OWQ WaQI Note

August 17, 2017

Office of Water Quality Water-Quality Information Note 2017.04

Subject: Correcting YSI EXO™ fluorescent dissolved organic matter (fDOM) sensor data for low-level non-linear response

YSI has recently made us aware that EXO fDOM sensors manufactured prior to June 2017 are affected by a non-linear response at very low fDOM concentration ranges. The problem is the result of an interaction between electrical and optical components in the sensor that affect fDOM values in two ways: (1) there is a region of the response curve less than about 5 relative fluorescence units (RFU) where measurements may appear to be negative, and (2) the linear portion of the slope above underestimates the true fDOM value. Review the attachment for a useful graphic and description of this phenomena. An RFU of 5 is comparable to 15 ppb quinine sulfate equivalents.

Sensors affected by this issue all have serial numbers earlier than 17E101416, and YSI has addressed the problem with a redesign of the hardware in new sensors manufactured in June 2017 or later. For sensors affected by this issue, there are two options for resolving data-quality issues described in the attached technical note from YSI. The methods described are intended to help USGS users understand the impact of this hardware issue on their low-level data and apply a correction, if needed.

If users find that their data cannot be satisfactorily corrected for their research or monitoring needs, please contact YSI technical support to discuss next steps (which may include replacement of sensors). If you have other questions about this topic, contact Brian Pellerin in the Office of Water Quality at bpeller@usgs.gov.

WaQI Notes are archived on the Office of Water Quality web site, http://water.usgs.gov/usgs/owq/WaQI/index.html

Signed,

Office of Water Quality

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Attachment

Correcting EXO fDOM sensor data for non-linear response

June 1, 2017
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Background

During recent testing to understand the effects of different matrix waters upon fDOM measurements, YSI learned that the fDOM sensor had a nonlinear response that was exaggerated at very low fDOM concentration ranges. The nonlinearity is the result of an interaction between electrical and optical components of the hardware and due to the way the sensors were evaluated when they were built, this effect was simply not apparent. The nonlinearity is only revealed when multiple measurements are made at very low concentrations. Through intensive investigation YSI's team has arrived at an engineering solution that will be implemented in a revised fDOM sensor available in June 2017.

Having found the hardware solution, we have worked with the USGS on approaches to correcting data that have been collected with sensors that have varying modalities of the nonlinearity effect. All EXO fDOM data from sensors built through May 2017 may be affected in two ways that are demonstrated in Figure 1: 1) there is a region near 5 RFU (or 15 ppb QSE, given that 1 RFU ~ 3 ppb QSE) where measurements will appear to be negative, and 2) the linear portion of the slope for the rest of the range up to 100 RFU (300 ppb QSE), beyond the non-zero X intercept, underestimates the true fDOM value.

The objectives of this document are twofold. First, we aim to better clarify the nonlinearity problem so that fDOM sensor users can assess the impact it may have had upon their data. As will be apparent from the description below, the nonlinearity will have the greatest impact upon low fDOM measurements. Because not all sensors have the same X intercept, this may also be the source of offsets of up to 10 ppb sometimes observed when fDOM sensors are swapped in the field (despite calibration in the same standards). The second aim of this document is to present approaches for correcting data collected using the fDOM sensors. These approaches were arrived at by testing with corrected fDOM prototype sensors that are the basis for the updated sensors that will be available in June 2017. It is likely that not all data, namely the data in the area of 5 RFU, will be correctable. But data beyond the X-intercepts can be corrected by users who perform some basic dilutions and measurements to calibrate their sensors.

Description of the problem

Figure 1 demonstrates the observed non-linearity in fDOM sensor response and the effect on the sensor slope. The X-axis refers to the true RFU value measured with a benchtop fluorometer, while the Y-axis is the "uncorrected fDOM," i.e. the raw output directly from the sensor. As mentioned previously, the non-linearity or "dip" in Region II results in two issues for fDOM data:

1) **fDOM values within the non-linear range (e.g. 0-5 RFU or 0-15 ppb QSE) are not accurate.** This dip in Region II causes an ambiguity in fDOM concentrations reported by the sensor below ~5 RFU, with the uncorrected fDOM minima located from 3-8 RFU rather than at zero (Figure 1). This may result in the loss of data for users in dilute water, as there is not a mathematical means for correcting this ambiguity.

