

Appendix 2. Model Archive Summary for Filtered Mercury Concentrations at Station 254543080405401: Tamiami Canal at S-12D Near Miami, Florida

Previous studies have established that fluorescence of chromophoric dissolved organic matter (fDOM) sensors can be used as surrogates for filtered mercury concentrations (Bergamaschi and others, 2011, 2012a, 2012b). This study focuses on the development of surrogate models for continuous monitoring of mercury in the Florida Everglades.

High density and long-term data will aid with the description of short- and long-term variability of carbon and mercury concentrations, which will improve understanding of carbon input and transport. Prior to this study, no continuous and long-term time-series data on carbon concentrations were available for the freshwater wetlands of the Florida Everglades.

The objectives of this study were to develop and document a surrogate model to calculate concentration and loads of filter-passing total mercury (FTHg) at site S-12D. This model archive summary describes the FTHg model developed to compute 15-minute frequency FTHg concentrations from temperature and fDOM data collected from September 5, 2013, to December 19, 2016, at site S-12D. The methods used follow U.S. Geological Survey (USGS) guidance as referenced in Rasmussen and others (2009).

Site and Model Information

USGS site number: 254543080405401

https://waterdata.usgs.gov/fl/nwis/inventory/?site_no=254543080405401&agency_cd=USGS

Site name: Tamiami Canal at S-12D near Miami, FL

Location: lat 25°45'43" N., long 80°40'54" W., referenced to North American Datum of 1927, in T. 54 S., R. 36 E., Miami-Dade County, Florida, hydrologic unit 03090202, on south bank 100 feet southwest of structure 12-D, near east boundary of Indian reservation on U.S. Highway 41.

Equipment: A YSI EXO water-quality monitoring system equipped with sensors for water temperature, specific conductance, turbidity, and an fDOM sensor. The monitor is housed in an 8-inch-diameter polyvinyl chloride (PVC) pipe on a diagonal extending off the end of the structure into the stream. Readings from the YSI EXO were recorded every 15 minutes and transmitted hourly by way of satellite. The model applies only to this site (254543080405401) and specified time period (September 5, 2013, to April 3, 2017).

Model number: 1.0

Date model was created: January 5, 2018

Model calibration data period: September 11, 2013, to December 19, 2016

Model application date: September 5, 2013, to April 3, 2017

Computed by: Amanda Booth, USGS Caribbean-Florida Water Science Center

Reviewed by: Mark Brigham, USGS Minnesota Water Science Center, Mounds View, Minnesota and Brian Downing, USGS California Water Science Center, Sacramento, California

Approved by: David Sumner, USGS Caribbean-Florida Water Science Center

Model Data

All data were collected using USGS protocols and are stored in the National Water Information System (NWIS) database (U.S. Geological Survey, 2019). fDOM data were corrected for the effects of temperature, turbidity, and inner filter effects. The regression model is based on 25 concurrent measurements of FTHg, fDOM, and temperature samples collected from September 11, 2013, through December 19, 2016. Samples were collected throughout the range of observed hydrologic, fDOM, and temperature conditions. Summary statistics and the complete model-calibration data are provided in the dataset. Studentized residuals from the final model were inspected for values greater than 3 or less than -3, which are considered potential outliers. No outliers were found within the dataset.

Filtered Mercury Data

Teflon equipment precleaned by the USGS Mercury Research Laboratory was used for the collection and transport of all mercury samples. A hydrokinetic nozzle, 200-milliliter bottle, and nozzle-bottle holder were used to collect enough water to fill a 2-liter bottle for each sample. Initially, two water samples were collected for mercury analysis: (1) a point sample next to the water-quality sensors and (2) a single vertically integrated sample at the location of highest water velocity. Samples were placed on ice for transport, filtered through a 0.7-micron quartz-fiber filter to separate dissolved and suspended sediment mercury species, and shipped to the laboratory within 24 hours. Filtered waters were acidified to 1 percent with concentrated hydrochloric acid within 5 hours of collection and were stored and shipped in coolers. Laboratory analyses were performed to obtain observed concentrations of FTHg using techniques and methods documented in U.S. Environmental Protection Agency (EPA) Method 1631 (EPA, 2002).

Elevated levels of turbidity are rare at this site other than immediately after a gate opening. To try to capture a wide range of conditions, a sampling event was coordinated on September 23, 2015, to collect a sample just after the gates were opened. Multiple samples were collected on this date at 8:02 a.m., 8:19 a.m., and 9:41 a.m. Eastern Standard Time. Only the 8:02 a.m. sample was included in model development.

Surrogate Data

The fDOM data used in this analysis were measured using a YSI EXO V2, serial numbers 13f100955, 14c101755, 14c100465, 14c100466, 15G100778, 15G100779, and 15c104523 (Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government). The fDOM data were corrected for temperature, turbidity, and inner filter effects (Downing and others, 2012). The equation for the turbidity correction was provided by B. Pellerin (U.S. Geological Survey, written commun. 2018) and was determined using YSI EXO, temperature, turbidity, and fDOM sensors. The equation was determined using Elliot silt loam and is provided below.

