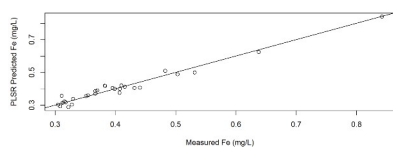
Photograph of field spectrophotometer setup.

C.) The spectrophotometer measures absorbance at 212 wavelengths (every 2.5nm from 200nm - 730nm)

Animated plot of field spectrophotometer absorbance measurements over a 24 hour period.

D.) A partial least squares regression (PLSR) model is fit using the absorbance data (factors) and manual sampling data (responses)

Example plot showing calibrated PLSR model results for Fe concentrations.

E.) The PLSR model is used to predict Fe and Mn concentrations

3. In-situ spectrophotometric analysis at a single depth

- In addition to the MUX system, a second spectrophotometer was suspended at 1.6m below the surface of the reservoir

- Higher-frequency data (absorbance at all 212 wavelengths was measured every 10 minutes)

- PLSR predictions were made using the same process as above

MONITORING RESULTS

Temperature, Dissolved Oxygen, and Redox Trends

The Hypolimnetic Oxygenation (HOx) system was active throughout the sampling period, resulting in oxic hypolimnetic conditions. The low DO concentrations near 5.0 m depth indicate the presence of a metalimnetic oxygen minimum (MOM), an artifact of the hypolimnetic oxygenation system

Oxidation-reduction potential was lowest in the MOM, where anoxia created reducing conditions conducive to anaerobic biogeochemical reactions
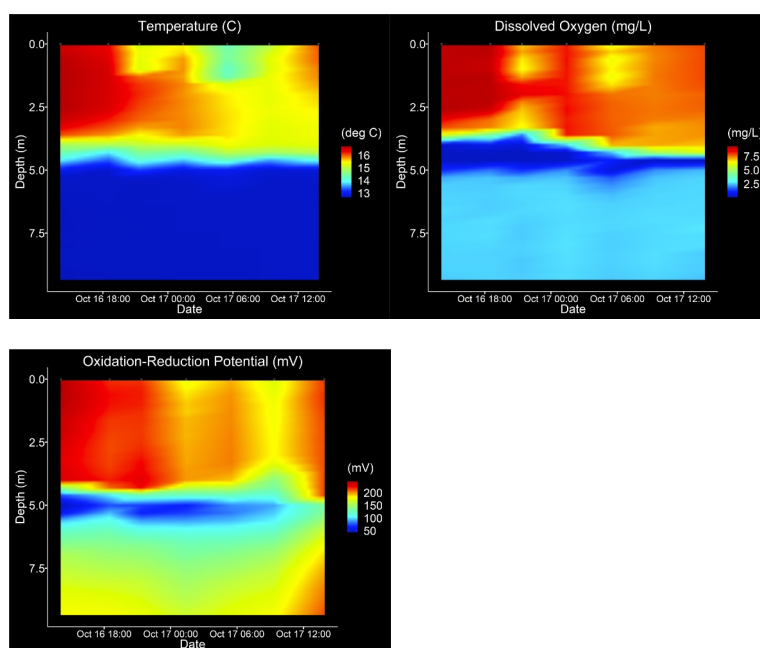

Figure 3: Temperature, dissolved oxygen, and oxidation-reduction potential during the 24 hour monitoring campaign. For visualization purposes, the data was linearly interpolated.

Fe and Mn Concentrations (manual sampling)

Sampling data show temporal and spatial heterogeneity in Fe and Mn concentrations:

