Appendix 3. Model Archive Summary for Filtered Methylmercury 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 methylmercury (FMeHg) at site S-12D. This model archive summary describes the FMeHg model developed to compute 15-minute frequency FMeHg concentrations from fDOM and temperature data collected from September 5, 2013, to April 3, 2017, 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: April 13, 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 FMeHg samples, fDOM, and temperature data 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 Methylmercury 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 particulate 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 FMeHg using techniques and methods documented in U.S. Environmental Protection Agency (EPA) Method 1631 (EPA, 2002) and DeWild and others (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 9:41a.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):

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

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:

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

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 (µS/cm @ 25 °C) on June 27, 2013, to 916 µS/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 by examining fDOM and other continuously measured data as explanatory variables for estimating FMeHg concentration. A variety of models that predict FMeHg 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 FMeHg were examined for homoscedasticity. fDOM and temperature were selected as the best predictors of FMeHg 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 FMeHg concentration at site number 254543080405401.

Filtered methylmercury concentration-based model:

$$FMeHg = 0.00021 * fDOM + 0.00527 * Temperature - 0.0534$$

where

> *FMeHg* = filtered methylmercury concentration, in nanograms per liter;
>
> *fDOM* = fluorescence of chromophoric dissolved organic matter, YSI EXO model, temperature and turbidity 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 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

FMeHg = 0.00021 * fDOM + 0.00527 * Temperature−0.0534

Variable Summary Statistics

	FMeHg	fDOM	Temperature
Minimum	0.060	118	18.2
1st Quartile	0.080	236	23.3
Median	0.140	303	26.4
Mean	0.143	290	25.6
3rd Quartile	0.190	343	29.1
Maximum	0.310	538	30.4

Exploratory Plots

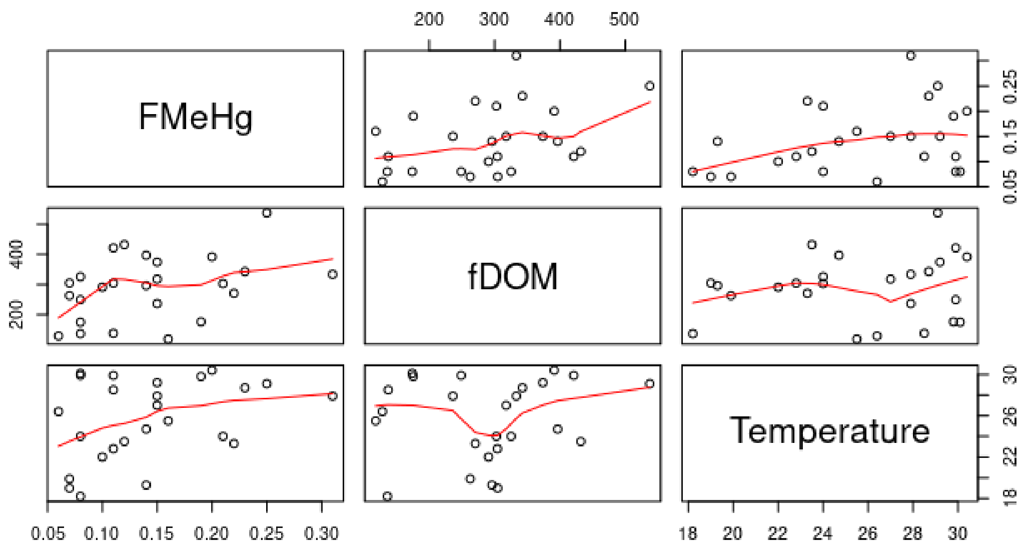


Figure 3.1. Comparison of filter-passing methylmercury (FMeHg) concentration, in nanograms per liter; fluorescence of chromophoric dissolved organic matter (fDOM), in quinine sulfate equivalents; and temperature, in degrees Celsius.

