The Municipal Water Quality Investigations Program

FDOM Final Report: A Two-Year Comparison of Dissolved Organic Carbon to Fluorescence of Dissolved Organic Matter

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Executive Summary

This report describes the results from the fluorescence of dissolved organic matter (FDOM) study comparing fluorescence data with dissolved organic carbon (DOC) data collected at the Harvey O. Banks Pumping Plant. In the previously completed *FDOM: A One Year Comparison of Dissolved Organic Carbon to Fluorescence of Dissolved Organic Matter (Interim Report)*, daily averages were calculated from 0.45 micrometer (µm) filtered water passing through a Cyclops 7 FDOM probe. Data used in the interim report were collected from July 2013 to July 2014 (*Year 1* data). In this report, additional data were collected from September 2014 to August 2015 (*Year 2* data). *Year 2* data were collected every 4 hours, resulting in greater data resolution for analysis. Additionally, in *Year 2*, a 100-µm-filtered water line was added for FDOM measurements, as well as a non-filtered water line to establish a baseline. This final report focuses on *Year 2* data, but also pulls in *Year 1* data to answer specific study questions. When data from both years are combined, they will be referred to as "*Year 1 + 2* data."

Organic carbon data is of interest to drinking water agencies because treatment disinfectants can react with naturally occurring carbon to form carcinogenic disinfection byproducts (DBPs). To date, organic carbon measurements have been made by directly measuring DOC through the collection of discrete samples or on a continuous basis using expensive organic carbon analyzers. Having the ability to use FDOM as a proxy for DOC would greatly reduce the time and cost of data production while continuing to provide necessary information about potential disinfection by-product formation.

Previous studies have shown that light attenuation resulting from suspended particles (high turbidity) is highly significant (Downing et al. 2012). In *Year 2*, the FDOM study looked to remove turbidity through filtration, with the hypothesis that doing so would improve the fluorescence-to-DOC relationship, even in high turbidity waters.

Year 2 results show that the three filtration states were not significantly different from one another. All three filter states also showed the same regressional breakdown once DOC approached 7 milligrams per liter (mg/L). At that level, FDOM continued to remain steady and decrease slightly when compared to carbon, which points to some unknown, dissolved constituent causing fluorescence to remain steady.

Regarding turbidity, the maximum observed at Banks never exceeded 200 nephelometric turbidity units (NTU) during the study period (and had not done so in the prior 30 years), and therefore may not have reached the level at which the regressions could be affected by turbidity. In Downing et al. 2012, attenuation of the FDOM signal as a function of turbidity was affected significantly after turbidity exceeded 600 NTU. FDOM *Year 2* results, coupled with the added effort and cost associated with filtration, demonstrates that the filtration step is unnecessary.

Year 2 data showed a decent relationship between FDOM and DOC (R^2 = 0.76), but not as good as observed during *Year 1* (R^2 = 0.93). Although the *Year 1 + 2* regression (R^2 = 0.88) is acceptable, in practice, seasonal variations in water quality make the use of a single regression to describe Banks DOC conditions too inaccurate for water agencies interested in DOC data. At times, estimated DOC could differ up to 1.5 mg/L from measured DOC. Further analysis attempting to account for this error showed that water quality conditions (such as elevated iron concentrations), the of source water, and operations at Banks Pumping Plant could possibly influence FDOM response and cause discrepancies in the fluorescence-to-DOC relationship.

In conclusion, the FDOM technology is a valuable tool that can be used as a proxy for direct DOC measurement, given that the regression being used is updated as deemed necessary. For new installations, it is imperative that the FDOM regression be adjusted based on hydrological conditions and that the sensor be calibrated. Based on the hydrology of Banks, an FDOM without a filtration system will provide the same quality of data as a filtered water system. New FDOM sensors (YSI brand) will be installed at Banks, Jones, and Gianelli stations. Further analysis between DOC and YSI FDOM is recommended for all three stations to confirm the data quality of these new sensors and to assess how the results compare with this report's findings.

Introduction

Since 1983, the California Department of Water Resources (DWR) has been monitoring dissolved organic carbon (DOC) as part of the comprehensive source-water monitoring program in the Sacramento-San Joaquin Delta (Delta) for drinking water. DOC is a constituent of concern for drinking water treatment plants and water purveyors because naturally occurring organic carbon can react with disinfectants during the treatment process. This can lead to the formation of carcinogenic disinfection byproducts (DBP), which are regulated by the Safe Drinking Water Act (SDWA).

Prior studies have shown that fluorescence can be used as a proxy for direct DOC measurements (Coble 2007; Cumberland and Baker 2007; Kraus et al. 2010). Other agencies, such as the U.S. Geological Survey (USGS), have used high-frequency in-situ fluorometers, like the fluorescing dissolved organic matter (FDOM) instrument, as a surrogate for DOC measurements in the fresh waters of California. Studies by Downing et al. (2008) and Saraceno et al. (2009) demonstrate there is a significant correlation between DOC and FDOM.

The use of in-situ instruments as surrogates for DOC could potentially save time and remove the need to purchase and maintain expensive DOC analytical instruments. Municipal Water Quality Investigations (MWQI) looked to evaluate the efficacy of FDOM as a surrogate for DOC at a complex source water site. This study assesses the DOC and data from a Turner Designs Cyclops 7 FDOM instrument installed at the MWQI monitoring station at Harvey O. Banks Pumping Plant (Banks) located on the State Water Project (SWP), approximately 17 miles southwest of Stockton, California.

Year 1 data presented in the FDOM interim report showed a strong relationship between FDOM and DOC ($R^2 = 0.93$), and that FDOM had a stronger relationship to DOC than ultraviolet absorbance measurements at 254 nanometers (UVA_{254}) ($R^2 = 0.45$). Those results led to uncertainty and to new questions worthy of further investigation. Consequently, this report looks to answer the following questions:

- How do different levels of filtration impact FDOM to DOC Correlation?

- Is the FDOM/DOC relationship consistent between the *Year 1* and *Year 2* data sets; when combined, does a two-year data set help improve the regression?
- What is the cause of the seasonal regression variance first observed in *Year 1* data?

To answer these questions, adjustments were required to instrument installation, station water delivery systems, and the programming of data management systems. This new data, plus analysis of pertinent external data, has given rise to some interesting results. These results showcase the strengths and limitations of the FDOM technology and inform our understanding of how hydrologic variability effects water quality at Banks.

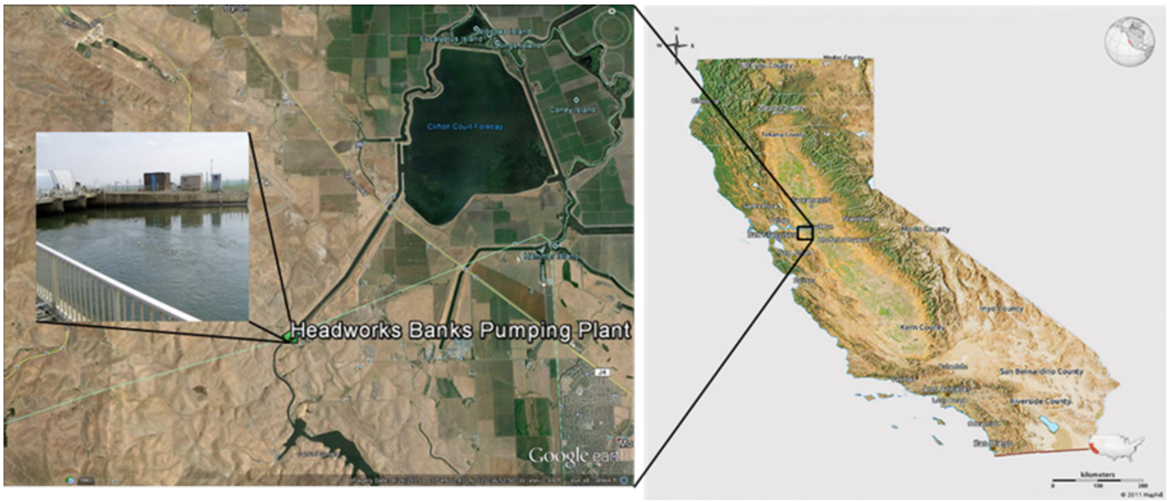
Methods

Study Area

The Harvey O. Banks Pumping Plant is located near Tracy, California and is one of the primary drinking water supply diversion points from the Delta (Figure 1). The plant is capable of pumping 10,300 cubic feet of water per second into the 444-mile-long California Aqueduct. Organic carbon concentrations measured at Banks represent the quality of Delta water at the point of entry into the California Aqueduct. Aqueduct water deliveries are made to the Bay Area and other south-of-Delta communities, so careful monitoring is important to inform drinking water agencies of water conditions and allow them time to adjust treatment processes based on these conditions.

Hydrology at Banks is complex because of multiple water sources (e.g., Sacramento and San Joaquin rivers, in-Delta return flows, and seawater intrusion), tidal influence, and source variability throughout the year. Fluctuating source water quality and stringent regulatory requirements make it challenging for water utilities to provide safe, reliable, and economical drinking water.