Elliot silt loam turbidity correction – exponential fit (table curve):

$$fDOM_{turbcorr} = \frac{fDOM_{tempcorr}}{e^{(-0.027567 - 0.06259 \cdot FNU)}}$$

where

$fDOM_{tempcorr}$ = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature corrected, in parts per billion quinine sulfate equivalents (QSE);

$fDOM_{turbcorr}$ = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature and turbidity corrected, in parts per billion quinine sulfate equivalents; and

FNU = turbidity (YSI EXO model), in formazin nephelometric units.

Serial dilutions were performed to determine the inner filter effect using Caloosahatchee River at S-79 (02292900) native water, filtered through a 0.45-micron filter, collected on August 16, 2017. Native water from S-12D was not used for this correction because we did not collect water at S-12D that had a high enough initial fDOM concentration to complete a serial dilution that would represent the range of fDOM concentrations observed during the study. Data collected at S-12D on September 28, 2017, indicate that the Caloosahatchee water is representative of S-12D with respect to the inner filter effect.

Inner filter effect correction:

$$fDOM_{corr} = 0.002 \cdot (fDOM_{turbcorr})^2 + 0.7608 \cdot fDOM_{turbcorr}$$

where

$fDOM_{corr}$ = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature corrected, turbidity and inner filter corrected, in quinine sulfate equivalents; and

$fDOM_{turbcorr}$ = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature and turbidity corrected, in quinine sulfate equivalents.

The $fDOM$ values at S-12D ranged from 79.9 QSE on February 14, 2014, to 610.5 QSE on August 1, 2014. Specific conductance at S-12D ranged from 260 microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ @ 25 °C) on June 27, 2013, to 916 $\mu\text{S}/\text{cm}$ @ 25 °C on September 22, 2015.

Model Development

Regression analysis was done using Microsoft Excel and the USGS Surrogate Analysis and Index Developer (SAID) tool (Domanski and others, 2015) by examining $fDOM$ and other continuously measured data as explanatory variables for estimating FTHg concentration. If data was not available for the minute the sample was collected, data from the minute before and the minute after were averaged together. A variety of models that predict FTHg were evaluated. The distribution of residuals was examined for normality, and plots of residuals (the difference between the observed and computed values) as compared to computed FTHg were examined for homoscedasticity. $fDOM$ and temperature were selected as the best predictors of FTHg based on residual plots, relatively high adjusted coefficient of determination (adjusted R^2), and relatively low model standard percentage error. Values for all aforementioned statistics and metrics were computed and are included below, along with all relevant sample data and more in-depth statistical information. When discharge (Q) equaled zero, a Q value of 0.001 was entered for the program to create the graphics.

Model Summary

Summary of final regression analysis for FTHg concentration at site number 254543080405401.

Filtered mercury concentration-based model:

$$FTHg = 0.00168 * fDOM + 0.0264 * Temperature - 0.293$$

where

$FTHg$ = filtered mercury concentration, in nanograms per liter;

$fDOM$ = fluorescence of chromophoric dissolved organic matter, YSI EXO model, temperature, turbidity, and inner filter effect corrected, in quinine sulfate equivalents; and

$Temperature$ = temperature, in degrees Celsius.

The use of $fDOM$ as an explanatory variable is appropriate physically and statistically. $fDOM$ refers to the fraction of chromophoric dissolved organic matter that fluoresces, and previous studies demonstrated that $fDOM$ data can be used to estimate filtered or dissolved mercury (Hg,) methylmercury (MeHg), and dissolved organic carbon (DOC) concentrations in water, allowing for the computation of continuous time-series data of

concentrations (Bergamaschi and others, 2011, 2012a, 2012b). The addition of temperature indicates an effect of seasonality.

Model Statistics, Data, and Plots

Model

$$\text{FTHg} = 0.00168 * \text{fDOM} + 0.0264 * \text{Temperature} - 0.293$$

Variable Summary Statistics

	FTHg	fDOM	Temperature
Minimum	0.480	118	18.2
1st Quartile	0.620	236	23.5
Median	0.790	303	26.4
Mean	0.878	292	25.7
3rd Quartile	1.030	348	29.1
Maximum	1.570	538	30.4