Basic Model Statistics

Number of Observations	25
Standard error (RMSE)	0.0593
Average Model standard percentage error (MSPE)	41.5

Coefficient of determination (R^2)	0.244
Adjusted Coefficient of Determination (Adj. R^2)	0.175

Variance Inflation Factors (VIF)

fDOM	Temperature
1.02	1.02

Explanatory Variables

	Coefficients	Standard Error	t value	Pr(>|t|)
(Intercept)	-0.05340	0.083900	-0.637	0.5310
fDOM	0.00021	0.000115	1.820	0.0817
Temperature	0.00527	0.003150	1.670	0.1080

Correlation Matrix

	Intercept	FDOM	Temperature
Intercept	1.000	-0.267	-0.908
fDOM	-0.267	1.000	-0.137
Temperature	-0.908	-0.137	1.000

Outlier Test Criteria

Leverage	Cook's D	DFFITS
0.360	0.261	0.693

Flagged Observations

One observation was flagged for difference of fits (DFFITS) greater than 0.693. All flagged observations were retained.

	FMeHg	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
9/23/2015 8:02	0.31	0.164	0.146	2.54	2.96	0.0586	0.134	0.738

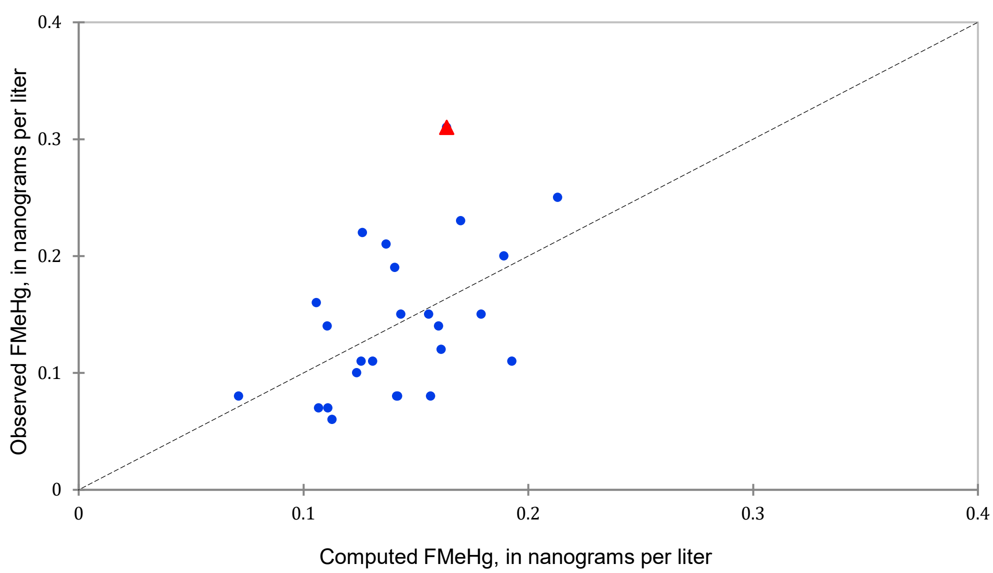


Figure 3.2. Relation between observed filter-passing methylmercury (FMeHg) and computed FMeHg; flagged observations are in red.