2) **All reported fDOM values in the linear range (e.g. 5-100 RFU or 15-300 ppb QSE) are underestimates due to an offset.** As evident in Figure 1, extending the linear portion of the curve (Region I) through the Y-axis would result in a negative intercept. This results in an underestimate of the true fDOM value as measured by the

sensor, the magnitude of which is dependent on the value (e.g. results in an offset of ~3 RFU on the lower end, but approaches difference of 0 RFU as RFU values increase). This can result in a large relative underestimate of measured fDOM compared to the actual fDOM value in the range common for most rivers, for instance (5-20 RFU or 15-60 ppb QSE).

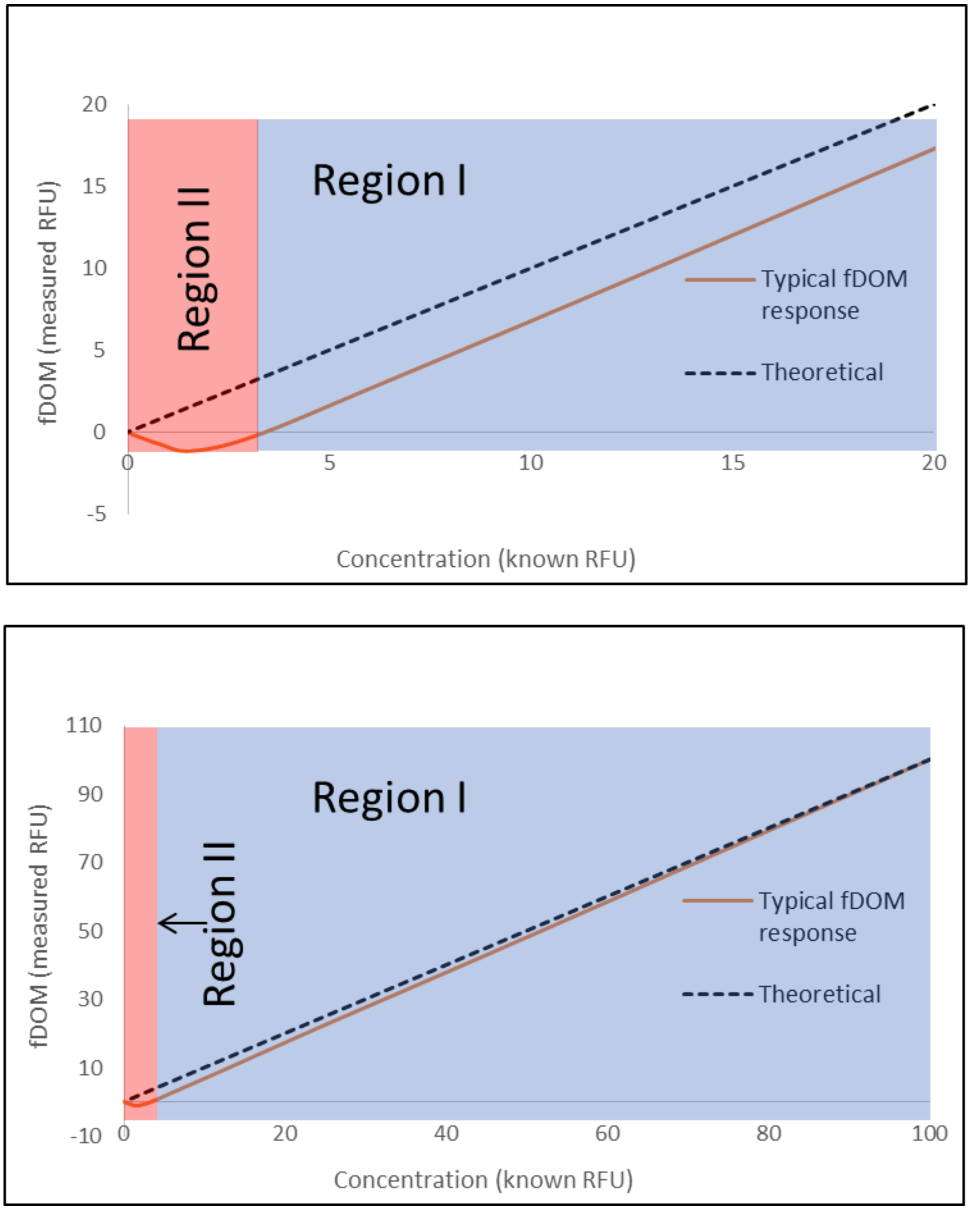

Figure 1. Region II represents the "dip," an area of sensor nonlinearity where the uncorrected RFU measurement can correlate to two known RFU concentrations. The top panel is a closer view of the same area shown in the bottom panel, which shows the full scale of the sensor.

