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Justification for Application of a Site-Specific Dissolved Oxygen Criterion to the Upper Tidal Fresh and Middle Oligohaline Pocomoke River Segments Due to Natural Conditions

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Introduction

The Pocomoke River, which forms the eastern border between Wicomico and Worcester Counties in Maryland, runs approximately 73 miles from its headwaters in Sussex County, Delaware to its mouth at Pocomoke Sound on the Chesapeake Bay. Nearly 14 percent of land in the Pocomoke River drainage is wetlands; forest lands cover nearly 48 percent of the watershed. The Great Cypress Swamp, which is located in southern Sussex County, is the origin of the Pocomoke River and the source of much of the organic material that gives the river its characteristic dark color. In addition to giving the Pocomoke River its dark hue, the organic matter generated by the Great Cypress Swamp and other non-tidal and tidal wetlands along the length of the Pocomoke River and its tributaries generate high rates of respiration, which can lead to significant natural reductions in dissolved oxygen concentrations. Together, the Great Cypress swamp and the tidal and non-tidal wetlands of the Pocomoke drainage basin result in a system with the highest total organic carbon concentrations of any Maryland tidal fresh tributary. Notched box and whisker plots comparing total organic carbon concentrations for Maryland's tidal fresh stations are presented in Figure 1. The concentrations for station ET10.1 in POCTF are significantly higher (non-overlapping notches) than any other station.

The tidal Pocomoke River is classified as "open-water" which includes those waters beyond the shoreline and shallow waters of the Chesapeake Bay and tidal tributaries (U.S. EPA, 2003). Based on requirements promulgated under the Clean Water Act, tidal waters designated as open waters of the State of Maryland are required to meet the dissolved oxygen criteria described in the State of Maryland Code of Regulations - COMAR 26.08.02.03-3(C)(8)(d)(i), COMAR 26.08.02.03-3(C)(8)(d)(v).

The graphical and statistical analyses that follow provide the basis for a site-specific 30-day mean dissolved oxygen criterion of 4.0 mg/L for the tidal fresh and oligohaline segments of the tidal Pocomoke River based on the presence of naturally occurring low dissolved oxygen that results from the presence of high concentrations of organic matter associated with large areas of headwater and fringing wetlands. These findings and the proposed site-specific dissolved oxygen criterion are fully consistent with EPA's amended Chesapeake Bay water quality criteria guidance published in 2004 (U.S. EPA, 2004). The data used in this report were obtained from the Chesapeake Information Management System (CIMS) data base, which is maintained by the U.S. Environmental Protection Agency Chesapeake Bay Program. The data are available to the public from the Chesapeake Bay Program web site: (http://www.chesapeakebay.net). Data were analyzed and figures were prepared using Statistical Analysis System (SAS®) software. All tables and figures are presented at the end of this report.

Water Quality Conditions

The water quality conditions that are described below and appear in Table 1 were based on summer (June through September) data for 2000 through 2002. These summers were found to have "moderate" flow conditions on a scale that ranges from record dry to record wet. Moderate flow conditions represent the middle third of the distribution of flows (greater than or equal to the 33rd percentile and less than the 66th percentile) for the Pocomoke River. The distribution of flows was based on a benchmark data set that included data for the 1975 through 1994 time period. Flow data used in the assignment of flow conditions for this investigation were obtained from the U.S. Geological Survey web site USGS Surface-Water Daily Data for the Nation:

(http://waterdata.usgs.gov/nwis/dv?referred_module=sw). The data were from Pocomoke River gage number 01485000, which is located near Willards, MD, for the 1 January 1975 through 20 June 2010 time period. Flow characteristics were assessed using methods developed for the Chesapeake Bay Program (Olson, 2003).