Statistical Plots

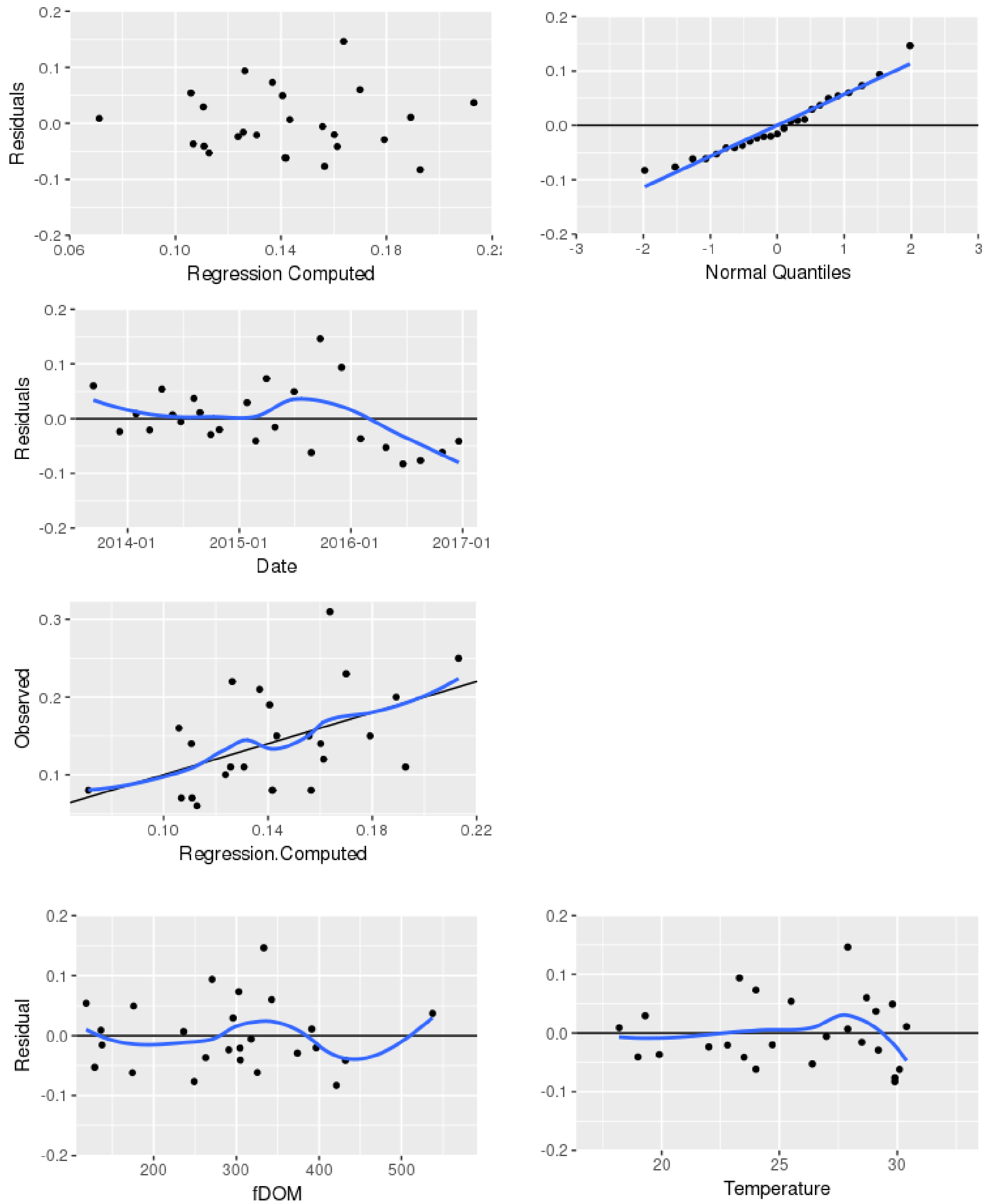


Figure 3.3. Residual and observed versus computed plots.

(fDOM, fluorescence of chromophoric dissolved organic matter)

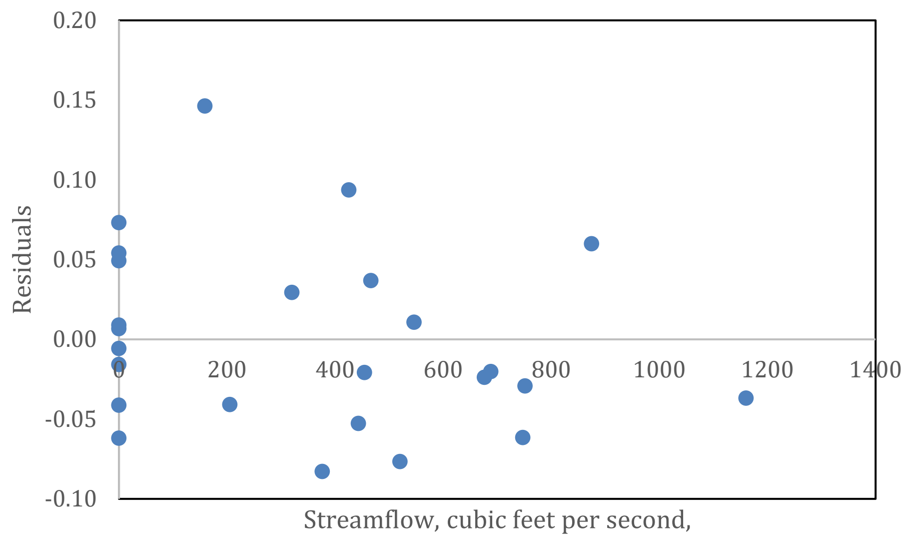


Figure 3.4. Relation between residuals and streamflow showing that the residuals had no systematic bias with respect to streamflow.