Correcting data for the non-linear response

We investigated whether previously-collected data might be corrected in light of these findings. Multiple curve-fitting approaches were tested before we arrived at what is proposed here. Our inquiry led us to conclude that **the slope off-set in Region I (slope) can be corrected** to where the measured fDOM crosses zero on the X axis (e.g. actual RFU). However, **the non-linearity (dip) below a zero (Region II) cannot be corrected** due to the fact that raw fDOM values below zero are associated with more than one actual fDOM value.

Slope (Region I) corrections

We investigated application of a sensor-specific correction factor as well as development of a of sensor-generic correction factor that might be applied to all sensors with some understandable margin of error. A third option is to accept the data as-is. Users may choose to not make a correction given that fDOM is a somewhat relative measure that has significant uncertainty given other corrections (*e.g.*, temperature and turbidity). However, users should make this decision based on the acceptable error ranges for their specific projects and sites, and performing a set of dilutions to evaluate one's sensor will aid in that decision. Users who choose to do nothing should also be aware that a difference of 1-5 RFU may also occur between the current generation fDOM sensors as well as with the hardware-corrected fDOM sensor available in June.

<u>OPTION 1: Apply a sensor-specific correction factor</u>. This correction factor would be unique to every fDOM sensor. The proposed approach involves measuring fDOM across a standard range that avoids the region of non-linearity (*e.g.* calibration at 50 and 100 RFU). Note that inner filtering effects will occur at fDOM > 25 RFU when using a natural DOM standard such as Suwanee NOM, but not with quinine sulfate (QS). Temperature would need to be measured and consistent during testing, and QS concentrations should be verified using a benchtop fluorometer or a separate "golden probe" used only in the lab. The steps are as follows:

1) Prepare quinine sulfate solutions of 300 and 150 ppb QSE (e.g. 100 and 50 RFU) as described in the EXO manual.
2) Record the fDOM response in each solution in RFU (note: do not calibrate the sensors to these solutions, but simply record values).
3) Calculate the uncorrected slope (m_{uncorr}) by plotting actual RFU of the standards on the X axis versus uncorrected sensor measured RFU on the Y axis, such as shown in Figures 1.
4) Calculate a corrected fDOM value ($fDOM_{corr}$) using the following equation:

$$\mathrm{fDOM_{corr}} = \left(\frac{1}{\mathrm{m_{uncorr}}}\right)\mathrm{fDOM_{uncorr}} + 100\left(1 - \frac{1}{\mathrm{m_{uncorr}}}\right)$$

Equation 1.

Where:

fDOMcorr = the fDOM value corrected for the slope overestimate (in RFU or QSE)
muncorr = uncorrected slope calculated from the measurements at 100 and 50 RFU (or 300 and 150 ppb QSE)
fDOMuncorr = the measured fDOM value without slope correction (in RFU or QSE).

Corrections can be made to ~ 5 RFU (actual) for all EXO fDOM sensors, but users may consider whether corrections to a lower actual fDOM value are appropriate. The lower limit can be estimated by determining the zero crossing point of the line (x-intercept) for their sensor using the same slope (m_{uncorr}) derived above using Equation 2:

$$X - intercept = 100(1 - \frac{1}{m_{uncorr}})$$

Equation 2.

The x-intercept may be more precisely identified with more quinine sulfate dilutions below 150, and used to determine m_{uncorr}. There will likely be greater relative uncertainty within this range (e.g. < 5 RFU) given some non-linearity, but the absolute error should be small. Data below the zero crossing, which identifies the boundary between Regions I and II of Figure 1, cannot be corrected.