Exploratory Plots

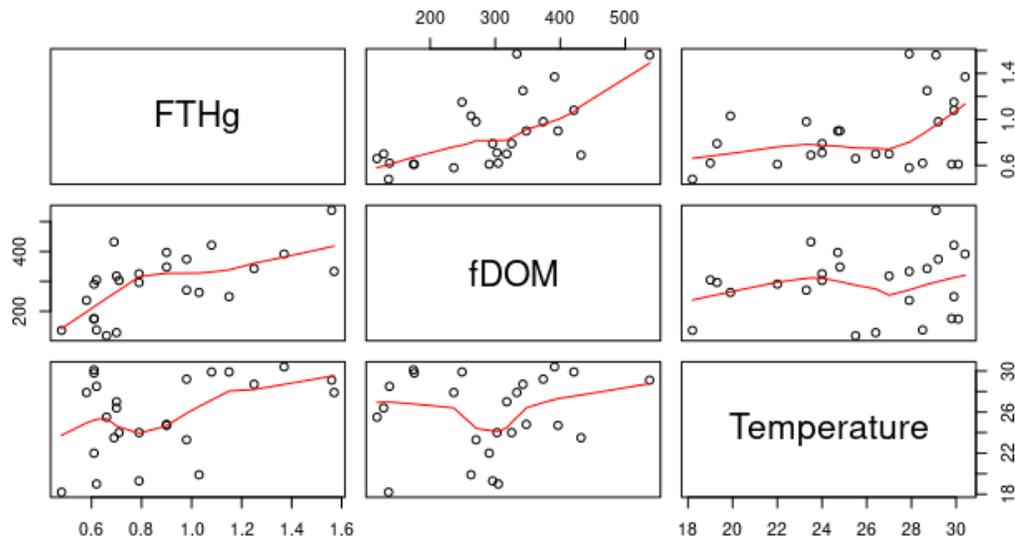


Figure 2.1. Comparison of filter-passing total mercury (FTHg) concentration, in nanograms per liter; fluorescence of chromophoric dissolved organic matter (fDOM), in quinine sulfate equivalents; and temperature, in degrees Celsius.

Basic Model Statistics

Number of Observations	25
Standard error (RMSE)	0.227
Average Model standard percentage error (MSPE)	25.9
Coefficient of determination (R^2)	0.499
Adjusted Coefficient of Determination (Adj. R^2)	0.454

Variance Inflation Factors (VIF)

fDOM	Temperature
1.02	1.02

Explanatory Variables

	Coefficients	Standard Error	t value	Pr(> t)
(Intercept)	-0.29300	0.32600	-0.899	0.378000
fDOM	0.00168	0.00044	3.820	0.000936
Temperature	0.02640	0.01220	2.170	0.041300

Correlation Matrix

	Intercept	fDOM	Temperature
Intercept	1.000	-0.263	-0.910
fDOM	-0.263	1.000	-0.136
Temperature	-0.910	-0.136	1.000

Outlier Test Criteria

Leverage	Cook's D	DFFITS
0.360	0.261	0.693

Flagged Observations

Three observations were flagged for difference in fits (DFFITS) values greater than 0.693. All flagged observations were retained in the model.

	FTHg	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
09/23/2015 08:02	1.57	1.000	0.566	2.56	2.99	0.0575	0.134	0.739
02/02/2016 09:48	1.03	0.675	0.355	1.68	1.76	0.1360	0.148	0.699
12/19/2016 10:16	0.69	1.050	-0.364	-1.72	-1.81	0.1360	0.156	-0.718

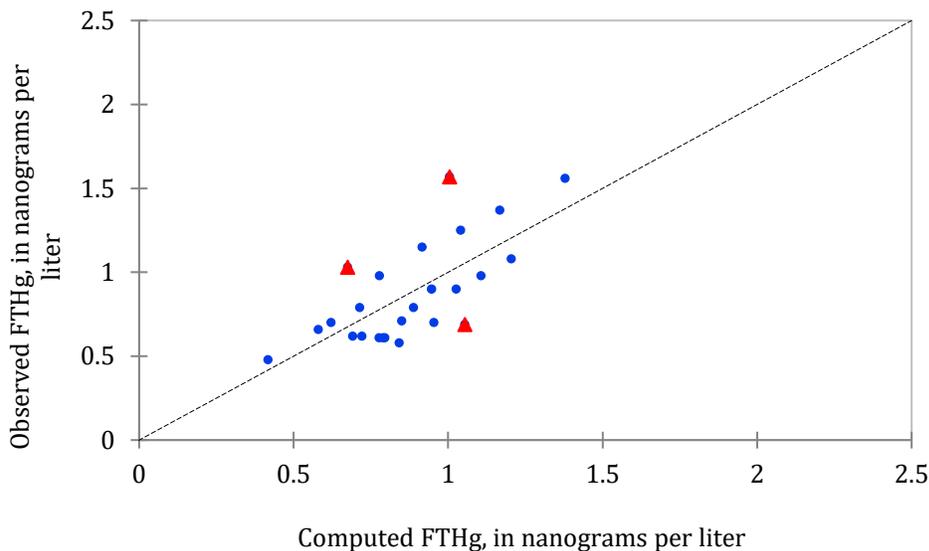


Figure 2.2. Relation between observed filter-passing total mercury (FTHg) and computed FTHg; flagged observations are in red.