The summary statistics presented in Table 1 were compared to similar statistics presented in Table VI-2 of *Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and its Tributaries – 2004 Addendum* (U.S. EPA, 2004). Chapter VI of the 2004 Bay criteria addendum document provides guidance for developing site specific dissolved oxygen criteria in naturally low dissolved oxygen concentration systems that are influenced by tidal wetlands. The document focuses on the tidal Mattaponi and Pamunkey Rivers, which are described as having "naturally lower ambient dissolved oxygen concentrations."[1]

As shown in Table 1, the summer mean 2000 through 2002 surface and bottom dissolved oxygen concentrations for monitoring station ET10.1 in upper tidal fresh river segment POCTF are 4.7 mg/L and 4.6 mg/L, respectively. These values are very close to the surface and bottom dissolved oxygen concentrations reported for the tidal fresh segments of the Mattaponi (MPNTF) (5.6 mg/L for surface and bottom) and Pamunkey (PMKTF) (5.3 mg/L surface and 5.5 mg/L bottom) rivers (U.S. EPA, 2004).

The summer surface 2000-2002 mean chlorophyll-a concentration at ET10.1 in POCTF (7.9 µg/L) is 2 µg/L larger than the concentration reported for MPNTF (5.9 µg/L) and 1.7 µg/L larger than the concentration reported for PMKTF (6.2 µg/L). The slightly larger mean concentration at ET10.1 is the result of one extreme observation (24.4 µg/L) that had an undue influence on the calculation of the mean. The mean summer surface 2000-2002 chlorophyll-a concentration at ET10.1 without that observation is 6.2 µg/L. Median values are more robust to outliers than means and thus are a more representative measure of central tendency in skewed data. The summer surface 2000-2002 median chlorophyll-a concentration at monitoring station ET10.1 in POCTF (5.98 µg/L) is comparable to those at TF4.4 in MPNTF (5.14 µg/L) and TF4.2 in PMKTF (5.86 µg/L). The data for all three stations are compared graphically using notched box and whisker plots in Figure 2. Notched box and whisker plots show the range in concentrations, the inter-quartile range, the median, and the mean (+ sign) of the distribution, the endpoint of the notches show the median plus and minus 1.58*(inter-quartile range/$\sqrt{n}$). The medians of notched box-and-whisker plots are significantly different at the 0.05 level if the notches do not overlap. The notches in Figure 2 do overlap, so the median concentrations of chlorophyll-a are not significantly different. Similarities were also found among these systems for total nitrogen and total phosphorus concentrations (U.S. EPA, 2004).

[1] In 2005, Virginia used the 2004 EPA published Bay criteria addendum (U.S. EPA, 2004) as the basis for promulgating a 30-day mean 4 mg/L site-specific dissolved oxygen criterion for the tidal Mattaponi and Pamunkey River segments within the Commonwealth's water quality standards regulations (Code of Virginia 9 § 62.1-44.15 3a; VAC 25-260).

Dissolved Oxygen Deficit

The dissolved oxygen deficit was calculated as the predicted saturation concentration minus the ambient concentration. Dissolved oxygen saturation concentration is a theoretical value that is calculated using ambient salinity and temperature (Weiss, 1970). The dissolved oxygen deficit provides an indication of the amount of oxygen being consumed in a particular system, but does not indicate whether the consumption rate is dominated by a geochemical or a biological process.

Summer surface and bottom dissolved oxygen concentrations and dissolved oxygen saturation concentrations monitoring station for ET10.1 for the water quality monitoring program data record are presented in Figures 3 and 4, respectively. With the exception of one datum, dissolved oxygen saturation concentrations exceed ambient concentrations.

Mean dissolved oxygen deficits were calculated for monitoring station ET10.1 for surface (3.3 mg/L) and bottom (3.4 mg/L) using June through September data for 2000 through 2002. These values are slightly larger than those reported for MPNTF (2.4 mg/L for surface and bottom) and PMKTF (2.5 mg/L for surface and 2.6 mg/L for bottom) for the same time period (dry flow conditions) (U.S. EPA, 2004). The dissolved oxygen deficits for MPNTF and PMKTF are described as being "among the highest observed in the Chesapeake Bay's tidal tributaries" (U.S. EPA, 2004).