Figure 1 Banks Water Quality Station



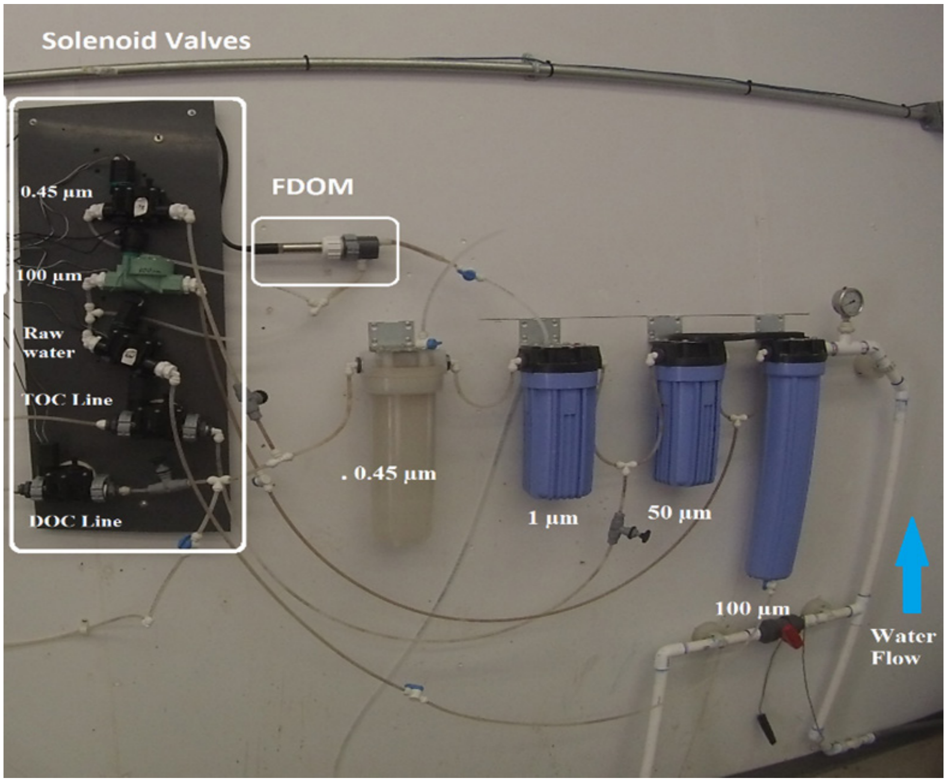
Map Source: http://www.maphill.com/united-states/california/3d-maps/satellite-map/cropped-outside/.

The water quality station at Banks sits on the aqueduct, uphill from the pumping plant (Figure 1). Currently, the station monitors total organic carbon (TOC), DOC, chloride, bromide, nitrate and sulfate, temperature, turbidity, specific electrical conductivity, pH, and fluorescence. As the station is uphill of the pumping plant, canal flow at Banks is directly related to the pumping rate at the pumping plant. Daily discharge pumping data are available and used in this report.

Water Delivery

Sample water is delivered into the station from the California Aqueduct using a progressing cavity pump. In Figure 2, water pumped into the station moves from right to left in the picture, and travels through a 100 micrometer (µm) filter followed by a 50 µm filter, before being delivered to the Sievers organic carbon analyzer. Some of the water that passes though the 50 µm filter continues through a 1 µm filter and a 0.45 µm filter before delivery to the Sievers for DOC analysis. For FDOM measurements, water is selectively pulled from the appropriate filter housing to measure 0.45 µm, 100 µm, or unfiltered water. Irrigation solenoid valves control what water type is delivered to the instruments. A Campbell Scientific datalogger controls the timing and actuation of solenoid valves.

Figure 2 Banks Pumping Plant Organic Carbon Filtration System for the *Year 2* Data Set



FDOM Sensor

Fluorometers work by emitting light at a particular wavelength into a water sample; the dissolved organic matter in the water absorbs the light and fluoresces at a different wavelength. A detector measures the response and outputs a signal in millivolts (mV) proportionate to the fluorescence. The sensor used in this study was a Turner Designs Cyclops 7 (FDOM) with an excitation wavelength (ex) of 350 nm and an emission wavelength (em) of 450 nm. The study conducted by Kraus et al. (2010) helped derive the 350ex/450em pair. In that study, 33 water samples were taken from the McKenzie River in Oregon, with the strongest correlation between DOC and FDOM pairs falling in the range of 320 nm to 370 nm for excitation and 420 nm to 475 nm for emission. The 350ex/450em pair for the Cyclops 7 falls in the middle of the ranges from the McKenzie River study. The Cyclops 7 was installed at Banks and recorded data between July 2013 and August 2015.

For *Year 2*, the FDOM instrument was configured to measure water at three levels of filtration: 0.45µm filtered, 100 µm filtered, and unfiltered water.

These filter states were selected, in part, because they were already available onsite for the Sievers DOC filtration requirements. The unfiltered stream was intended as a baseline against which to judge the other streams during high turbidity events. The FDOM measurements would then be compared against DOC, with turbidity as an additional variable for assessment.

The FDOM was installed in a flow-through cap which was integrated into the water delivery system. The three filter states were sequentially delivered to the FDOM by the irrigation solenoid valves. These valves were programmed to operate on a 4-hour cycle. From 0:00 hours to 2:00 hours, unfiltered water flowed; from 2:00 to 3:00 hours, 100-µm filtered water flowed; and from 3:00 to 4:00, 0.45-µm filtered water flowed.

A 4-hour program cycle results in six measurements per day, per filter state, for the 0.45 µm and 100 µm sample streams, and 12 measurements per day for the unfiltered stream. Each FDOM measurement recorded is an average of readings taken every 15 seconds from the preceding hour. At the top of the hour, all 15-second readings from the previous hour are averaged into a single reported value.

Sievers TOC Analyzer

For each organic carbon measurement (Sievers 5310C analyzer), the concentration of inorganic carbon species (CO_2^*, HCO_3^-, and CO_3^{2-}) is determined and, after oxidation of the organic compounds, the total carbon (TC) content of the sample is measured. The concentration of the organic compounds is then calculated from the difference between concentrations of TC and total inorganic carbon (TIC), generally referred as inorganic carbon (TC - IC = TOC). This method is EPA approved for determining organic carbon concentrations in water and is the same method employed by DWR's Bryte Water Quality Laboratory.

The Sievers analyzer has a flow-through system that initiates sampling when water is present. Like the FDOM sensor, solenoid valves control what water source (TOC or DOC) is delivered to the Sievers. These valves are programmed to operate on a 4-hour cycle. From time 0:00 to 1:00 hours, the Sievers makes 6 TOC measurements; from time 01:00 to 2:00 hours, it makes 6 DOC measurements; from time 2:00 to 4:00 hours, the Sievers is idle.

Discrete Sample Collection and Analysis at Bryte Laboratory

For DOC samples submitted to Bryte Laboratory, water is collected directly from the canal. DOC samples are processed in the field by passing sample water through a 0.45-µm filter. A comparison between delivery system water and direct-from-canal samples gives a sense of the representativeness of continuous measurements produced in the station, which is an important consideration when looking at FDOM results. For the purposes of this study, the discrete DOC samples measured by Bryte Laboratory are considered the “gold standard” result when discrepancies exist between Bryte and Sievers results. Aside from organic carbon, metals samples submitted to Bryte lab are discussed in this report.

Turbidity and Temperature

Turbidity and temperature were the variables investigated in this study. In Downing et al. 2012, changes in turbidity and temperature were linked to the attenuation of FDOM signal. The FDOM model used in this study (Cyclops 7) was part of the Downing experiment. Because of Downing, it is understood that both factors can influence FDOM response. Since MWQI did not have temperature and turbidity instruments installed, Delta Field Division instruments were used in analysis. Although all Banks instruments are in the same station, the MWQI and Delta Field Division instruments are supplied water from two separate pumps, each pulling from a slightly different location in the canal. Temperature and turbidity data used were downloaded from the CDEC website, where data are described as provisional in nature.