- Total Fe concentrations near the reservoir bottom increased overnight, then dissipated
- A "hot spot" of soluble Fe in the MOM was observed, likely resulting from anaerobic Fe reduction
- Mn concentrations were more stable over the 24 hour period, due to the slower reaction kinetics of Mn
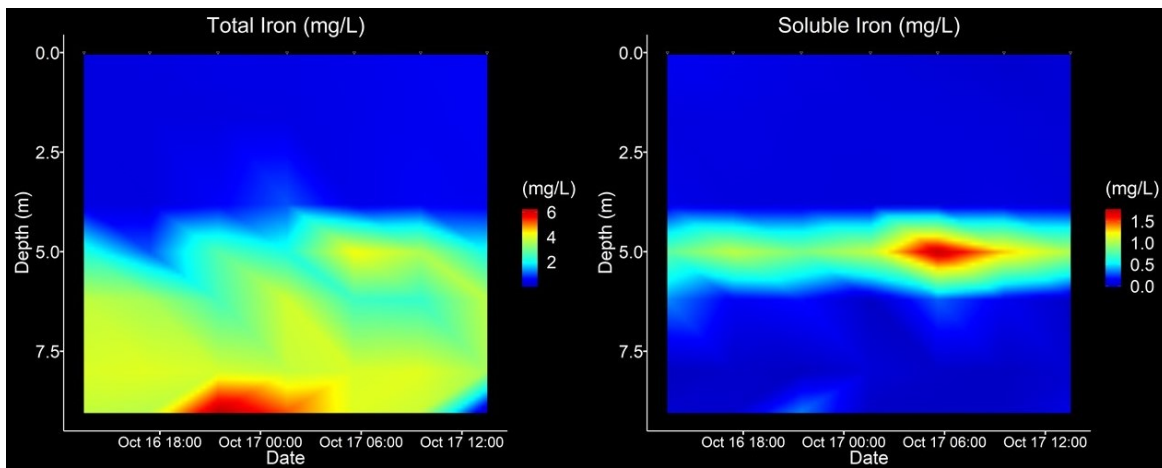
Figure 4: Total and soluble iron concentrations during the 24 hour monitoring campaign. For visualization purposes, the data was linearly interpolated.
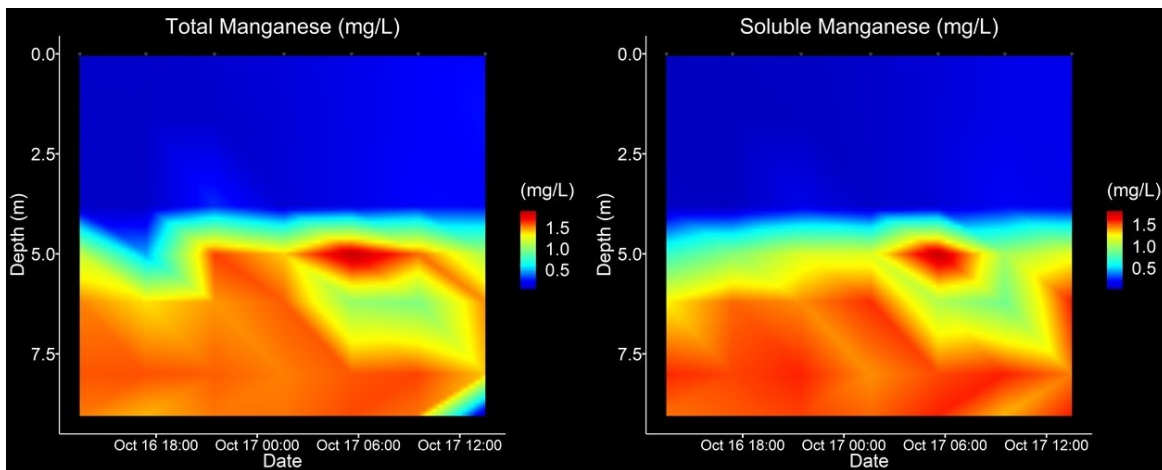

Figure 5: Total and soluble manganese concentrations during the 24 hour monitoring campaign. For visualization purposes, the data was linearly interpolated.

MODELING RESULTS

MUX PLSR Results

The PLSR model using multiple-depth data predicted Fe and Mn concentrations at 7 depths that mirrored the general trends in the observed data, but the model was unable to accurately predict large deviations