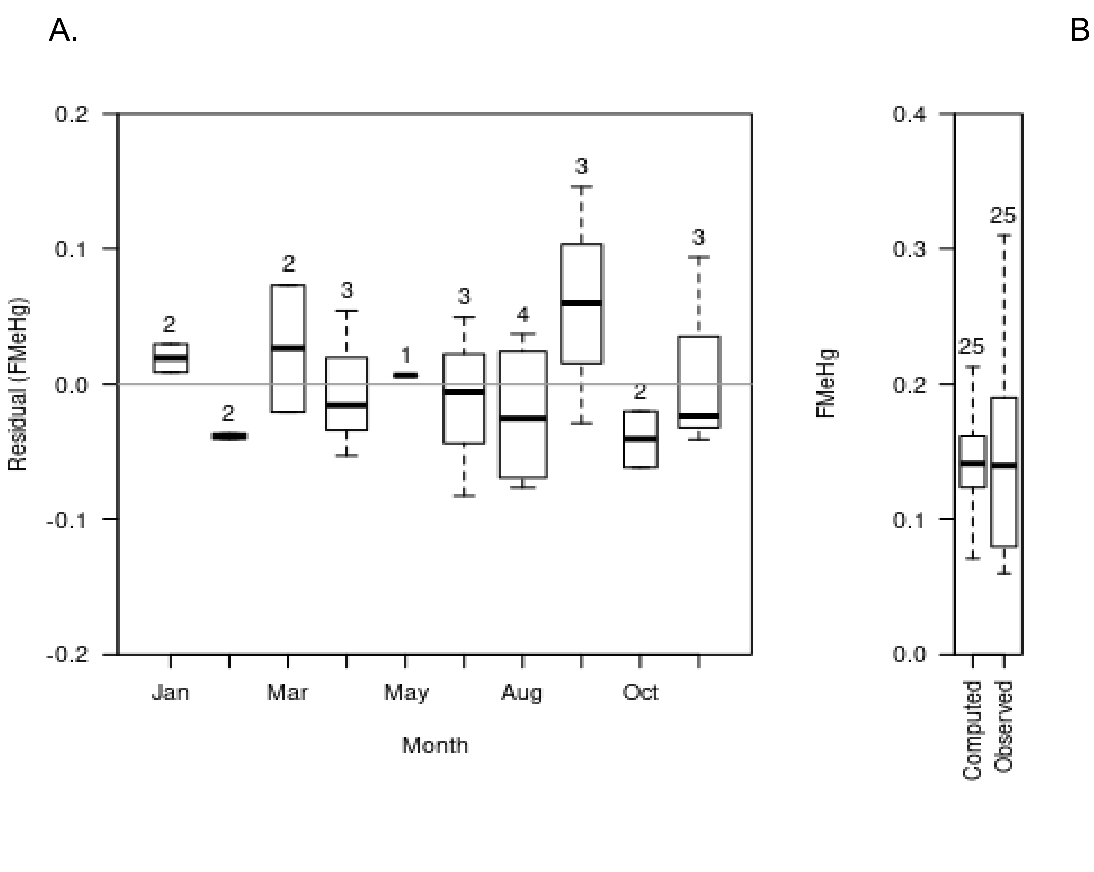


Figure 3.5. *A*, Seasonal variation in residuals, and *B*, computed and observed filter-passing methylmercury (FMeHg), in nanograms per liter.