The dissolved oxygen deficits for the moderate flow condition summers of 2000 through 2002 are similar to those observed over the 1986 through 2009 data record, which includes a variety of flow regimes, for surface (Figure 5) and bottom (Figure 6). If the dissolved oxygen deficits for ET10.1 were the result of external non-point source nutrient loads they should be related to flow, because high flows would result in higher nutrient loads to the system and higher dissolved oxygen deficits. The opposite would be expected during periods of low flow, i.e., low flows would result in lower non-point source nutrient loads and therefore lower dissolved oxygen deficits. The null hypothesis that dissolved oxygen deficits are not related to flow and by extension not to external non-point source nutrient loads, was tested using a general linear model that used dissolved oxygen deficit as the dependent variable and flow and month (to account for seasonality) as explanatory variables. Although the overall model was significant ($p<0.0001$), the significance level for the model was the result of month ($p<0.0001$) and not flow ($p=0.3388$). This indicates that dissolved oxygen deficits are highly seasonal, though not significantly related to flow (Figure 7) and that the observed dissolved oxygen deficits are not related to external nutrient loads. Based on this analysis it seems reasonable to infer that the large dissolved oxygen deficits observed at monitoring station ET10.1 in segment POCTF are a function of internal processes.

Dissolved Oxygen/Water Temperature Relationships

Another feature of black-water systems, where respiration is dominated by biological and geochemical processes, is a relationship between dissolved oxygen concentration (and dissolved oxygen deficit) and water temperature. Figure 8 shows the dissolved oxygen concentration and dissolved oxygen deficit for ET10.1 plotted against water temperature using surface data for the period of record. A LOESS curve was fitted to the dissolved oxygen data using water temperature as an independent (explanatory) variable to better illustrate the functional relationship. Figure 8 shows dissolved oxygen concentrations decreasing as water temperature

increases due to decreasing dissolved oxygen saturation concentrations and increased respiration from biological sources. The pattern in Figure 8 is similar to that of MPNTF and PMKTF (U.S. EPA, 2004), which is described as being "evidence of the lack of a strong influence of planktonic algal photosynthesis on dissolved oxygen concentrations…." If algal photosynthesis were influencing dissolved oxygen concentrations in POCTF, one would expect to see an upturn in the daytime, surface dissolved oxygen concentrations at higher water temperatures as opposed to a flattening of the curve. As stated above, the summer surface median chlorophyll-a concentration for station ET10.1 in POCTF (5.98 μ/L) is similar to TF4.4 in MPNTF (5.14 μ/L) and TF4.2 in PMKTF (5.86 μ/L).

Low Variability in Dissolved Oxygen Concentrations

If the hypothesis that low dissolved oxygen in segment POCTF is a natural condition resulting from its status as a wetland dominated system is correct, dissolved oxygen levels should be relatively consistent between night and day and between surface and bottom layers. Evidence which supports that hypothesis is provided in Table 2. The Maryland Department of Natural Resources (DNR) has measured surface and bottom dissolved oxygen concentrations on a monthly basis at water quality monitoring station ET10.1 in POCTF from 1986 to the present. These samples are collected at a depth of 0.5 meters during the daylight hours when photosynthesis activity by phytoplankton and concentrations of waste oxygen should be at their highest levels.

Between 1998 and 2002 DNR deployed in-situ continuous monitoring devices at three locations on the tidal Pocomoke River at Rehobeth, Cedar Hall Wharf, and Shelltown. The location closest to the POCTF segment was the Rehobeth station, in the upper portion of the POCOH segment, approximately 1 mile down-river from the established boundary with the tidal fresh POCTF segment. Continuous monitors are programmed to take readings for dissolved oxygen and other field parameters every 15 minutes, 24 hours a day. The meter at the Rehobeth station was suspended from a surface float that was configured to position the probe sensors at a consistent depth of one meter below the water surface.

For the comparisons in Table 2, the mean and other statistics of the 1986 through 2009 daytime data at water quality monitoring station ET10.1 were calculated for May through July for surface and bottom layers and compared to the 2002 continuous monitoring data at Rehobeth for day (6:00 A.M through 5:59 P.M) and night (6:00 P.M. through 5:59 A.M.) periods. The low standard deviations and small range in concentrations as measured by the difference between the 5th and 95th percentiles for the long-term data indicate low variability within those months. The dissolved oxygen concentrations for surface and bottom within a month are identical (May and June) or almost identical (July). If the system were dominated by phytoplankton one would expect to see larger differences due to seasonal algal production and differences between surface and bottom dissolved oxygen concentrations due to differences in light availability.