Analytical Methods

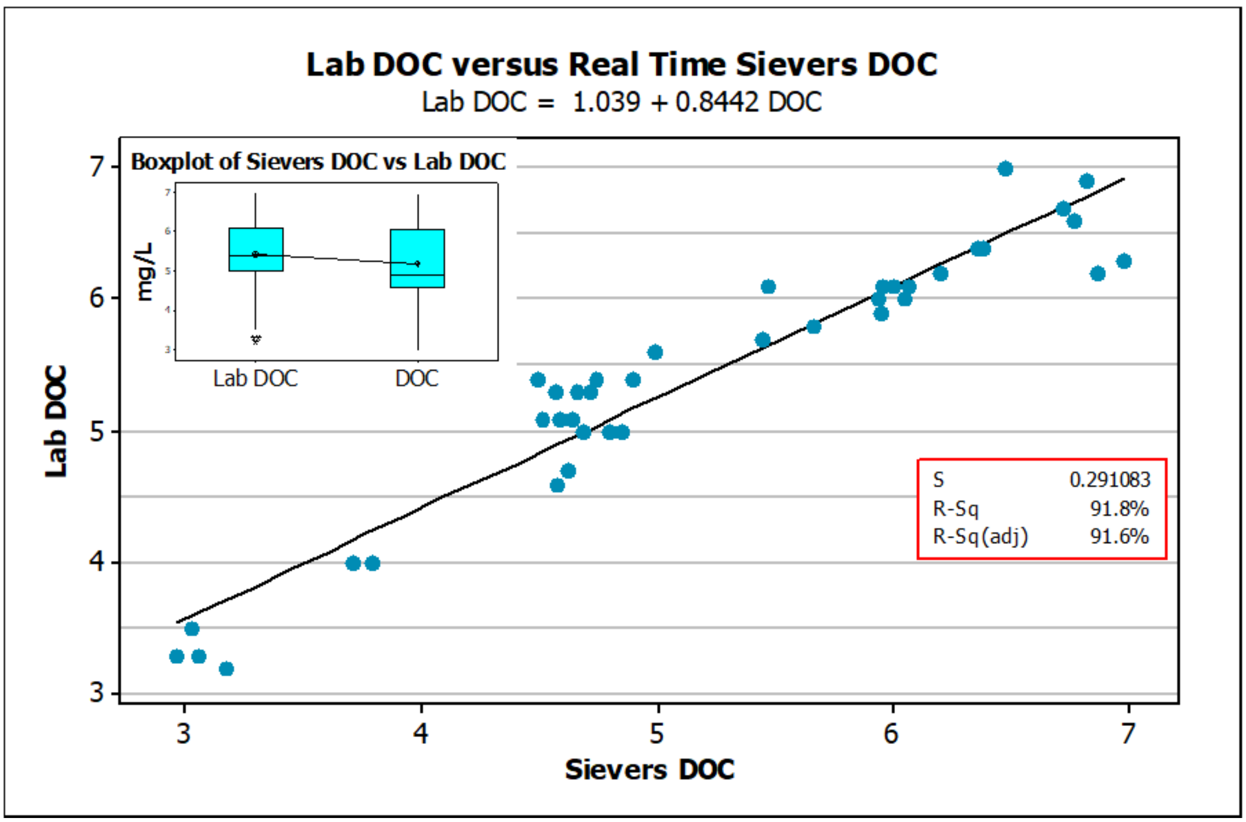
To answer the study questions, data from each FDOM filter state were compared to the DOC data (both Sievers and Bryte data). A regression was then developed between Bryte DOC and Sievers DOC, and between Sievers DOC and FDOM. FDOM/DOC regressions were developed using 80 percent of the available data, with the other 20 percent (randomly selected) being set aside for post-regression verification. The resulting data sets were analyzed using a non-stacked analysis of variance (ANOVA) method to compare Bryte DOC, Sievers DOC, and FDOM values from each filter state. Excel and Minitab software were used to test, create, and run statistical analyses like ANOVA and correlations. Because of the larger amount of Sievers DOC data compared to FDOM, an Excel macro was used to interpolate FDOM values that would match the collection times of Sievers DOC data.

In this report, the unfiltered FDOM and 0.45-µm-filtered FDOM streams are both used in analysis. The reason for this is, that in *Year 1*, the 0.45-µm data set was the only data collected. Therefore, it is necessary to use the 0.45-µm data to conduct analysis over the whole two-year study period. Because the unfiltered FDOM was proven to be the most cost-effective and the most likely to be used in future applications, the remainder of analysis is completed using that data set.

Results

Prior to developing regressions between DOC and FDOM, the first step was to confirm the data quality of the Sievers DOC instrument. The Sievers DOC data quality was assessed by comparing it with Bryte Laboratory DOC data (Figure 3). The assumption for this study was that Bryte Lab produced the true value against which the Sievers would be compared.

Figure 3 Banks Sievers DOC Versus Bryte Lab DOC Regression and Boxplot



Sievers online data were selected to match collection times of the Bryte Lab samples. Bryte Lab DOC and Sievers online DOC data from September 2014 to August 2015 were used for this analysis. Discrete samples were collected from the canal near the station intake, while the Sievers samples traveled through the station water delivery system. Considering this difference, the regression (R^2 = 0.916) proved to be strong for this period (Figure 3). Based on these results, the Sievers DOC provides an accurate measurement of DOC in the canal. With the Sievers data verified, comparisons between Sievers DOC and the different FDOM filter states could begin.

The boxplot in Figure 3 shows that DOC mean values between Bryte and Sievers are very comparable. This reinforces the similarity between lab-grade instrumentation and the real-time instrument at Banks. In Exhibit 1, the statistical results of the unstacked ANOVA were obtained using the real-time data produced by the Sievers DOC and the discrete lab data from Bryte. With a P value of 0.345 (P > 0.05), the ANOVA test confirms that no significant difference was found between Bryte DOC and Sievers DOC.

Exhibit 1 ANOVA Result Comparison Between Real Time DOC and Lab DOC

```
Source  DF     SS    MS     F      P
Factor   1   1.04  1.04  0.90  0.345

Error  76  87.75  1.15

Total   77  88.79

S = 1.075   R-Sq = 1.18%   R-Sq(adj) = 0.00%


                                Individual 95% CIs For Mean Based on
                                Pooled StDev
Level     N   Mean  StDev  ------+---------+---------+---------+---
Lab DOC  39  5.413  1.005           (-------------*------------)
DOC      39  5.181  1.140  (------------*-------------)
                           ------+---------+---------+---------+---
                              5.00      5.25      5.50      5.75
```

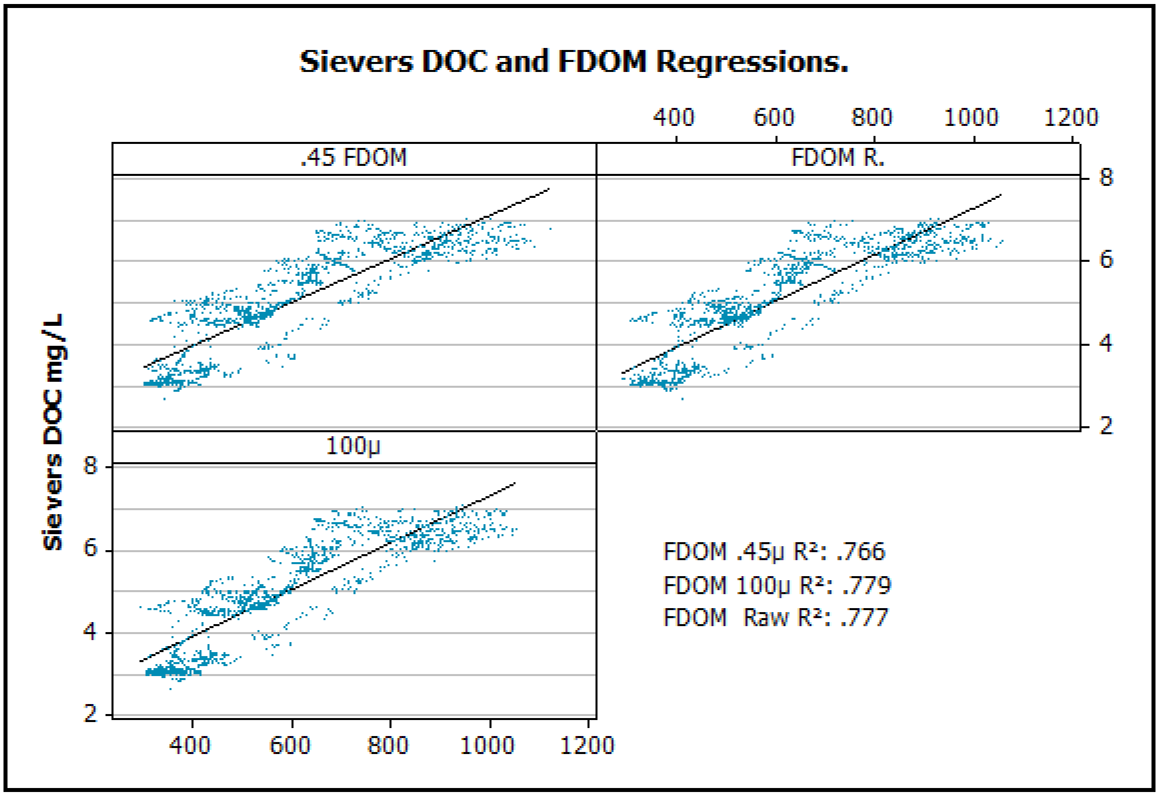
For DOC data analysis, 80 percent of the total data (randomly selected, ~1300 data points) were used to develop the FDOM-to-DOC regressions. The remaining 20 percent (~300 data points) were set aside to test the regression’s real-world application. This procedure was used to minimize the chance that the results would be influenced by the data used to create the equation.