Predictions were most accurate at 5.0m and 9.0m depths, where Fe concentrations were highest, indicating model bias towards higher concentrations
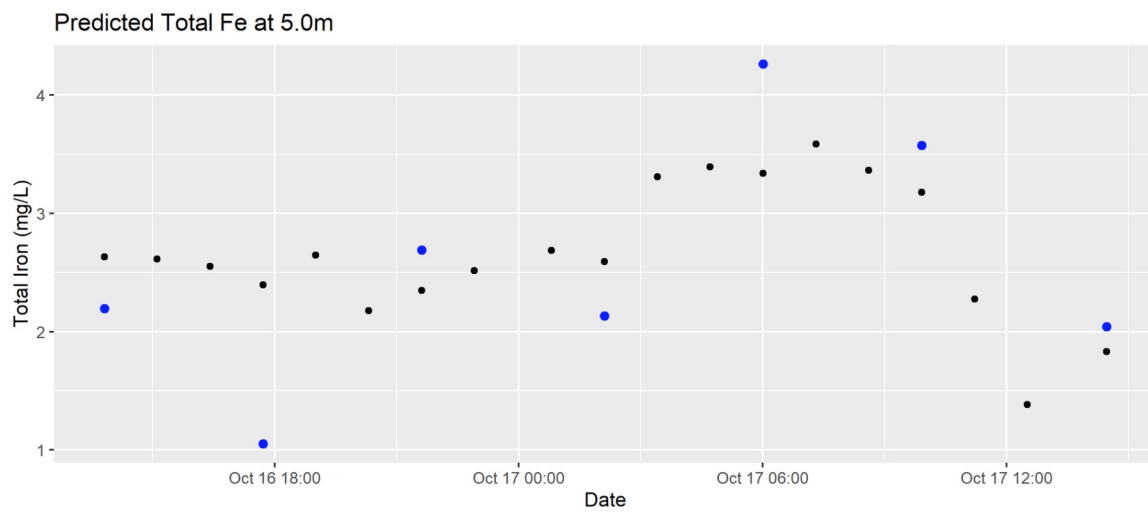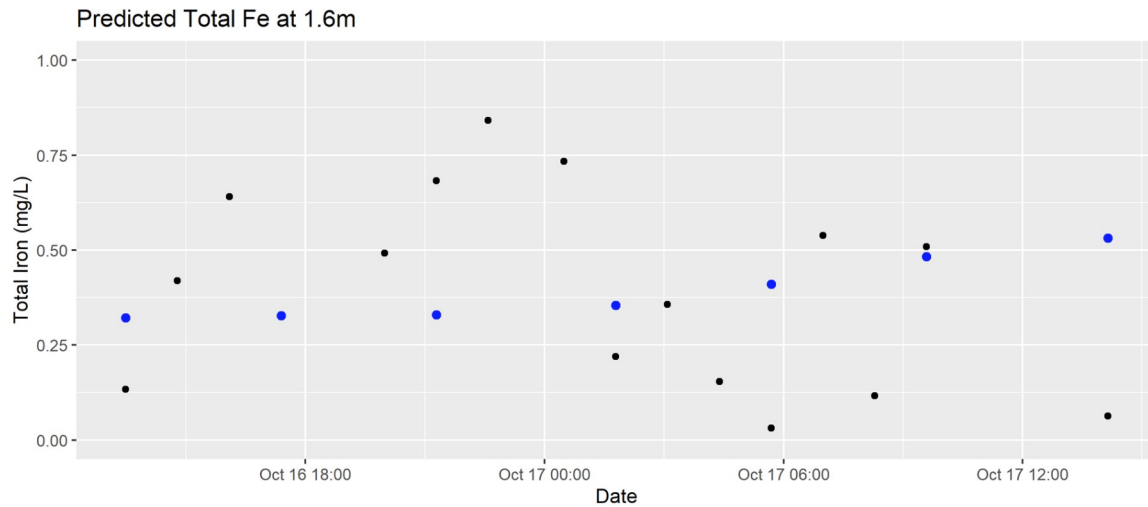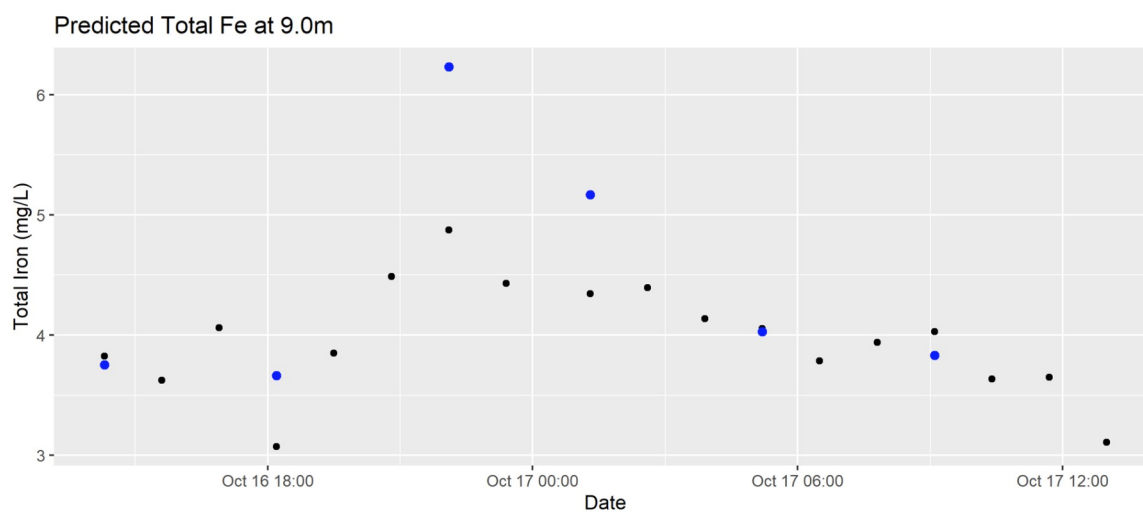
Figure 6: Predicted (black) vs. observed (blue) total Fe concentrations at 1.6, 5.0, and 9.0 m depths using the multiplexor data.