OPTION 2: Apply a sensor-generic (estimated) correction factor. As an alternative to a sensor-specific correction, we explored developing a generic correction factor that could be applied to all EXO fDOM sensors with reasonable accuracy. In November 2016, YSI evaluated the potential for this correction using ~ 20 EXO sensors manufactured from 2012-2016 that were sent in to YSI by USGS collaborators and others. As shown in Figure 2, the slopes and intercepts varied between sensors and were offset from the relationship between known and measured RFU for an ideal sensor ("theoretical" in Figure 2). Sensor variability was also not as large per production lot, though Figure 2 does suggest that from year to year sensor variability becomes more apparent, especially in concentrations of quinine sulfate that yield measurements below 50 RFU (~150 QSU).

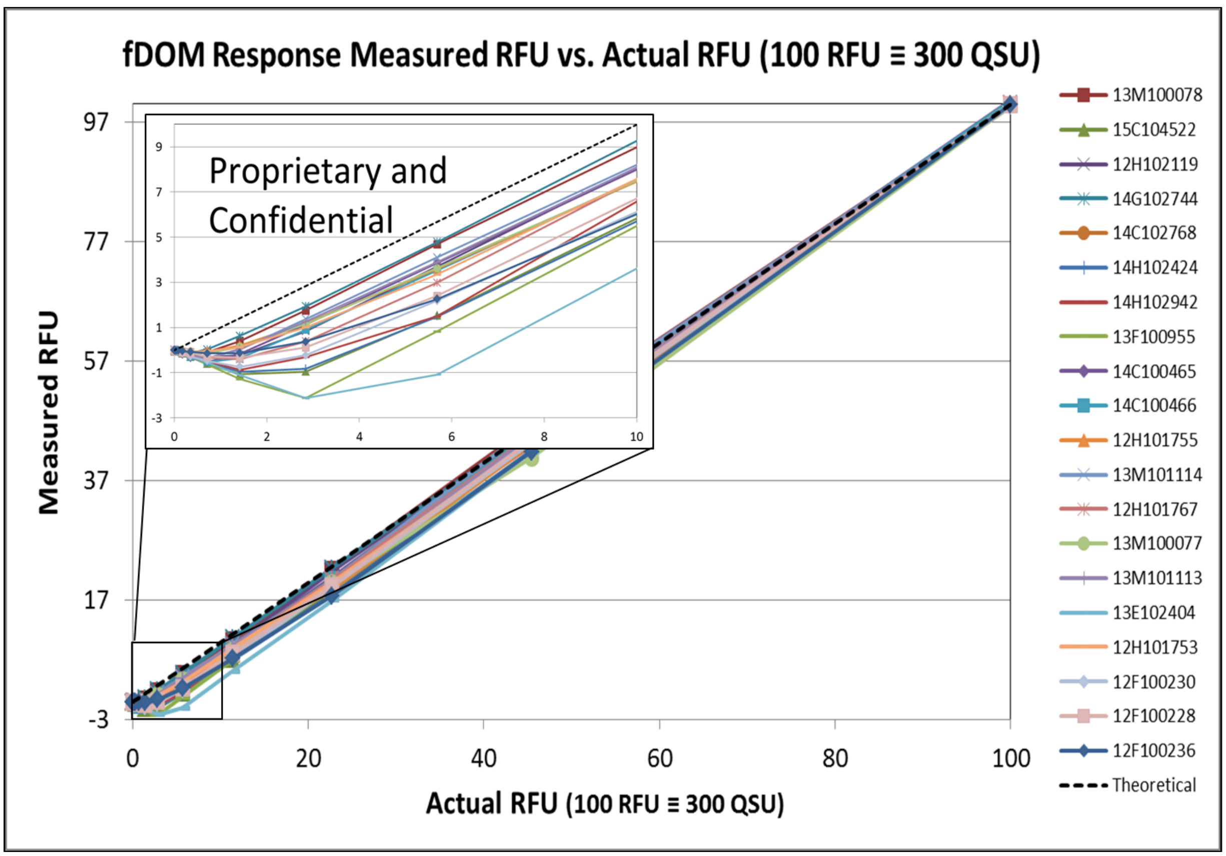

Figure 2. Demonstration of nonlinearity across the range of fDOM measurements for 20 individual sensors.