Do different levels of filtration impact FDOM-to-DOC Correlation?

In Figure 4 below, FDOM data from the three filter states were compared against Sievers DOC concentrations. The three resulting regressions were not significantly different ($P > .05$) from one another: 0.45-µm filtered ($R^2 = 0.766$), 100-µm filtered ($R^2 = 0.779$), and unfiltered water ($R^2 = 0.777$).

Additionally, for all three filter states, the relationship with DOC appears to break down once the FDOM reads above 800 mV. DOC concentrations topped out near 7 milligrams per liter (mg/L) during the study period. At 7 mg/L DOC, FDOM ranged anywhere from 650 mV to 1100 mV. Since DOC is not the cause of FDOM response beyond 800 mV, the additional florescence is likely because of some unknown, dissolved inorganic component. The relational breakdown is present during both study years and shows that filtration of particulate matter does nothing to improve the FDOM-to-DOC regression. Since there is no significant difference between the three filter states, and since filtration does not improve the regression’s high end, the relatively maintenance-free unfiltered water stream should be selected for field applications.

Figure 4 Sievers DOC and FDOM Regressions



Is the FDOM/DOC relationship consistent between *Year 1 and Year 2* data sets; and when combined, does a 2-year data set help improve the regression?

Figure 5 shows Sievers DOC and 0.45-µm FDOM over a two-year period. Good agreement was observed between FDOM and DOC during the summer and fall of 2014, but in the spring of 2015, a relational change occurred. This period is referred to as the *phase shift* and is similar to what occurred during 2013–2014 (the shift can be observed highlighted in red). After observing this phenomenon in 2014, a goal in *Year 2* was to look at the same time period in 2014–2015 to determine if the phase shift was a real, repeatable event, or if there was some other cause. To answer this question, in 2014–2015, 0.45-µm FDOM data was collected. For consistency, 0.45-µm filtered water was provided in *Year 2* to match what was supplied to the FDOM in *Year 1*, as seen below.

Figure 5 Observed Sievers DOC and 0.45-µm FDOM Filtered for Year 1 and Year 2 Data

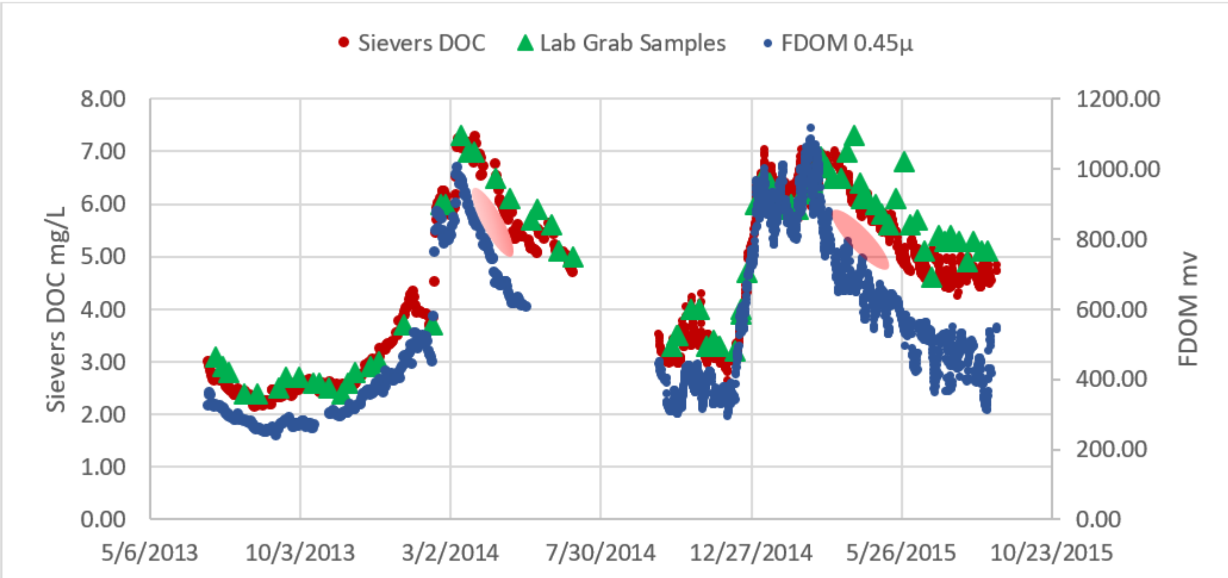
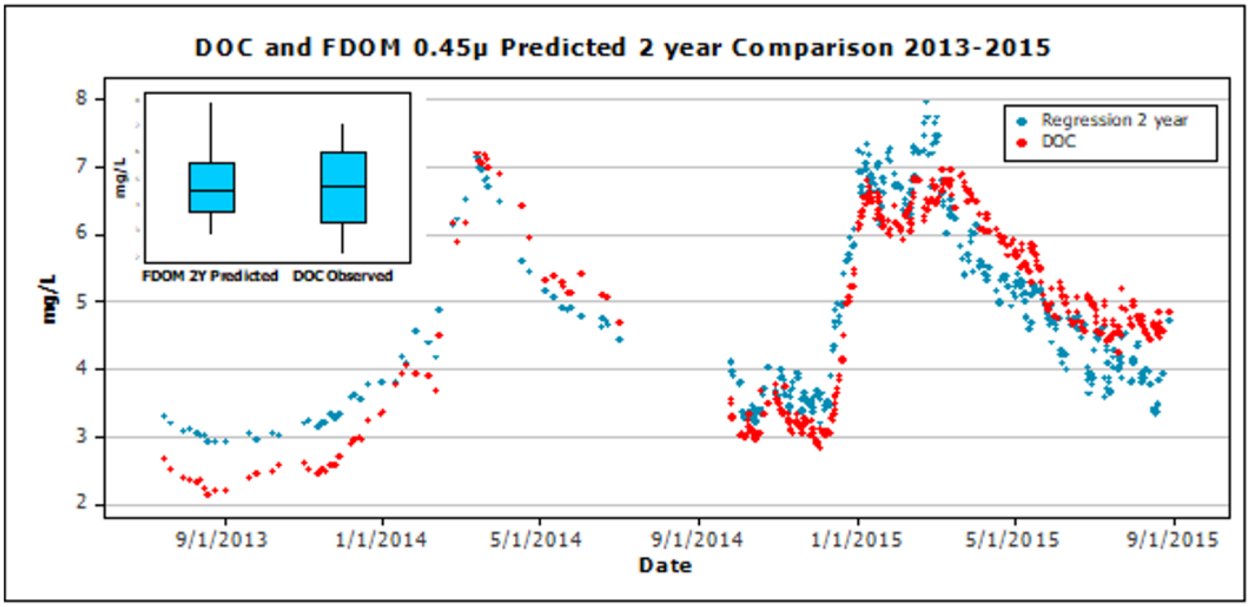


Figure 5 shows 0.45-µm FDOM data and Sievers DOC. Lab DOC discrete data were added to show the accuracy of Sievers DOC. As seen in *Year 1*, a significant gap developed between the FDOM and the Sievers data in March 2015. The fact that the spring-time gap occurred in both years shows that the phase shift is likely not because of instrument error. The causes of the phase shift will need to be accounted for if an accurate prediction model for FDOM is to be developed — more on the possible causes of the phase shift can be found in the discussion section, below.

Although consistent variance (phase shift) occurred between the two sample years, a goal of this study was to determine if the regression could be improved with an additional year of data. Therefore, Figure 6 shows predicted 0.45-µm FDOM and observed DOC for *Year 1 + 2* data, combined. Using 80 percent of samples pulled at random, a regression ($y = 0.006063x + 1.375$) was developed to predict DOC concentrations for the remaining 20 percent of data. The R^2 value for the two years of 0.45-µm FDOM filtered data combined was 0.810. During the first year, the R^2 value was 0.937 while the second year alone was 0.766.

Figure 6 Sievers DOC and Predicted 0.45-µm FDOM Filtered for Year 1 and Year 2 Data



The predicted values sometimes differed from the observed values by more than 1 mg/L. One benefit of the two-year regression is that because lower DOC values were observed in *Year 1*, the higher DOC concentrations seen in *Year 2* were more accurately predicted by the regression. This shows that the FDOM technology can do a reasonable job of estimating DOC concentrations within a defined margin of error (± 1 mg/L), but since water agencies are most interested in time periods of elevated DOC, further analysis might be needed to have a better understanding of the FDOM's response at high concentrations. In the future, for example, if a behavior seems repetitive enough, we could account for the error with a modified FDOM regression equation (ideas for further analysis are covered in the *Recommendations* section at the end of this report). Overall, the predicted FDOM mean and the observed DOC mean were not statistically different using ANOVA, as observed in the Figure 6 inset.

Regardless of regression improvements, the phase shift observed over the two-year study shows that some unknown cause is driving the separation between predicted FDOM mean and observed DOC mean. For the FDOM technology to replace analytical DOC in complex waters such as Banks, the cause of the phase shift must be understood.