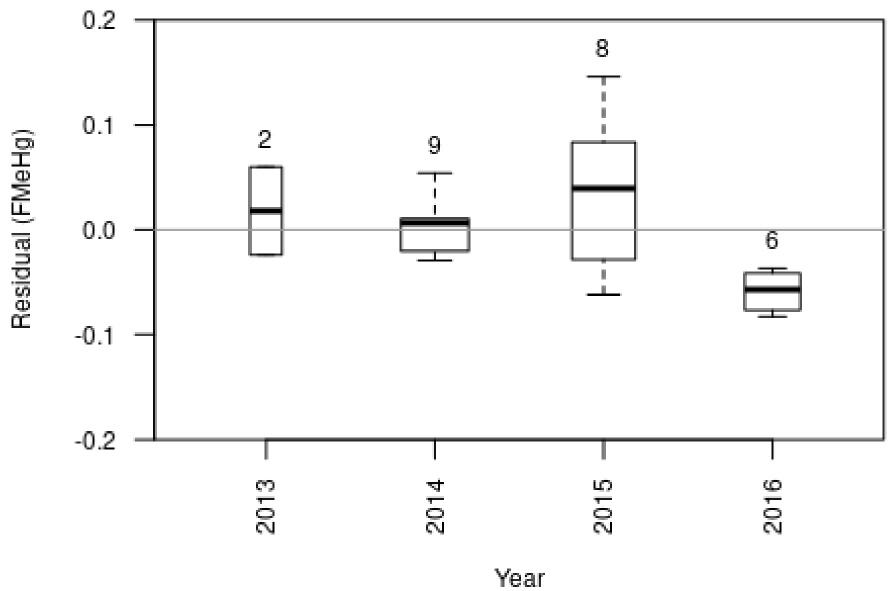
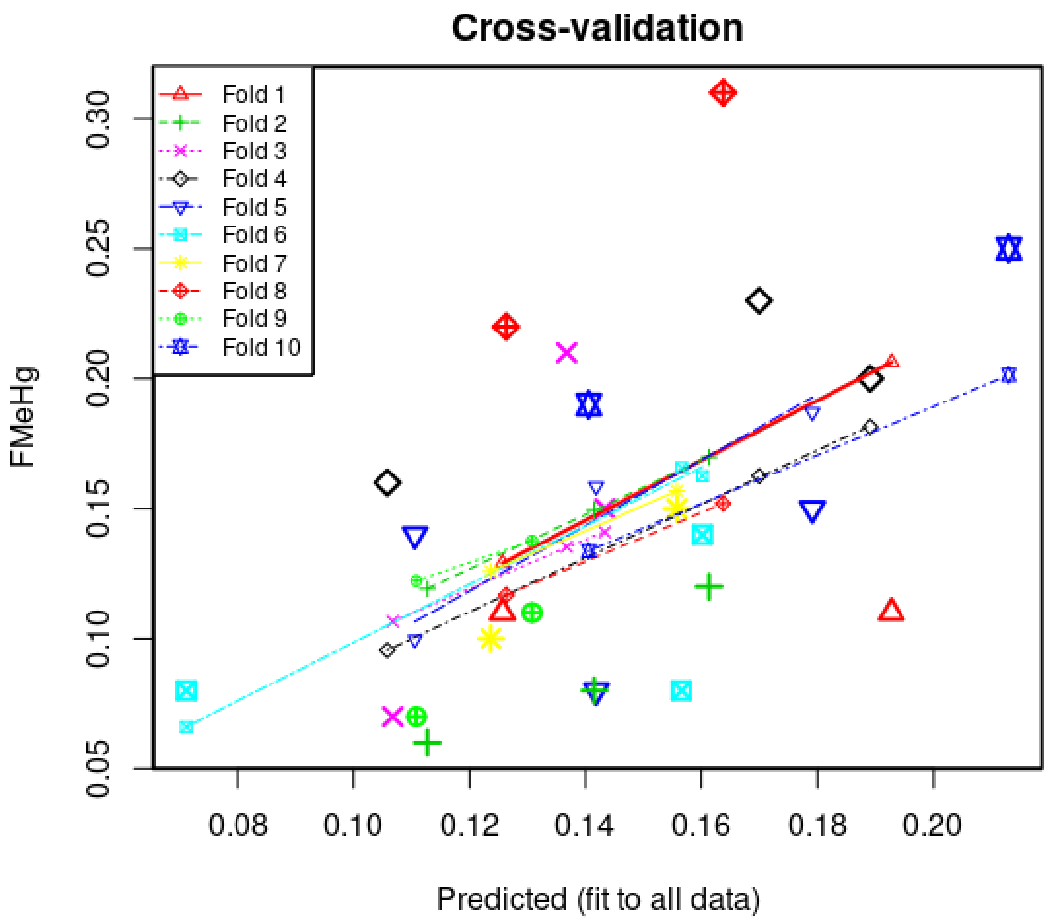