Variable	RMSE	R²
Fe	0.5278	0.90
Mn	0.2173	0.89

Table 1: Skill metrics for PLSR model using MUX data at 7 depths.

Single Depth PLSR Results

The PLSR model using the single-depth data at 1.6m depth produced more accurate predictions, albeit within a narrower range of concentrations
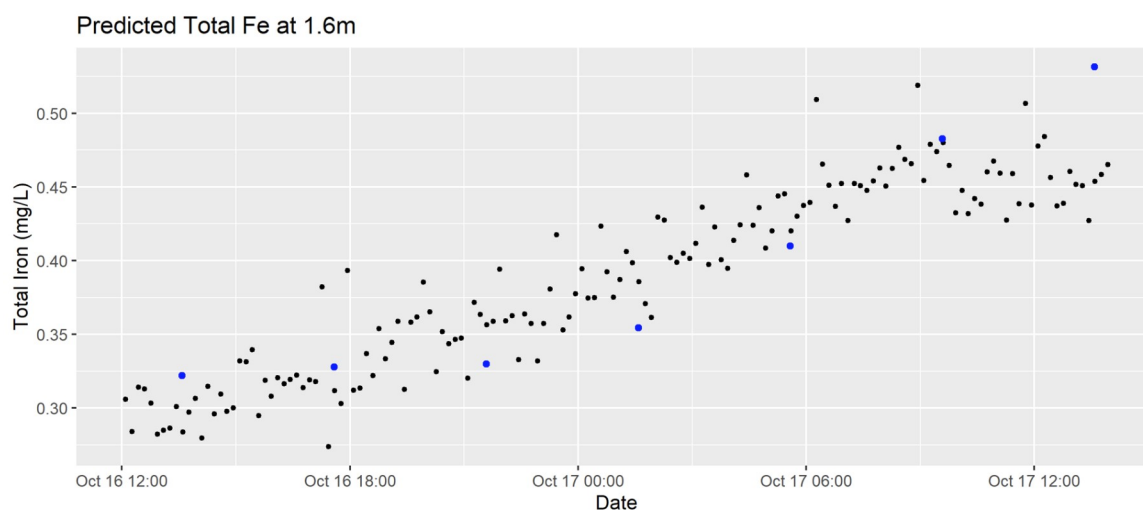
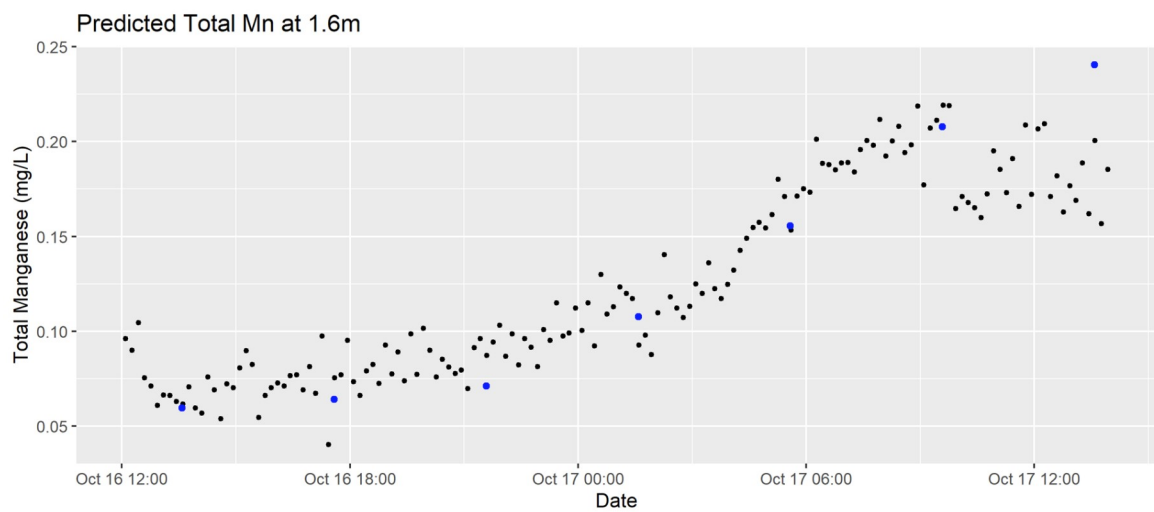Figure 7: Predicted (black) vs. observed (blue) total Fe and Mn concentrations at 1.6 m depth.