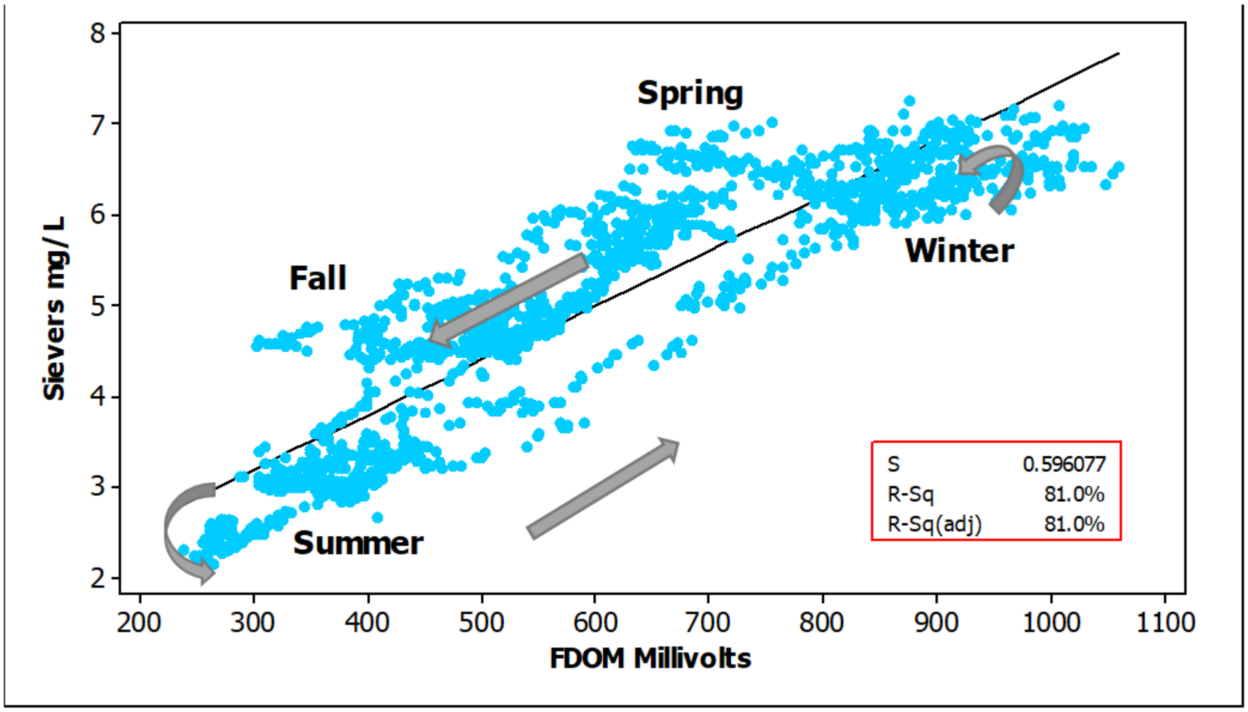
Discussion

The results have shown that a single regression to estimate DOC is useful for observing general trends in DOC but is too inaccurate for use by DWR modelers and water agencies. Whether developing a regression from *Year 1* data, from *Year 2* data, or from the whole dataset combined, the phase shift occurs in the spring and the relationship between FDOM and DOC breaks down. Because the phase shift is consistent from season to season and from year to year, trends observed within the dataset can be further assessed.

What is the cause of the seasonal regression variance first observed in FDOM Year 1 data?

Looking at the relationship between Sievers DOC and FDOM 0.45-μm data (Figure 7), a circular pattern is apparent. This hysteresis effect is observed as the relationship between DOC and FDOM changes seasonally based on some unknown variable. *Hysteresis* is defined as the time-based dependence of a system output on present and past outputs (Baker & Showers 2019). At Banks, the relationship between DOC and FDOM changes seasonally. That is, there looks to be two states, and therefore two relationships between DOC and FDOM. As the one condition is replaced with the other, the memory of the prior state persists in the system until an inflection point is reached. Investigating this regression variance is a difficult task because Banks is a complex system. Based on the timing of relational changes, it would make sense that storm-driven seasonal flows cause the hysteresis effect, but many other possible causes exist. Some of these possible causes are considered in the following text.

Figure 7 Linear Regression of Sievers DOC and 0.45µ FDOM for Year 1 and Year 2 Data



Temperature

Testing temperature variance was one of the goals of this report. Downing et al. (2012) observed that fluorescence decreases about 1 percent for every 1 °C increase in temperature; this relationship was explored as a cause of observed regression error. The following version of Downing's temperature correction was applied to the *Year 2* data:

FDOM corr = FDOM raw + p (Tmeas – 25)/ rp(FNU) ¥ rd(UVA254)

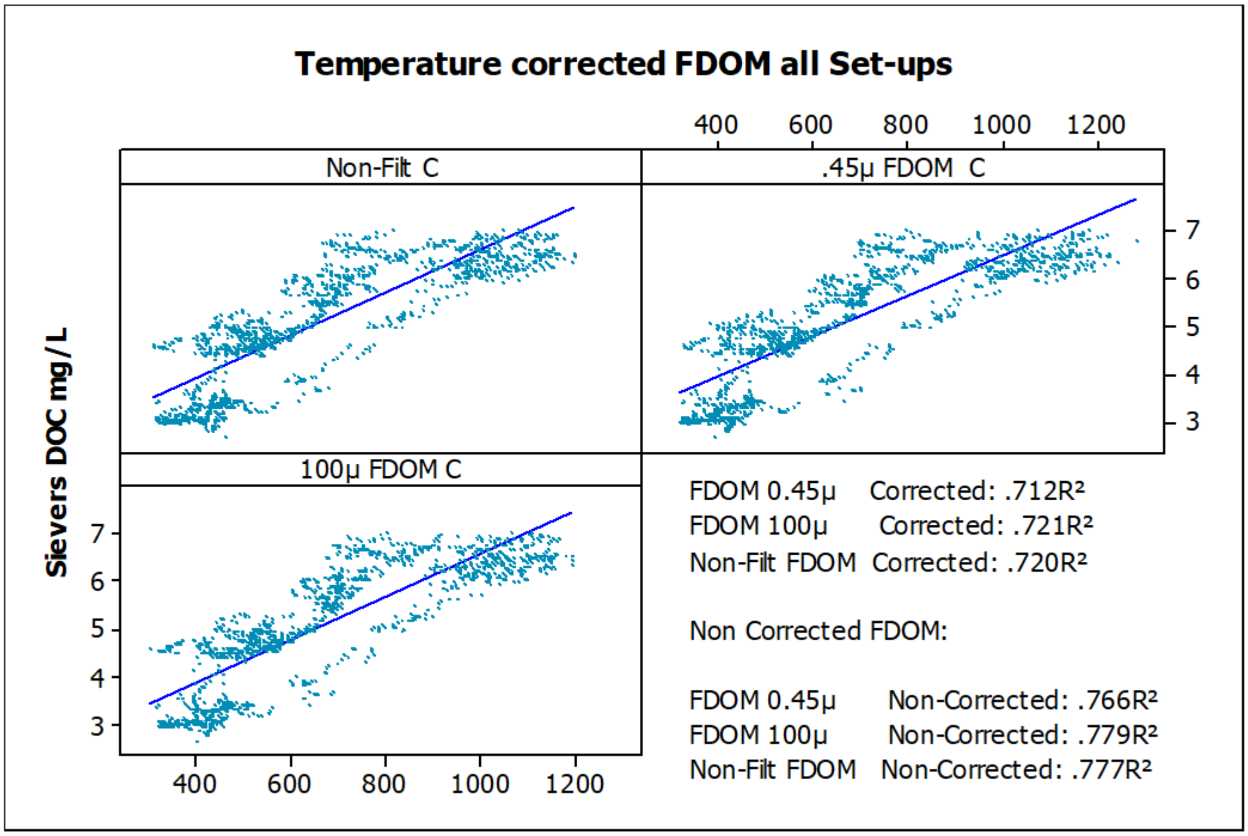
The turbidity (FNU) and interpolated UVA254 were removed since these corrections were not needed. The new adjusted equation only provides a temperature correction:

FDOM Tcorr = FDOM raw+(FDOM raw (p(25-Tmeas)))

Where FDOM raw means FDOM values in millivolts, Tmeas is the continuous measured water temperature, and p is a constant of 0.011.

In Figure 8, all three regressions for temperature-corrected FDOM are shown. The temperature correction decreased the quality of the relationship for all three filter states ($R^2 \sim 0.71$), whereas the non-temperature corrected FDOM regression was roughly 0.77. Further, the temperature correction did nothing to correct for the hysteresis effect.

Figure 8 All FDOMs Temperature Corrected Regression Results



One caveat with using this temperature correction — the equation used was intended to test a natural river system, not water at a pumping station. Taking this in to account, a better temperature correction for a canal (influenced by pumping) *could* be developed but based on the continued presence of hysteresis shown in Figure 8, it is unclear if there is value in developing this. That, and the fact that most modern FDOM probes automatically incorporate temperature correction. Regardless, an improvement in the relationship was expected but did not occur.