Statistical Plots

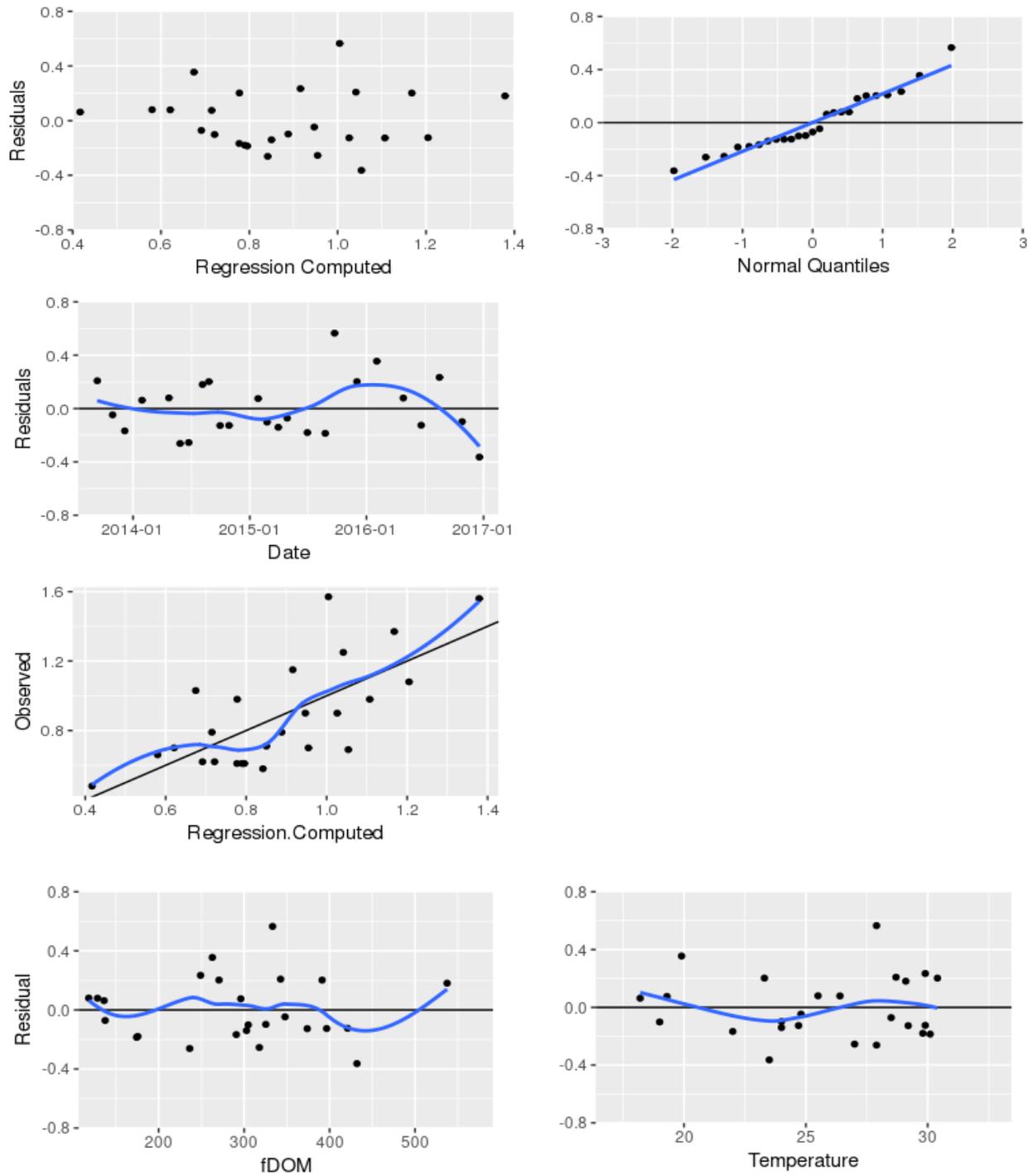


Figure 2.3. Residual and observed versus computed plots.

(fDOM, fluorescence of chromophoric dissolved organic matter)

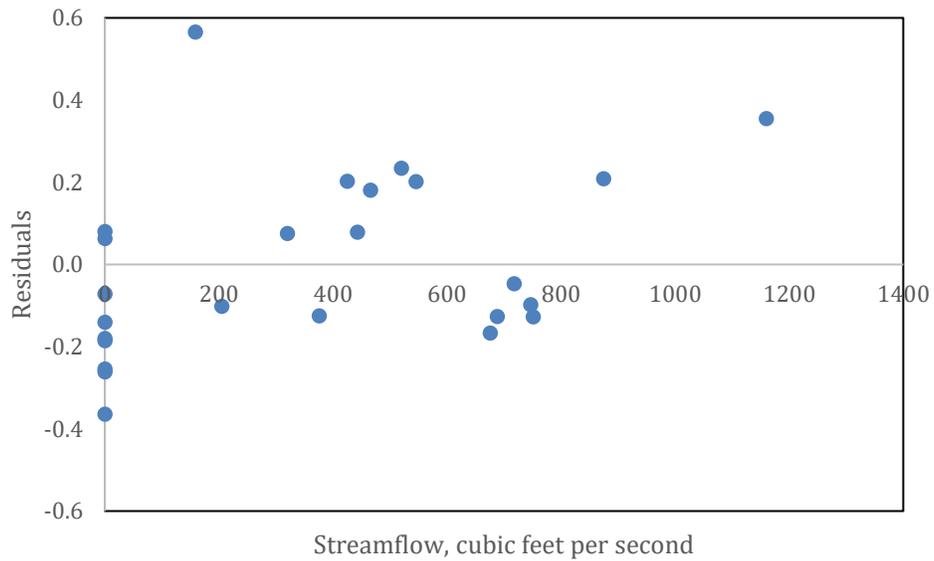


Figure 2.4. Relation between residuals and streamflow showing that the residuals had no systematic bias with respect to streamflow.