Variable	RMSE	R²
Fe	0.028	0.96
Mn	0.016	0.94

Table 2: Skill metrics for PLSR model using single-depth data.

KEY TAKEAWAYS & NEXT STEPS

Key Takeaways

1. Over a 24 hour period, significant changes in both total and soluble Fe concentrations were detected. Mn concentrations were less variable

2. Total Fe concentrations increased overnight in the oxic hypolimnion, whereas soluble Fe fluctuated significantly in the anoxic metalimnion

3. The patterns are suggestive of biogeochemical hot moments: short time periods of high Fe reactivity

4. A high-frequency monitoring system was implemented and was able to accurately predict Fe and Mn concentrations at multiple depths, although our current model missed some of the larger variations in the observed data

Next Steps

1. Increase the sample size of our observational data (manual samples). This should improve the predictive accuracy of our multi-depth PLSR model

2. Address issues caused by fouling of the multiplexor system by applying corrections to data that show a strong fouling signal

3. Investigate changes in Fe and Mn chemisty that occur during reservoir turnover

4. Use the methodology outlined here to predict other ecological variables (i.e. C, N, and P)

ABSTRACT

The biogeochemical cycles of iron (Fe) and manganese (Mn) in freshwater lakes and reservoirs have impacts on water quality, primary productivity, as well as organic carbon sequestration and mineralization. Dissolved oxygen (DO) has a strong influence on Fe and Mn cycling, as changes in redox state largely control the transformations of both metals. The relationship between seasonal anoxia in lakes and reservoirs and metals cycling has been well established, but less is known about the effects of short-term fluctuations in DO on Fe and Mn cycling.

We developed and applied a novel high-frequency monitoring system to assess the dynamics of metals chemistry in response to rapid changes in DO concentration in a seasonally-stratified drinking water reservoir located in Vinton, VA, USA. The reservoir contains a hypolimnetic oxygenation (HOx) system, which is designed to increase the hypolimnetic DO concentration. Water chemistry data are collected using an in-situ spectrophotometer connected to a multiplexor pump that can retrieve samples from multiple depths in the water column. The spectrophotometer measures UV-visible absorbance spectra for 216 wavelengths at a 10-minute resolution, and then partial least-squares regression (PLSR) models, calibrated on weekly water chemistry sampling data, are used to predict total and soluble Fe and Mn concentrations from absorbances. Preliminary results suggest that rapid increases in hypolimnetic DO facilitate higher rates of Fe and Mn oxidation in the water column, and rapid decreases in hypolimnetic DO quickly stimulate Fe and Mn release from the sediments. During summer 2020, this monitoring system is being used to measure Fe and Mn concentrations over the course of a reservoir-scale oxygenation experiment using the HOx system to induce shifts from anoxic to oxygenated conditions in the hypolimnion, and vice versa. By comparing the fluxes of metals observed during rapid shifts in DO concentration to those observed during periods of relatively static DO concentrations, we will elucidate the timing and magnitude of potential biogeochemical hot moments. Results from this study will aid drinking water managers in mitigating water quality issues, as well as improve our fundamental understanding of metals biogeochemistry in freshwater lakes and reservoirs.