Turbidity

During past FDOM studies by USGS (Downing et al. 2009), turbidity was found to play a major role in how FDOM responded during certain flushing events. The report described that high turbidity (~800 NTU) caused FDOM values to increase because large particles caused additional fluorescence. To test if removing turbidity could improve the regression during high turbidity conditions, 0.45µm, 100µm, and unfiltered water were delivered to the FDOM sensor. Unfortunately, during *Year 2* of this study, turbidity at Banks never exceeded 150 NTU, even during flushing events. Moreover, looking at the last 12 years, turbidity at Banks never exceeded 190 NTU. The location of the Banks station upstream of the pumping plant and the operation of Clifton Court control gates likely buffered turbidities and limited this study's ability to (1) test Downing's theory and (2) test if turbidity could explain the phase shift.

Even though there were occasional elevated turbidities observed at Banks, most data collected over the year showed less than 10 NTU. Elevated turbidities over the winter (~130 NTU) could show significant variance between FDOM and DOC, but because these were short-lived events, developing a turbidity correction for the entire data set was ineffective and showed no overall improvement. That said, turbidity could still be playing some role in regression variance during times of elevated turbidities, just not in a way that would explain the phase shift.

Iron

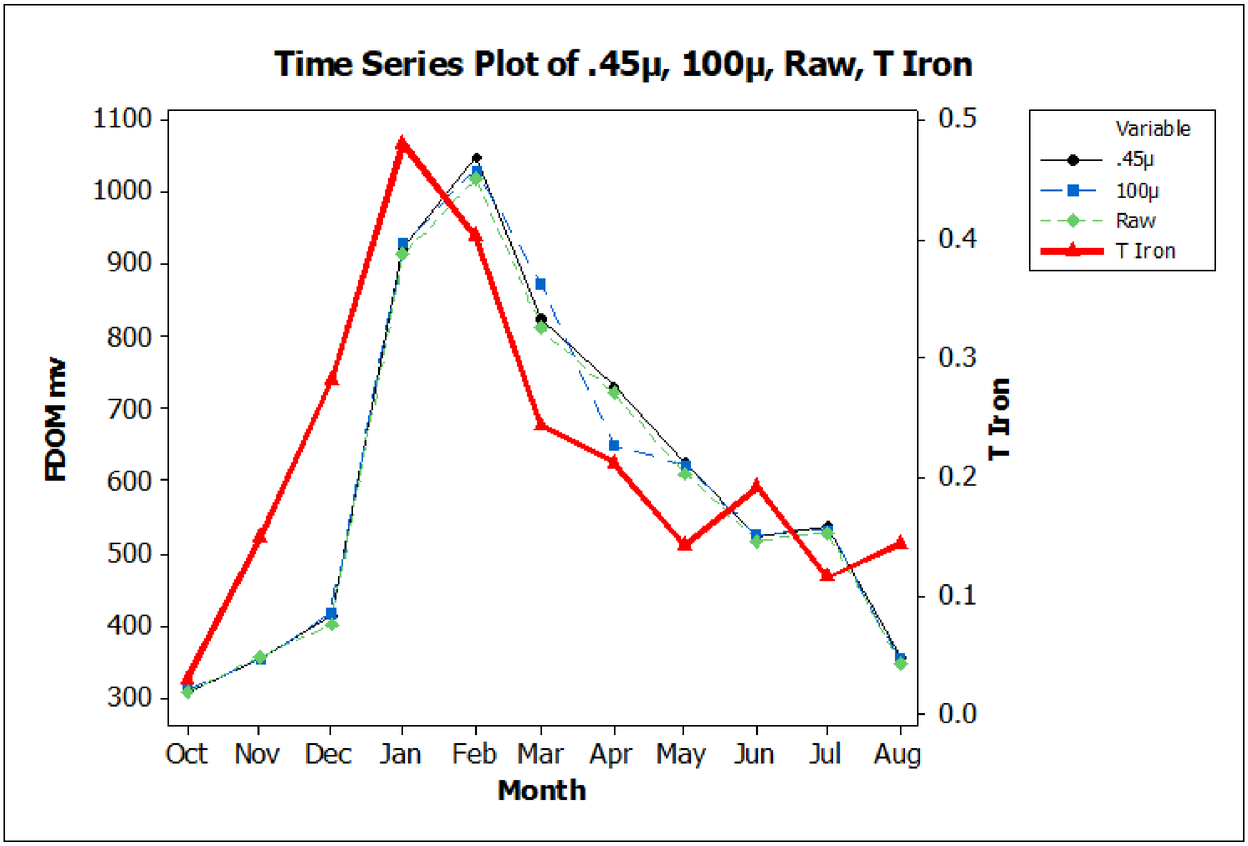
Natural dissolved organic matter (DOM) is composed of a variety of organic compounds, and these compounds can interact with metals in aquatic environments. Fluorometers are known to be affected by this interaction. Previous studies (Poulin et al. 2014) observed that as iron concentrations increase, the fluorescence response will also increase until quenched. At Banks, the Division of Operations and Maintenance (O&M) has monitored water quality for over 35 years. They discretely sample every two weeks for various constituents, including iron. This data set was used to assess iron's relationship with FDOM (Table 1).

Table 1 Correlation Between DOC, FDOM, Dissolved and Total Iron with the Respective P Values

DOC	0.45µ FDOM	100µ FDOM	Non-Filtered FDOM
T iron: N/A	T iron: 0.807 (0.005)	T iron: 0.789 (0.004)	T iron: 0.789 (0.004)
D iron: 0.661 (0.027)	D iron: 0.806 (0.003)	D iron: 0.799 (0.003)	D iron: N/A

Mirroring previous studies, the Banks data shows a relatively stronger relationship between iron and all FDOM filtration states. To further investigate iron's effect on DOC/FDOM relationship, a time series of total iron and FDOM was developed for *Year 2* data (Figure 9). At a glance, the data sets correlate well and follow the same pattern. But when analyzed, it becomes apparent that iron concentrations were not the driver of the phase shift. During the phase shift period, iron concentrations were well below their annual maximum. The relationship between DOC and FDOM was better at times of elevated iron concentrations at Banks (November–January). Therefore, iron may affect the DOC/FDOM relationship on some level, but it does not explain the variance observed during the phase shift period.