There is also good agreement between the long-term data and the 2002 continuous monitoring data from the Rehobeth station and no difference between the day and night mean dissolved oxygen concentrations for the continuous monitoring data, which further suggests POCTF is not an algal-dominated system. These lines of evidence suggest that low ambient dissolved oxygen concentrations in the POCTF and POCOH segments are largely influenced by extensive natural

wetland systems as opposed to phytoplankton populations, findings fully consistent with those reported by U.S. EPA (2004).

Shortnose sturgeon

The State of Maryland has adopted a dissolved oxygen water quality criterion for the protection of shortnose sturgeon (*Acipenser brevirostrum*) under the open-water fish and shellfish subcategory, which states "For protection of the endangered shortnose sturgeon, (dissolved oxygen shall be) greater than or equal to 4.3 milligrams/liter as an instantaneous minimum at water column temperatures greater than 29°C (77°F)" COMAR 26.08.02.03-3(C)(8)(d)(v). The State of Maryland does not currently collect the necessary data to calculate an instantaneous minimum water column dissolved oxygen concentration; however, DNR does measure on a monthly basis dissolved oxygen and water temperature at a number of water column depths at ET10.1 through the Department's ambient water quality monitoring program.

The nominal depth at ET10.1 is 5 meters and physical parameters such as dissolved oxygen and water temperature are generally measured at the surface, one meter off the bottom, and at 1 meter intervals between surface and one meter off the bottom. The actual number of water column measurements on any particular date does vary depending on tide state and occasional equipment problems. As a result, it is possible to calculate a water column average temperature and dissolved oxygen concentration. The water temperatures and dissolved oxygen concentrations presented in Figure 9 were calculated by averaging the data by sample date over the sample depths that were measured during each site visit. On average, six discrete depths were used in the water column calculations; the number of depths for the entire data record ranged from one to a maximum of nine. As shown in Figure 9, the water column average temperature exceeds 29°C only five times over the period of record. Of those five events, there is only one case where the data indicates a violation occurred such that both the temperature exceeded 29°C and the dissolved oxygen concentration was less than 4.3 mg/L. Thus, based on monthly data collected from 1986 through 2009 it appears that the open-water criterion for the protection of the endangered shortnose sturgeon was violated one time (~0.4 percent of the data fail to meet the criterion).

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Table 1. Summer (June through September) averaged water quality conditions at ET10.1 in the Pocomoke tidal fresh segment (POCTF) for 2000 to 2002, moderate flow conditions summers.

CBP Segment	Water Column Layer	Water Column Depth (meters)	Salinity (ppt)	Temperature ^{o}C	Dissolved Oxygen Conc. (mg/L)	Dissolved Oxygen Deficit (mg/L)	Chlorophyll-*a* Conc. µg/L	TSS Conc. (mg/L)	TN Conc. (mg/L)	TP Conc. (mg/L)
POCTF	S	0.5	0.7	26.1	4.7	3.3	7.9	12.9	1.64	0.120
POCTF	B	4.9	0.7	26.0	4.6	3.4	7.7	25.7	1.60	0.141

Table 2. Dissolved oxygen concentrations (mg/L) for 1986 through 2009 for ET10.1 in POCTF and the 2002 continuous monitoring dissolved oxygen measurements collected at the Rehobeth station in POCOH.

CBP Segment	Station	Depth (meters)	Month	Year	Period	Mean	Standard deviation	5th percentile	Median	95th percentile
POCTF	ET10.1	0.5	May	NA	Day	5.8	0.9	4.1	5.7	7.3
POCTF	ET10.1	4.9	May	NA	Day	5.8	0.9	4.0	5.7	7.4
POCTF	ET10.1	0.5	June	NA	Day	4.6	1.1	3.4	4.5	6.7
POCTF	ET10.1	5.1	June	NA	Day	4.6	1.1	3.0	4.6	6.6
POCTF	ET10.1	0.5	July	NA	Day	4.4	1.0	3.0	4.5	5.8
POCTF	ET10.1	4.7	July	NA	Day	4.3	0.9	3.2	4.4	5.7
POCOH	Rehobeth	1.0	May	2002	Day	6.0	0.5	5.0	6.1	6.7
POCOH	Rehobeth	1.0	May	2002	Night	6.0	0.4	5.1	6.2	6.4
POCOH	Rehobeth	1.0	June	2002	Day	5.4	0.8	4.0	5.4	6.6
POCOH	Rehobeth	1.0	June	2002	Night	5.4	0.7	4.0	5.5	6.4
POCOH	Rehobeth	1.0	July	2002	Day	5.6	1.0	4.2	5.5	7.5
POCOH	Rehobeth	1.0	July	2002	Night	5.6	0.8	4.3	5.6	7.0