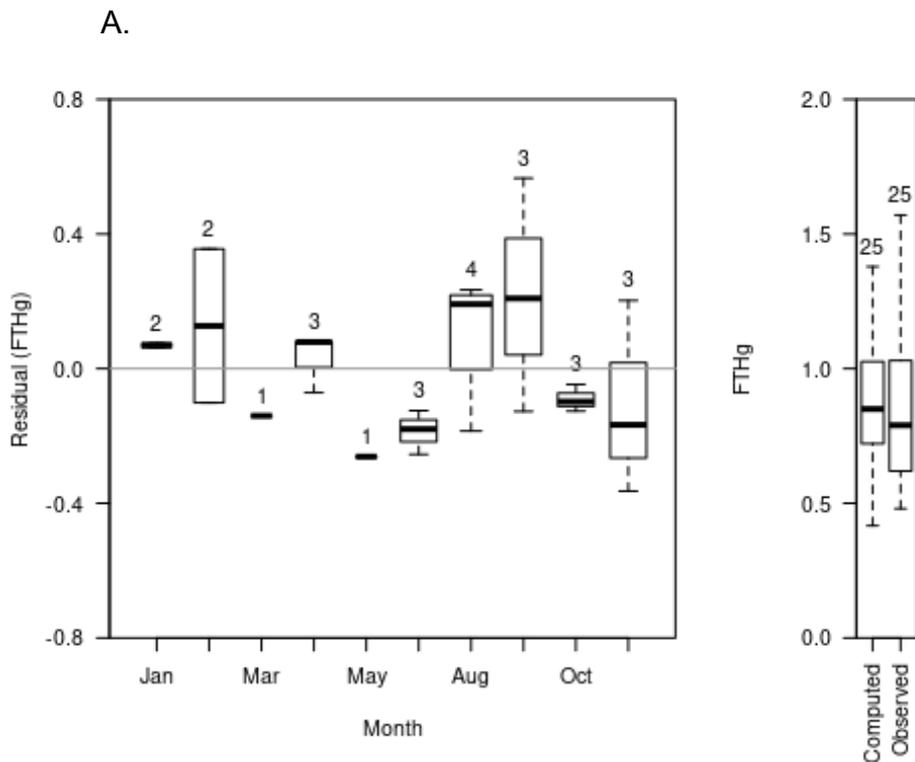


Figure 2.5. A, Seasonal variation in residuals, and B, computed and observed filter-passing total mercury (FTHg), in nanograms per liter.