Figure 9 **Time Plot of Various FDOM Filter States and Iron**

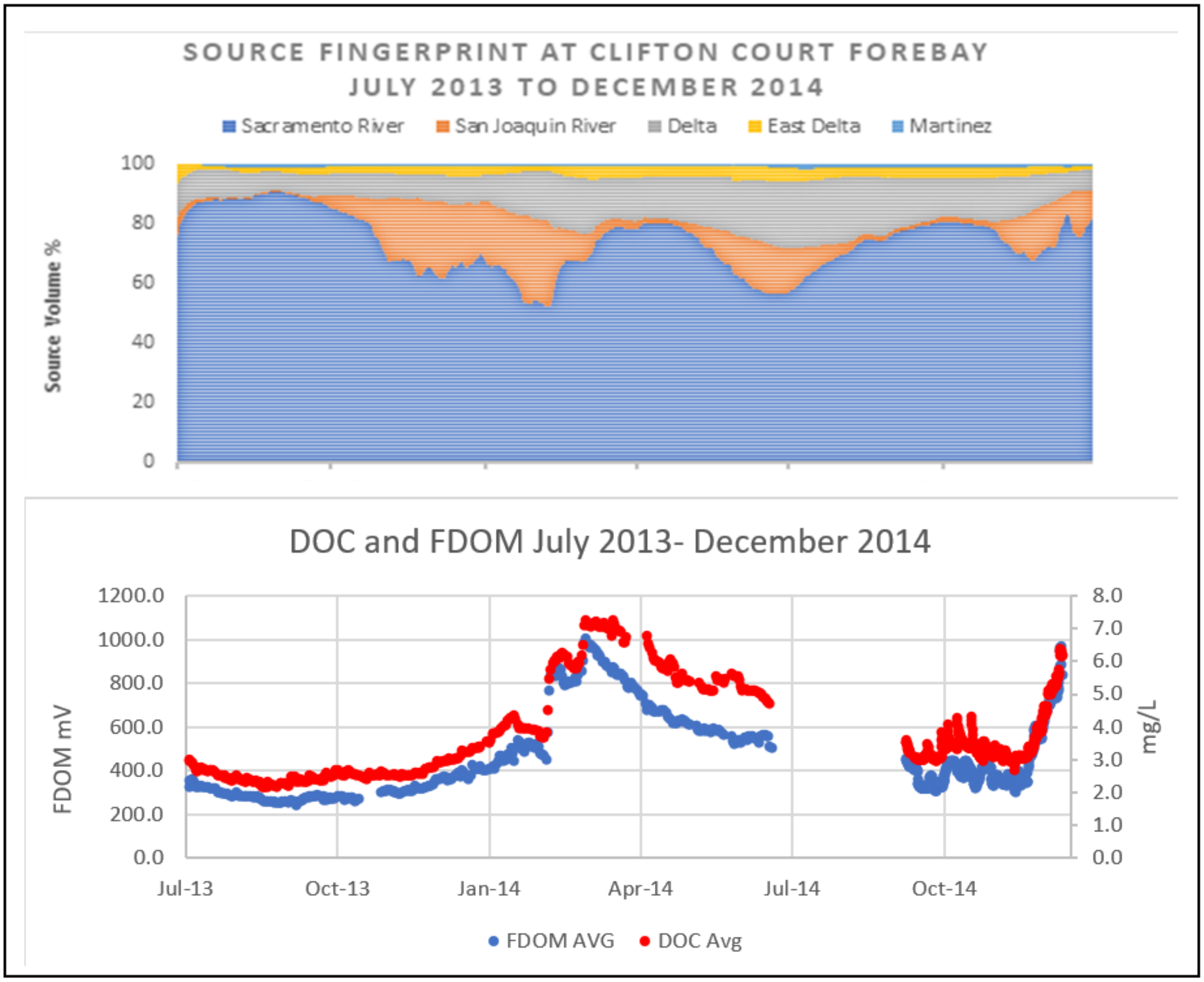


Source and Seasonality

Watershed hydrology and State Water Project operations result in a constantly changing mix of water at Clifton Court Forebay. Water at Clifton Court can be sourced from the Sacramento River, San Joaquin River, other smaller tributaries (e.g., eastside streams), from in-Delta sources, and from the San Francisco Bay (Martinez). Although it varies across the year, the Sacramento River generally provides about 70 percent of the total volume available at Clifton Court, the San Joaquin River provides between 15–35 percent, the in-Delta source provides about 5–25 percent, and other sources provide the remainder. Higher DOC concentrations at Banks during the spring months, as compared with Sacramento and San Joaquin River DOC, are mostly because of the in-Delta DOC influence. In the spring, the Sacramento and San Joaquin rivers do not generally exceed 5 mg/L, while in-Delta sourced water can be as high as 11 mg/L. In the interim report, it was speculated that the water source could be a driver of regression variance. Using DWR's source fingerprinting model, the plan was to look more closely at source inputs in this report. But the 2015 fingerprint model was deemed too inaccurate by DWR modelers (likely because of the extreme drought conditions) and was cancelled for the 2015 calendar year. Since no additional fingerprint data were available for *Year 2*, analysis continued looking only at the *Year 1* data.

In Figure 10, seasonal source fluctuations can be observed. In general, the ratio of Sacramento River water decreases during the winter months and then increases during the spring at the same time as the phase shift. Although this would point to the Sacramento River causing the phase shift, there are other periods of time where phase shift conditions occur at times of lower Sacramento River influence. Similarly, the ratio of San Joaquin River water at Clifton Court does not track consistently with the phase shift.

Figure 10 Bay Delta Office's Delta Source Fingerprint at Clifton Court Forebay with Corresponding FDOM and DOC Values

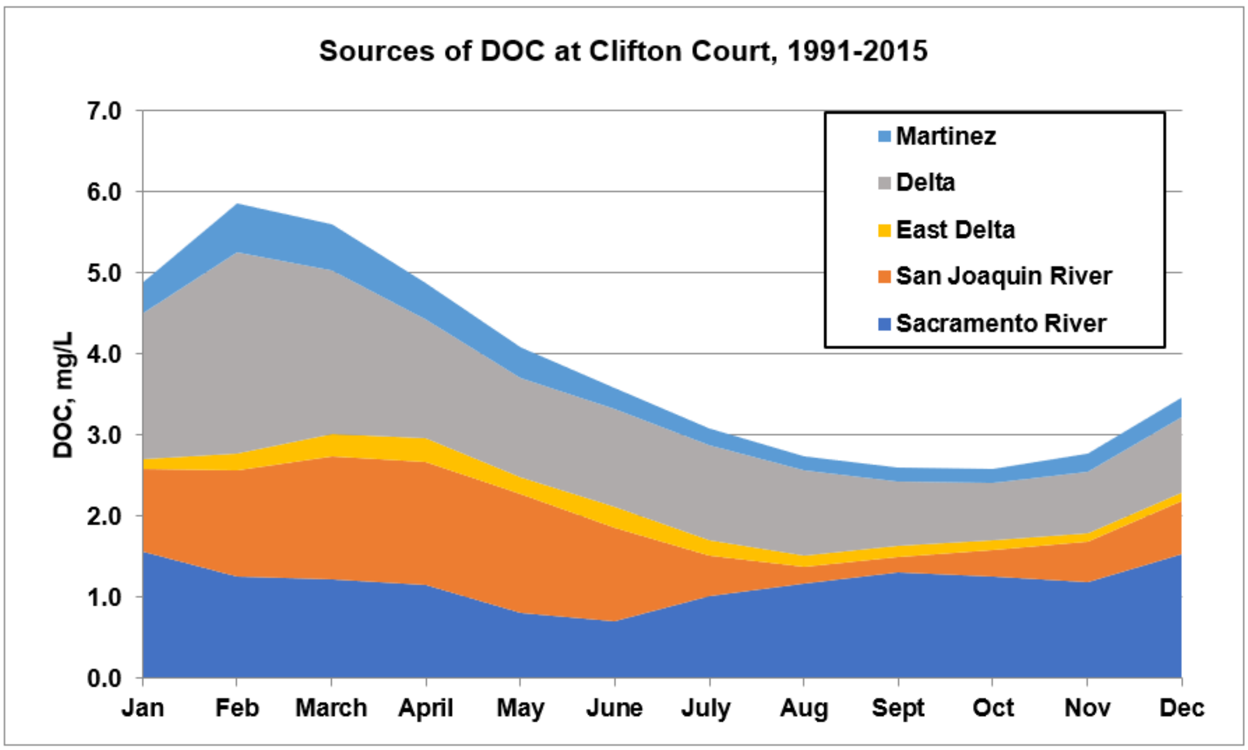


Note: The date range for both graphs is the same.

In March 2014, an increase of Sacramento River water was observed along with a decrease in San Joaquin River water. At this time, the ratio of in-Delta sourced water had roughly doubled over what had been present in late 2013. A higher proportion of in-Delta sourced water makes sense for this time of year, as farmers need to increase Delta islands pumping to remove excess water for flood control and to prepare fields for planting. The high ratio of in-Delta sourced water was maintained over the summer and into the fall of 2014, which also tracks well with the expectation that island irrigation needs to be pumped out during the growing season.

Looking at the historical record of *Source Fingerprints* at Clifton Court, the annual cycle in source ratios can be observed. Shown in Figure 11, on average, the February-to-April period provides for the highest amount of in-Delta sourced DOC at Clifton Court (Palencia Consulting Engineers and Starr Consulting 2017). This matches up quite well with the phase shift period observed in FDOM *Year 1 + 2* data and is further evidence that in-Delta-sourced water is driving the regressional variance observed during the early spring.

Figure 11 Average Monthly DOC Contribution for Each Fingerprint Source at Clifton Court Forebay from 1991 to 2015



Note: Data set part of analysis conducted in the 2017 State Water Project Sanitary Survey.

FDOM data were missing from July to September 2014, as this was the transition point between *Year 1* and *Year 2* data periods. Based on the elevated in-Delta source during this period, it can be assumed that the phase shift would have continued over the summer. At this point, this is only a hypothesis. The theory would have been further testable had the 2015 source fingerprints been valid. It is recommended that once new FDOM sensors are installed at Banks, this theory be revisited.

Beyond water source, seasonal variations in water quality are a possible cause of the changing DOC/FDOM relationship. That is, in summertime, controlled reservoir releases likely have a different fluorescence signature than seen in winter runoff, regardless of river source. Determining seasonal differences in source river fluorescence was outside the scope of this study but is worth considering in future refinements of the DOC-to-FDOM relationship.