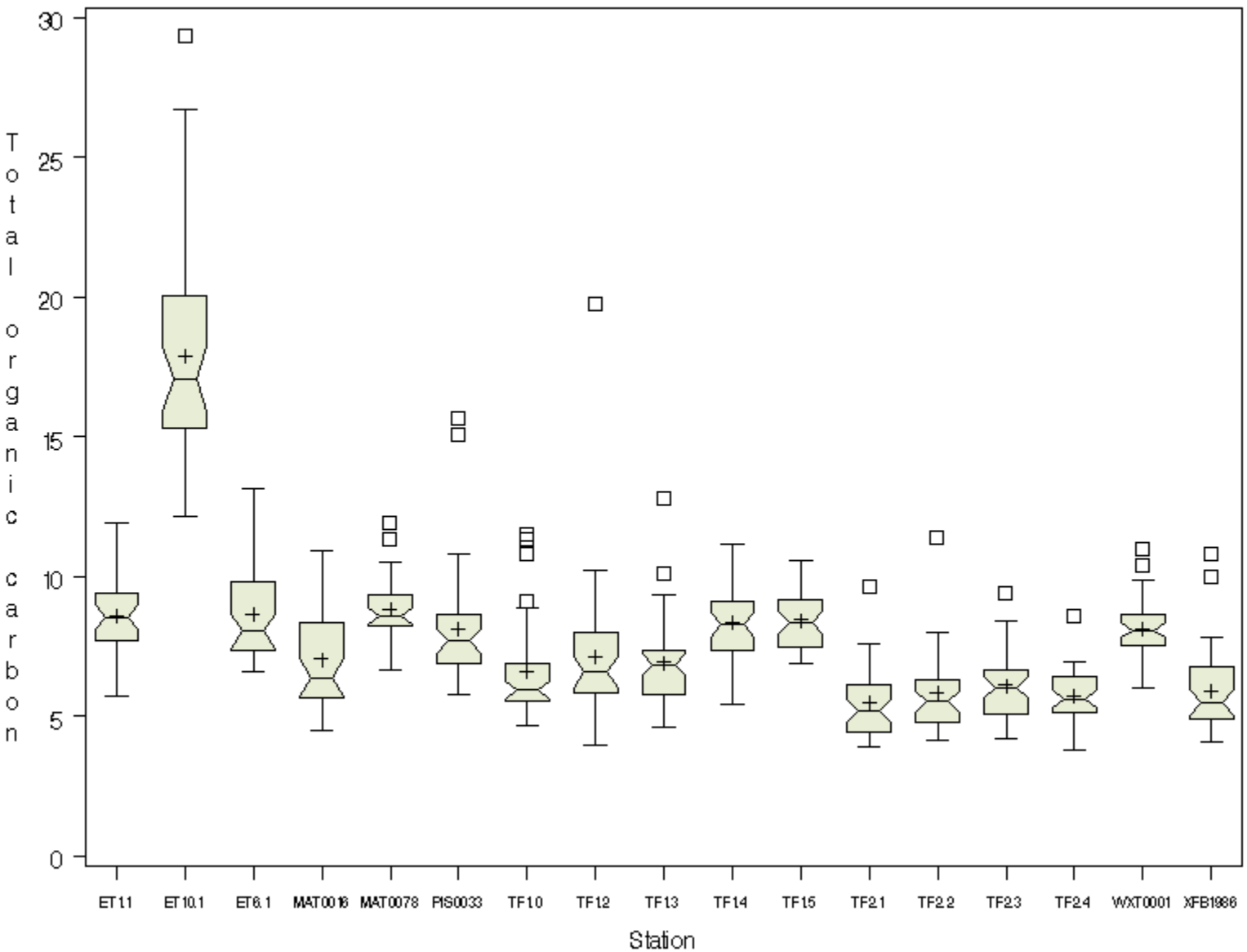

Figure 1. Notched box and whisker plots showing monthly mean summer total organic carbon concentrations (mg/L) at tidal fresh stations for 1999 through 2008.