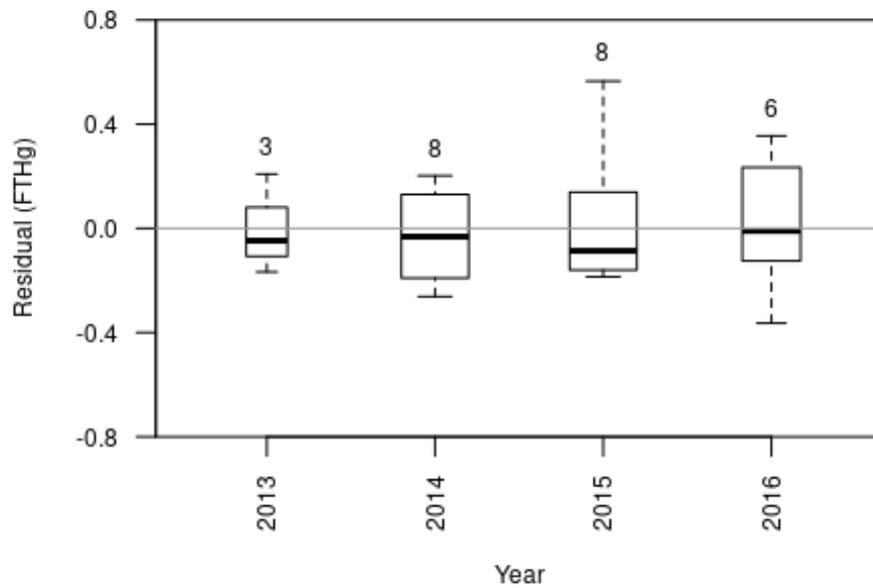
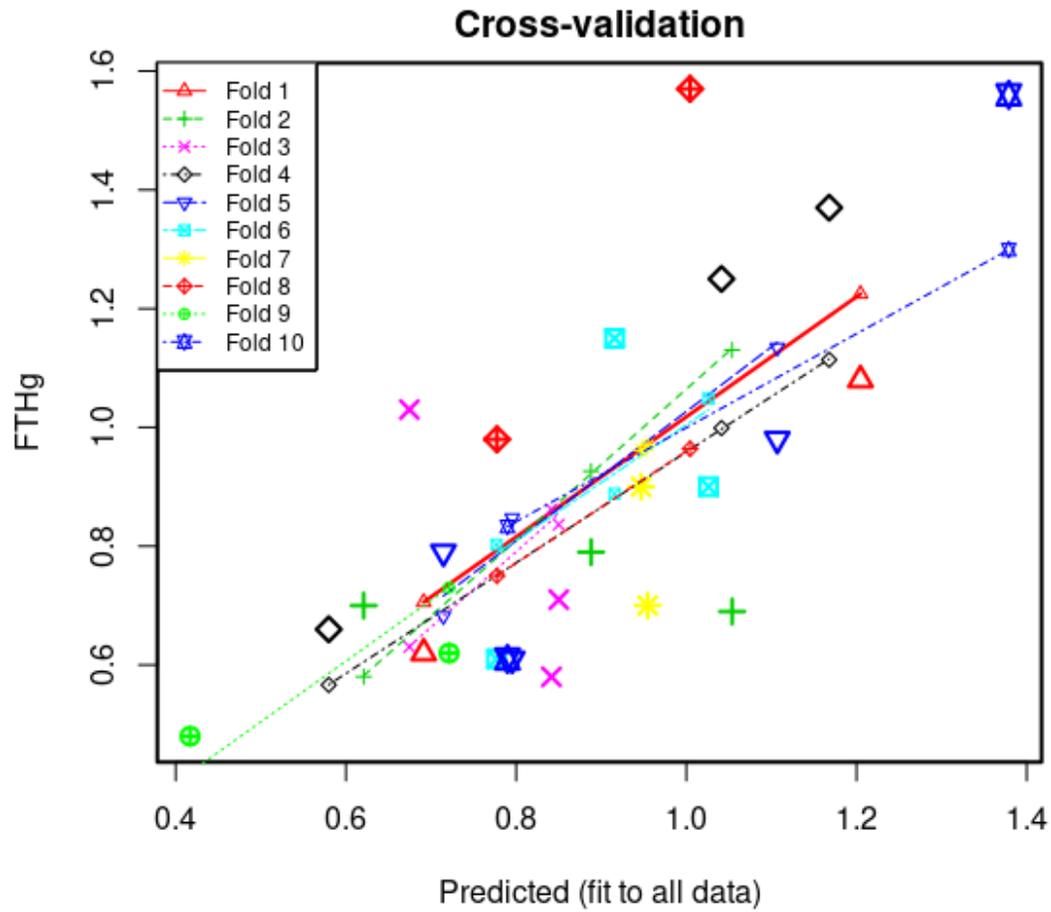


Figure 2.6. Annual variation in residuals.

(FTHg, filter-passing total mercury)

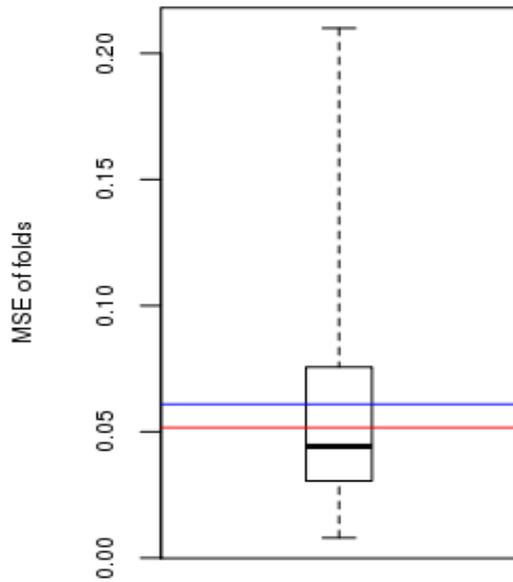
Cross Validation

K-fold cross-validation was used to validate the model. The advantage of K-fold cross validation is that all the examples in the dataset are eventually used for both training and testing. The data were split randomly into 10 experiments or folds.



Minimum MSE of folds: 0.00794
 Mean MSE of folds: 0.06090
 Median MSE of folds: 0.04420
 Maximum MSE of folds: 0.21000
 (Mean MSE of folds) / (Model MSE): 1.18000

Figure 2.7. Cross-validation plot.
(FTHg, filter-passing total mercury)



Red line - Model MSE

Blue line - Mean MSE of folds

Figure 2.8. Mean standard of error (MSE) of folds boxplot.