Based on the data collected from the 20 sensors an average m_{uncorr} of **1.035** could be used to estimate the correction in lieu of sensor specific data down to the zero crossing point. Results from the 20 sensors tested suggest that the generic correction will result in a lower percent error relative to no correction for most sensors. For example, the generic correction results in a lower percentage error when slopes are greater than ~ 1.017 (95th percentiles = 1.028 to 1.041; intercepts ~ -1.5 RFU, 95th percentiles = -2.74 to -4.19) as shown in Figure 3 for fDOM samples at both 10 and 50 RFU.

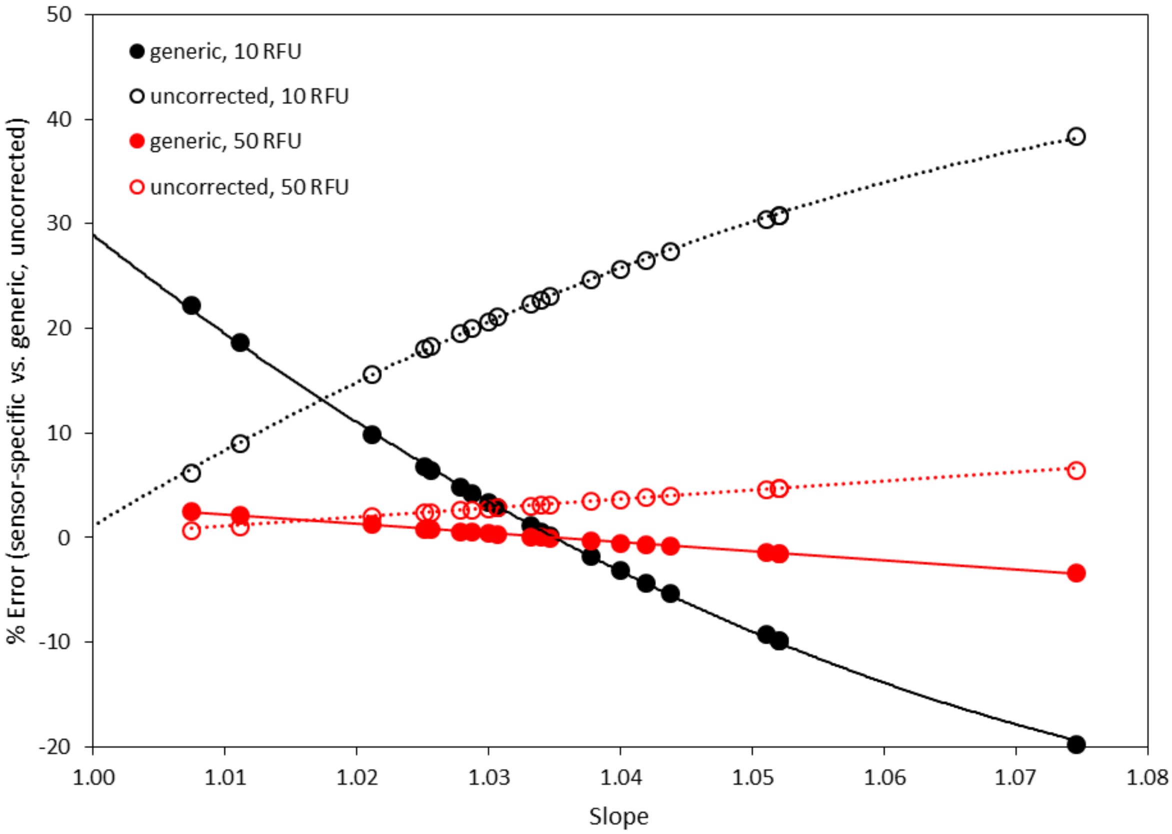

Figure 3. Percent error for the generic correction and uncorrected fDOM values relative to the sensor-specific corrections at 10 and 50 RFU.

The methods described above will hopefully assist users in investigating the impact of this hardware anomaly on their data, and once understood the same correction approach can be applied throughout the lifetime of the sensor. If users find that their data cannot be suitably corrected for their research needs, please contact our technical support team (+1 (877) 726-0975) so that we can discuss next steps with you, which may include replacement of sensors with the most aggravated nonlinearities.

We want to thank Brian Pellerin of the USGS for his assistance in investigation of this issue, and we invite fDOM users to share their findings with us and others so that we all might benefit from what is learned and continuously strive for sensor improvements.