Figure 3.6. Annual variation in residuals.

(FMeHg, filter-passing methylmercury)

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.

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              Minimum MSE of folds:  0.000358
                 Mean MSE of folds:  0.004220
               Median MSE of folds:  0.002890
              Maximum MSE of folds:  0.017800
 (Mean MSE of folds) / (Model MSE):  1.200000
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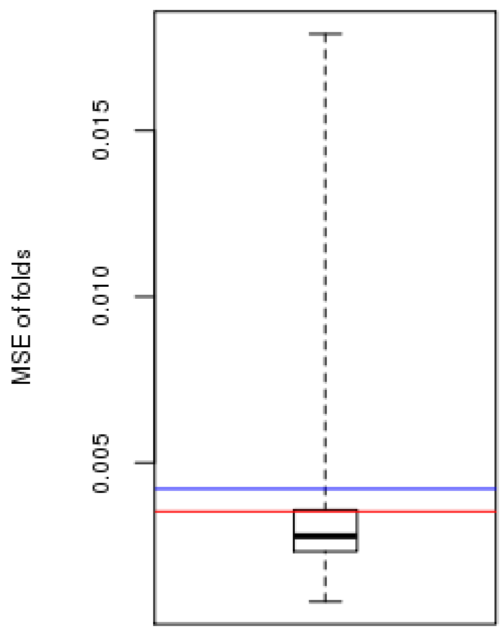
Figure 3.7. Cross-validation plot.

(FMeHG, filter-passing methylmercury; MSE, mean standard of error)

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Red line - Model MSE

Blue line - Mean MSE of folds
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Figure 3.8. Mean standard of error (MSE) of folds boxplot.

Model Calibration Dataset

0	Date	FMeHg	fDOM	Temperature	Computed FMeHg	Residual	Normal Quantiles	Censored Values
1	2013-09-11	0.23	343	28.7	0.17	0.0601	1.07	--
2	2013-12-06	0.1	291	22	0.124	-0.0237	-0.303	--
3	2014-01-29	0.08	136	18.2	0.0711	0.00887	0.303	--
4	2014-03-14	0.11	304	22.8	0.131	-0.0208	-0.2	--
5	2014-04-23	0.16	118	25.5	0.106	0.0542	0.906	--
6	2014-05-28	0.15	236	27.9	0.143	0.00667	0.2	--
7	2014-06-24	0.15	318	27	0.156	-0.00574	0.0996	--
8	2014-08-06	0.25	538	29.1	0.213	0.037	0.637	--
9	2014-08-26	0.2	391	30.4	0.189	0.0109	0.409	--
10	2014-09-30	0.15	374	29.2	0.179	-0.0291	-0.409	--
11	2014-10-28	0.14	397	24.7	0.16	-0.0202	-0.0996	--
12	2015-01-27	0.14	296	19.3	0.111	0.0294	0.52	--
13	2015-02-24	0.07	305	19	0.111	-0.0408	-0.637	--
14	2015-03-31	0.21	303	24	0.137	0.0732	1.26	--
15	2015-04-28	0.11	137	28.5	0.126	-0.0157	0	--
16	2015-06-30	0.19	176	29.8	0.141	0.0494	0.765	--
17	2015-08-25	0.08	174	30.1	0.142	-0.0619	-1.26	--
18	2015-09-23	0.31	333	27.9	0.164	0.146	1.98	--
19	2015-12-02	0.22	271	23.3	0.126	0.0937	1.53	--