Model Calibration Dataset

	Date	FTHg	fDOM	Temperature	Computed FTHg	Residual	Normal Quantiles	Censored Values
0					FTHg			
1	2013-09-11	1.25	343	28.7	1.04	0.209	1.07	--
2	2013-10-29	0.9	348	24.8	0.947	-0.0469	0.0996	--
3	2013-12-06	0.61	291	22	0.777	-0.167	-0.765	--
4	2014-01-29	0.48	136	18.2	0.417	0.0631	0.2	--
5	2014-04-23	0.66	118	25.5	0.58	0.0802	0.52	--
6	2014-05-28	0.58	236	27.9	0.842	-0.262	-1.53	--
7	2014-06-24	0.7	318	27	0.955	-0.255	-1.26	--
8	2014-08-06	1.56	538	29.1	1.38	0.181	0.637	--
9	2014-08-26	1.37	391	30.4	1.17	0.202	0.765	--
10	2014-09-30	0.98	374	29.2	1.11	-0.127	-0.52	--
11	2014-10-28	0.9	397	24.7	1.03	-0.126	-0.409	--
12	2015-01-27	0.79	296	19.3	0.715	0.0754	0.303	--
13	2015-02-24	0.62	305	19	0.721	-0.101	-0.2	--

14	2015-03-31	0.71	303	24	0.85	-0.14	-0.637	--
15	2015-04-28	0.62	137	28.5	0.691	-0.0714	0	--
16	2015-06-30	0.61	176	29.8	0.79	-0.18	-0.906	--
17	2015-08-25	0.61	174	30.1	0.795	-0.185	-1.07	--
18	2015-09-23	1.57	333	27.9	1	0.566	1.98	--
19	2015-12-02	0.98	271	23.3	0.778	0.202	0.906	--
20	2016-02-02	1.03	263	19.9	0.675	0.355	1.53	--
21	2016-04-25	0.7	128	26.4	0.621	0.0791	0.409	--
22	2016-06-20	1.08	421	29.9	1.2	-0.125	-0.303	--
23	2016-08-16	1.15	249	29.9	0.916	0.234	1.26	--
24	2016-10-26	0.79	325	24	0.888	-0.098	-0.0996	--
25	2016-12-19	0.69	432	23.5	1.05	-0.364	-1.98	--

Model Limitations

Errors in the FTHg surrogate model can be attributed to several factors, including those related to fDOM and specific conductance data. There is error associated in the calibration of the standards, and corrections were applied only when the instrument value was more than 5 percent from the standard value for fDOM and 3 percent for specific conductance. Additionally, corrections for turbidity and inner filter effects may change over time on the basis of the size and makeup of the sediment and organic matter. While the influence of changes in particle size and composition and its effect on turbidity influence on fDOM values at this location is small, the change in inner filter effect is potentially substantial. After Hurricane Irma in September 2017, the inner filter effect changed substantially at the Caloosahatchee River at S-79 (02292900), figure 2-9, indicating that variations are possible at this location as well. Unfortunately, changes in the inner filter effect were not monitored throughout this study.