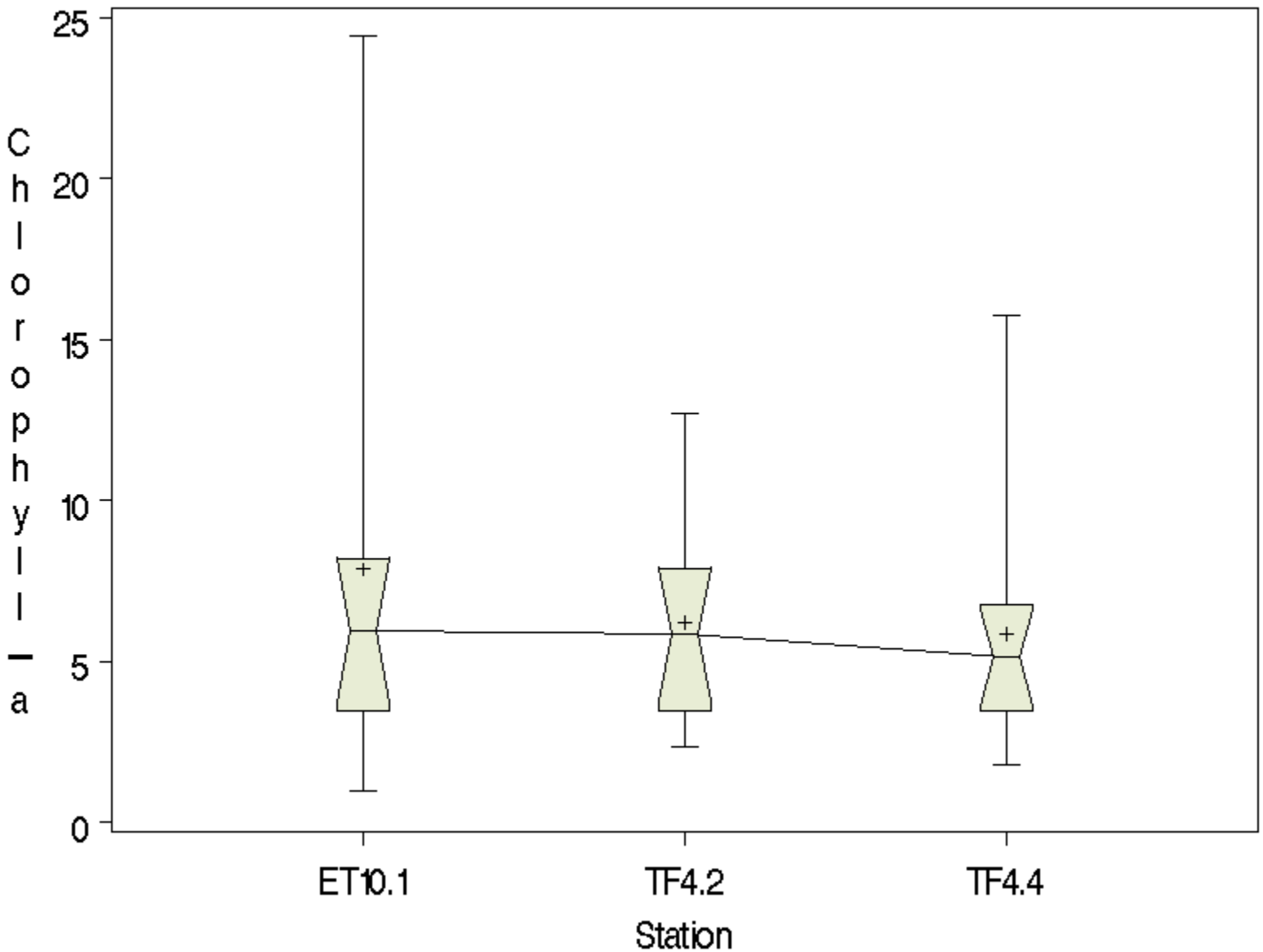

Figure 2. Notched box and whisker plots showing the distribution of chlorophyll for June through September 2000 through 2002 for ET10.1 (POCTF), TF4.2 (PMKTF), and TF4.4 (MPNTF).