20	2016-02-02	0.07	263	19.9	0.107	-0.0367	-0.52	--
21	2016-04-25	0.06	128	26.4	0.113	-0.0527	-0.906	--
22	2016-06-20	0.11	421	29.9	0.193	-0.0828	-1.98	--
23	2016-08-16	0.08	249	29.9	0.157	-0.0765	-1.53	--
24	2016-10-26	0.08	325	24	0.142	-0.0615	-1.07	--
25	2016-12-19	0.12	432	23.5	0.161	-0.0413	-0.765	--

Model Limitations

Errors in the FMeHg 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 3-9, indicating that variations are possible at this location as well. Unfortunately, changes in the inner filter effect were not monitored throughout this study.

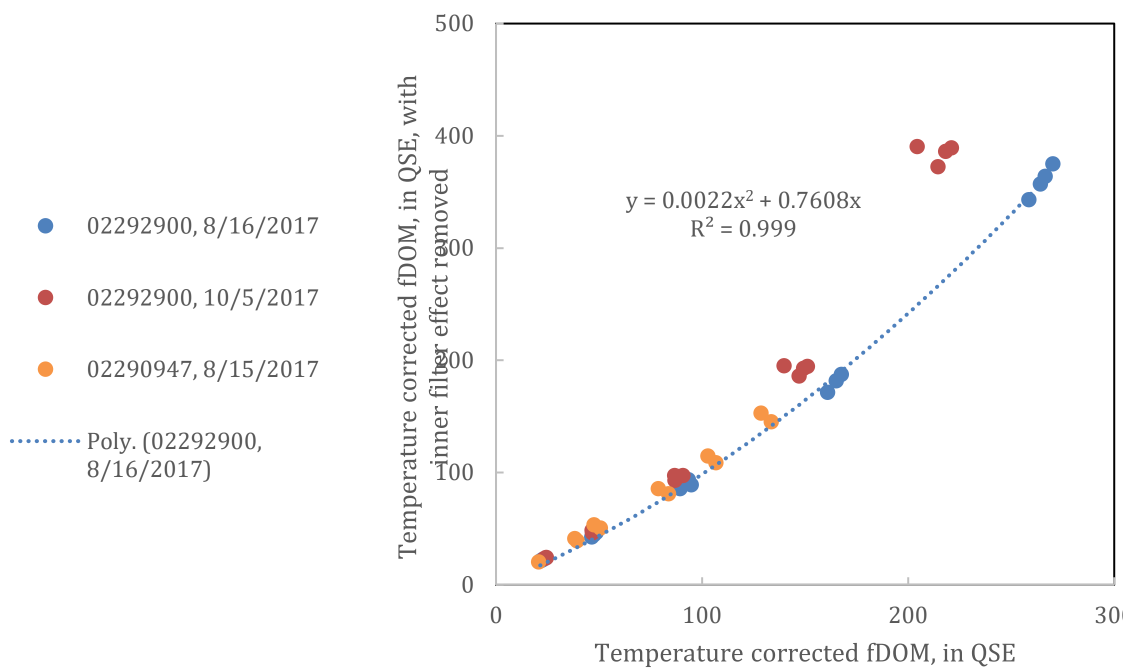

Figure 3.9. Relation between temperature corrected fluorescence of chromophoric dissolved organic matter (fDOM), in quinine sulfate equivalents (QSE), with the inner effect removed and temperature corrected fDOM, in QSE, without the inner filter effect removed.

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. For filtered methylmercury, the percent recovery for matrix spikes and matrix-spike duplicates was provided by the Wisconsin Mercury Lab and ranged from 88.6 percent to 129.4 percent, with a mean of 106.4 percent between October 2013 and November 2016. The percent recovery for check standards averaged 104.5 percent and ranged from 87.8 percent to 127.5 percent.

Definitions

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FMeHg: Methylmercury(1+) in ng/l (50285)
fDOM: Colored dissolved organic matter (CDOM) in ug/l QSE (32295)
Temperature: Temperature, water in deg C (00010)
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App Version 1.0

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