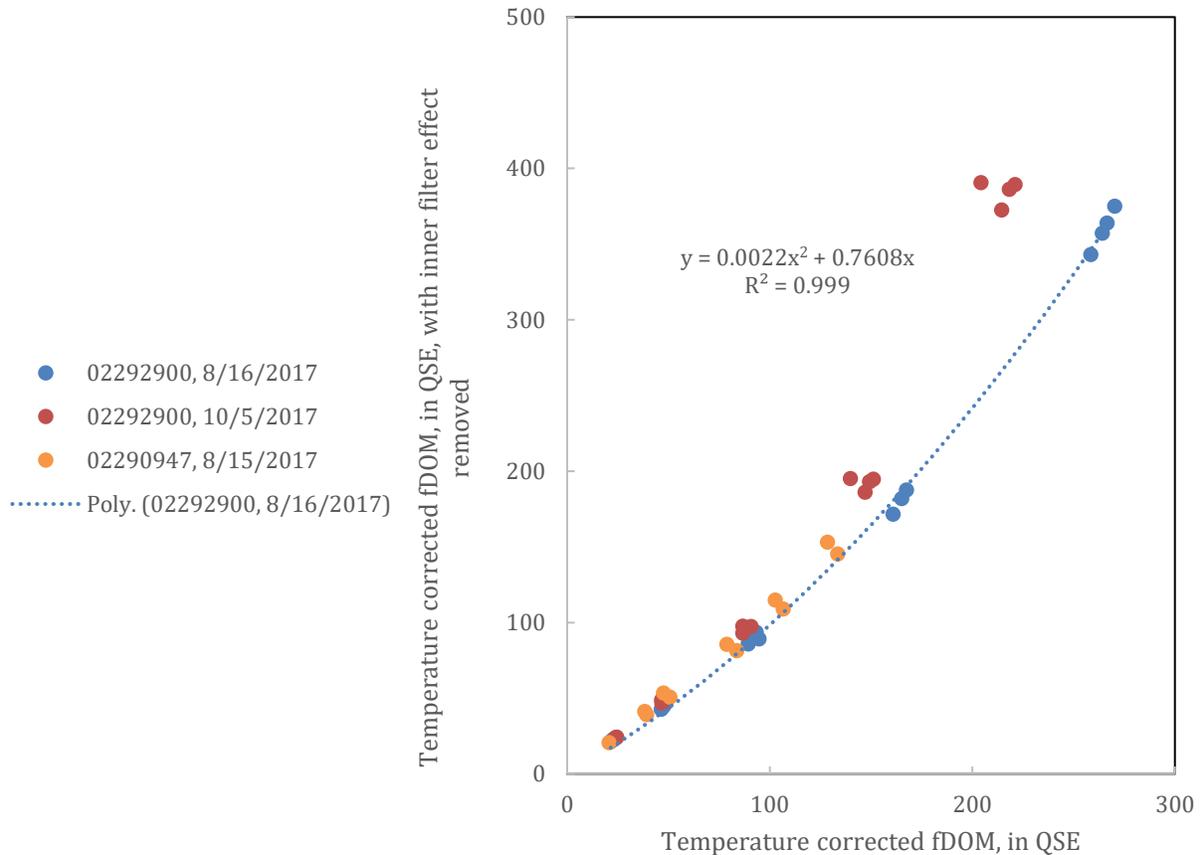


Figure 2.9. Relation between temperature corrected fluorescence of chromophoric dissolved organic matter (fDOM), in quinine sulfate equivalents (QSE), with the inner effect removed and temperature corrected fDOM, in QSE, without the inner filter effect removed.

Another limitation to this model is in the assumption that the sensor data and the discrete data collected at the station are representative of the mean channel. Width- and depth-integrated samples were not collected and the sensor profiles were used to determine the variability of the channel cross section.

An additional source of model error comes from the processes used to collect and analyze discrete samples.

Definitions

FTHg: Mercury in ng/l (50287)

fDOM: Colored dissolved organic matter (CDOM) in ug/l QSE (32295)

Temperature: Temperature, water in deg C (00010)

References Cited

- Bergamaschi, B.A., Fleck, J.A., Downing, B.D., Boss, E., Pellerin, B., Ganju, N.K., Schoellhamer, D., Heim, W., Stephenson, M., and Fujii, R., 2011, Methylmercury dynamics in a tidal wetland quantified using in situ optical measurements: *Limnology and Oceanography*, v. 56, no. 4, p. 1355–1371, accessed October 1, 2017, at <https://doi.org/10.4319/lo.2011.56.4.1355>.
- Bergamaschi, B.A., Fleck, J.A., Downing, B.D., Boss, E., Pellerin, B.A., Ganju, N.K., Schoellhamer, D.H., Byington, A.A., Heim, W.A., Stephenson, M., and Fujii, R., 2012a, Mercury dynamics in a San Francisco estuary tidal wetland—Assessing dynamics using in situ measurements: *Estuaries and Coasts*, v. 35, no. 4, p. 1036–1048, accessed October 1, 2017, at <https://link.springer.com/article/10.1007/s12237-012-9501-3>.
- Bergamaschi, B.A., Krabbenhoft, D.P., Aiken, G.R., Patino, E., Rumbold, D.G., and Orem, W.H., 2012b, Tidally driven export of dissolved organic carbon, total mercury, and methylmercury from a mangrove-dominated estuary: *Environmental Science and Technology*, v. 46, no. 3, p. 1371–1378, accessed October 1, 2017, at <https://doi.org/10.1021/es2029137>.
- Domanski, M.M., Straub, T.D., and Landers, M.N., 2015, Surrogate analysis and index developer (SAID) tool (version 1.0, September 2015): U.S. Geological Survey Open-File Report 2015–1177, 38 p., accessed October 1, 2017, at <https://doi.org/10.3133/ofr20151177>.
- Downing, B.D., Pellerin, B.A., Bergamaschi, B.A., Saraceno, J.F., and Kraus, T.E., 2012, Seeing the light—The effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers and streams: *Limnology and Oceanography—Methods*, v. 10, no. 10, p. 767–775, accessed April 19, 2017, at <https://doi.org/10.4319/lom.2012.10.767>.
- Rasmussen, P.P., Gray, J.R., Glysson, G.D., and Ziegler, A.C., 2009, Guidelines and procedures for computing time-series suspended-sediment concentrations and loads from in-stream turbidity-sensor and streamflow data: U.S. Geological Survey Techniques and Methods, book 3, chap. C4, 53 p., accessed October 1, 2017, at <https://doi.org/10.3133/tm3C4>.
- U.S. Environmental Protection Agency [EPA], 2002, Method 1631, revision E—Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry: U.S. Environmental Protection Agency Report EPA–821–R99–05, accessed October 1, 2017, at https://www.epa.gov/sites/production/files/2015-08/documents/method_1631e_2002.pdf.
- U.S. Geological Survey, 2019, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed May 8, 2019, at <https://doi.org/10.5066/F7P55KJN>.