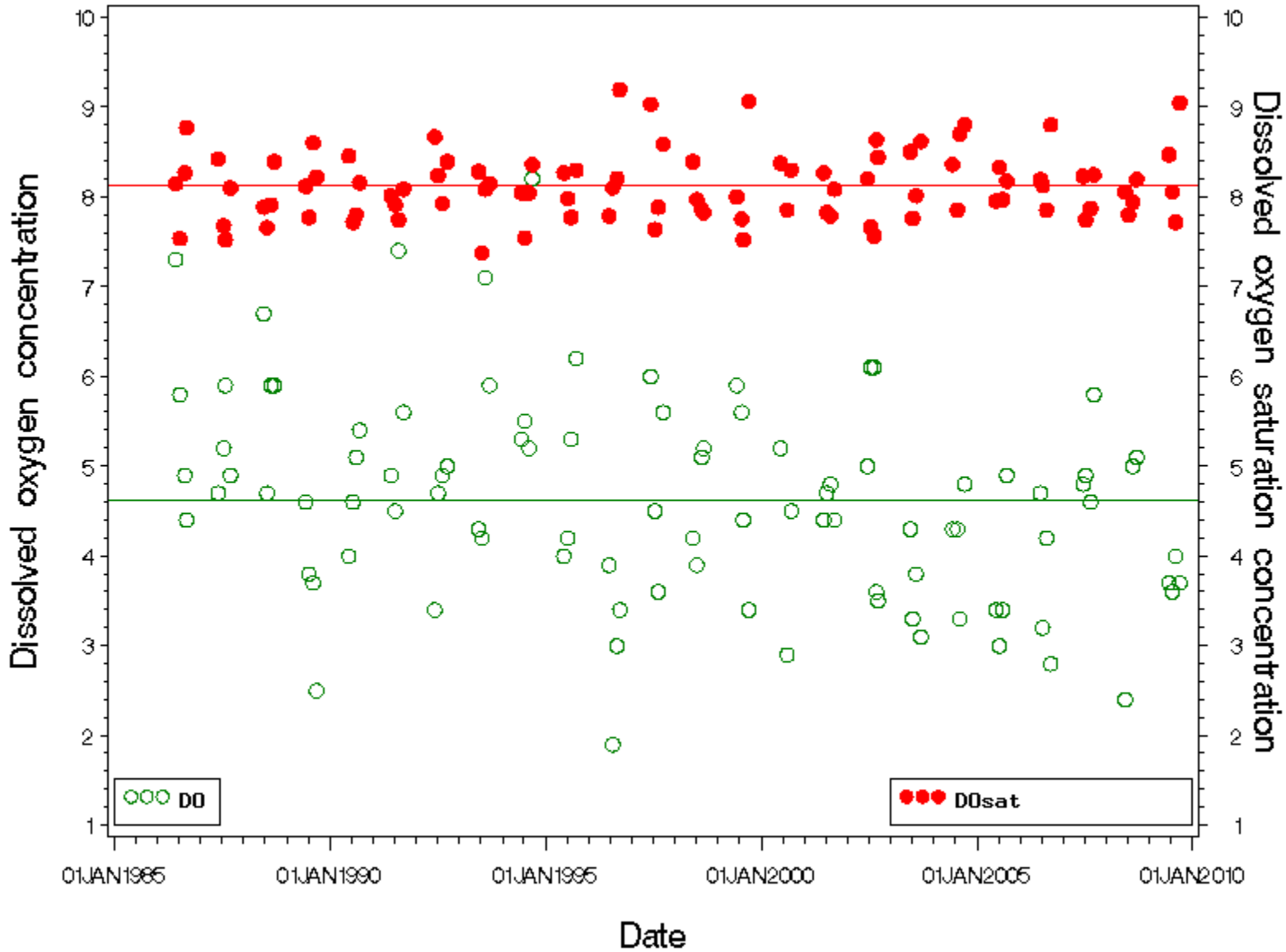

Figure 3. Station ET10.1 in POCTF June through September surface dissolved oxygen concentration (mg/L) and dissolved oxygen saturation concentration (mg/L), with mean of both (red and green lines).