Pumping Regime and Clifton Court Gate Operations

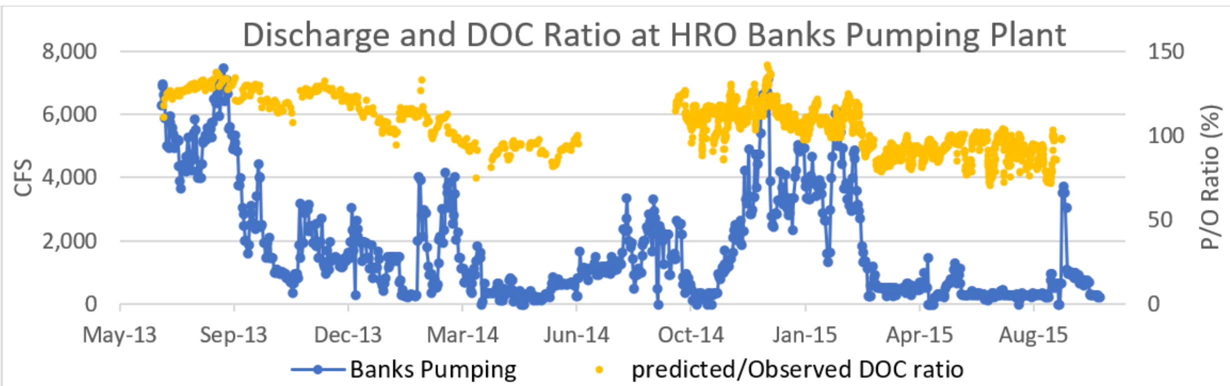
Pumping is a major factor in determining the water quality available at the Banks Station uphill of the pumping plant. Pumping rates and timing are based on many variables (e.g., demand, legal restrictions), but are also dependent on the amount of water available in Clifton Court Forebay. The gates at the entrance to the forebay are operated to allow in high tide water. Based on the system's operation, high tide water generally has a lower EC than Sacramento River water. Although Clifton Court gate operation is worth consideration, its operation was consistent across the whole FDOM study period. Because of this, gate operation was not considered as a viable explanation for DOC/FDOM regression variance. Pumping, on the other hand, was examined more closely.

During the winter of 2014, pumping occurred continuously (on a daily timestep) from November to March 2015. During these months, the DOC-to-FDOM regression was quite good ($R^2 = 0.93$). Because 2015 was a drought year, pumping at Banks decreased in early spring (March 2015). Limited pumping at this time could possibly explain the phase shift. Canal water quality conditions can change when there is limited-to-no pumping and can result in stagnation. Stagnant water loses suspended materials, allows more light infiltration, and may result in more algal development.

In Figure 12, pumping at Banks is compared with the predicted-to-observed (P/O) DOC ratio. Low P/O DOC ratios are observed during most periods of low pumping (spring time), while the ratio increases during most periods of higher pumping. This is not completely consistent throughout the year, as can be seen during October of 2014 when a high ratio is associated with low pumping. Although stagnation does occur from time to time, it seems unlikely for water quality to be sufficiently altered prior to pumping recommencing.

Pumping on its own does not explain regression variance, but building on the theory that in-Delta sourced water is the cause, it is possible that pumping has a hand in the phase shift. In the spring of 2014, low pumping occurred at Banks. Low pumping results in less Sacramento River water being present at Clifton Court, and in turn, a greater amount of in-Delta sourced water being present. In this way, pumping rates would have a hand in determining the source of the water at Clifton Court.

Figure 12 Discharge Pumping from Banks Pumping Plant Compared to the Predicted-to-Observed DOC Ratio.



Conclusion

FDOM *Year 2* data showed a strong relationship between FDOM 0.45µm and DOC ($R^2 = 0.76$), although not as good as that seen with *Year 1* data ($R^2 = 0.93$). Both years' data combined still yielded a strong regression of $R^2 = 0.88$. At the top end of the FDOM readings, the relationship between FDOM and DOC looks to break down for all filtration types. This is not necessarily tied to high turbidity and points to the presence of some unknown dissolved inorganic component that increased the fluorescence signature.

Previous studies have shown that increasing turbidity interferes with the fluorescence-to-DOC relationship. For *Year 2* data, turbidity was removed from the water through filtration. By developing regressions for the three FDOM filter states (0.45µm, 100µm, and non-filtered), turbidity's effect on the DOC-to-FDOM relationship could be assessed. Despite the different filtration methods, there was not a significant difference between the filtered and non-filtered samples, likely caused by low turbidity at Banks. Since Banks very rarely sees high turbidities (historical, discrete samples have never exceeded 200 NTU), it makes sense for future FDOM installations at Banks to run unfiltered water exclusively. Doing so will provide the same quality of results as filtered water, with fewer maintenance costs.

One of the major obstacles in this study was to explain why FDOM and DOC had such dramatic drift during the spring months, causing the regression to break down. Looking for causes of seasonal variance proved very challenging. Temperature is a well-known factor that affects the fluorescence of DOM. During this study, a temperature correction was applied in the hopes that it would explain the drift between instruments. But the correction did not provide the expected improvement or explain the phase shift. Iron was also explored because of its known effect on DOM fluorescence. The results suggested a strong correlation between iron and FDOM; however, iron-based interferences are based on iron quenching fluorescence, which was not observed during this study.

One variable that showed some promise was source water. Looking at the 2013–2014 fingerprint models, regression variance aligned reasonably well with source water changes. Looking at the different sources, the in-Delta component looks to be the most likely driver of regression variance. Unfortunately, confirmation of this with *Year 2* data was not possible because the 2015 fingerprints were unavailable because of fingerprint model error, possibly caused by the extreme drought conditions of the year.

Pumping at Banks was another variable that seemed to align well with the phase shift. Coupling the source fingerprint data with the pumping at Banks produced the clearest explanation for regression variance. With additional FDOM data, fingerprint modeling, and with varying water year types, this hypothesis could have been further tested.

Outside of developing a working theory to explain the phase shift, the data analyzed in this project has allowed for a deeper understanding of the DOC-to-FDOM relationship and has provided a roadmap for future use of the FDOM technology. Leveraging this experience will be essential when planning for future projects. In conclusion, the FDOM technology is a great tool for use as a proxy for direct DOC measurements, given that the data produced are calibrated and adjusted based on the specific hydrological conditions of each site. With a good understanding of the site characteristics, and with careful observation and adjustment, this technology can be used to further the understanding of water quality at Banks, in the Delta region, and beyond.

Recommendations

As with all scientific explorations, questions answered beget new questions worthy of consideration. The FDOM study is no different. Out of this study, some recommendations have been developed for future FDOM installations. Also, some questions remain about how to improve the quality of FDOM data to better fit with DOC. These recommendations include:

For Installations

- One lesson learned is that timely instrument calibration is a necessity. Although the instrument was factory calibrated when new, the lack of a calibration verification protocol left some uncertainty with the results. With no calibration verification, instrument drift was not able to be quantified. When new FDOM sensors are deployed, it will be essential to provide routine calibration using verified standards to remove this uncertainty.
- Based on the results of this study, no filtration is necessary when installing FDOM sensors. Filtration will not improve the regression for the turbidity levels seen at Banks (< 200 NTU). Also, filtration does not improve the FDOM-to-DOC regressional breakdown observed at FDOM measurements above 800 mV. Therefore, raw water delivered to the FDOM is the best option.
- To make data comparisons more efficient, it would be beneficial if DOC and FDOM measurements were taken at the same time and on the same interval. A great deal of time was spent building the tool used to interpolate data so that time stamps would match. If the instruments are programmed at the onset to synchronize measurements, a lot less effort will be required during data processing.

For Future Study

- In this study, a single regression was built from a one- or two-year data set. Instead of using a single regression, consider using regressions that are built from shorter time periods and that are active over smaller periods of time. Regression adjustments could occur monthly, seasonally, or even based on changes in the fingerprint source model. This approach may provide better results than those observed from annually adjusted regressions. If implemented, regressions could be built from the existing 2013–2015 data set or could be built using new data, depending on what seems most appropriate. If new data is preferred, a YSI EXO sonde (with FDOM sensor) has recently been installed at Banks, so new data will be available for analysis.

- Although a working theory to explain the phase shift has been developed, more data and analysis are needed to improve confidence in that theory. Assuming the theory is accurate, a correction method to improve the regression at the times of changing in-Delta influence needs to be developed. The main goal is to provide an answer to what exactly is causing the phase shift, and how can the phase shift be avoided in future predictions. Because of technical issues, the Clifton Court fingerprint data for the spring of 2015 in-Delta water was not available. Because of the missing fingerprint data, there was no comparison done between in-Delta correlation and FDOM for the last half of the *Year 2* data. In the future, though, this data will likely be available, and a comparison will be possible. Developing short time-period regressions or regressions built on the source fingerprint, when available (covered above), should solve for the variance seen from high in-Delta sourcing; but if not, other methods to solve for the phase shift regression variance should be considered.
- Water agencies tend to be interested in time periods of elevated DOC, which happen to be when the FDOM-to-DOC regression is the least accurate. For the FDOM to become a viable alternative to analytical DOC, the relationship at the top end of the regression must be improved. This issue may also be resolved using short time-period data sets and regressions; but like the phase shift, should be considered separately from general regression imprecision. If a behavior like the phase shift seems repetitive enough, the error could be accounted for with a modified FDOM regression equation.
- Once new YSI FDOM data are available from Banks, Jones, and Gianelli, further analysis between DOC and YSI FDOM is recommended. This will help test the precision of these new sensors and assess how the results compare to the findings in this report. Other questions worth assessing with new instruments:

- Is the phase shift observable in the new data? At all three stations?
- Are the same patterns in calculated DOC at Banks observable at Jones and Gianelli?
- At Gianelli, how is the regression affected by the water source change when operations switch from pumping to generating at San Luis?

Also, since the data used in this report only covers drought year conditions, new YSI FDOM data collected during different water-year types should be assessed and compared against the drought data used in this report.

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