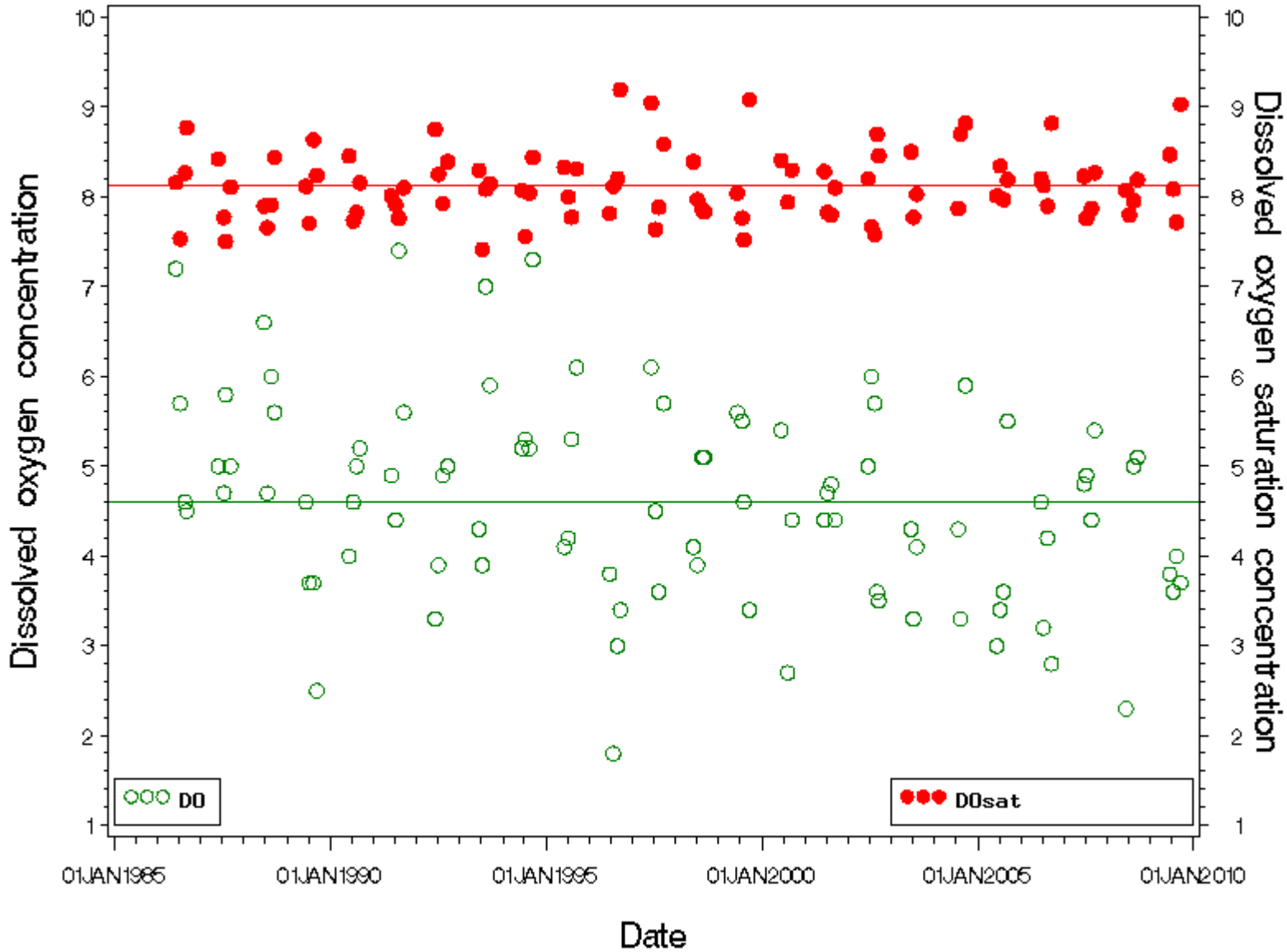

Figure 4. Station ET10.1 in POCTF June through September bottom dissolved oxygen concentration (mg/L) and dissolved oxygen saturation concentration (mg/L), with mean of both (red and green lines).

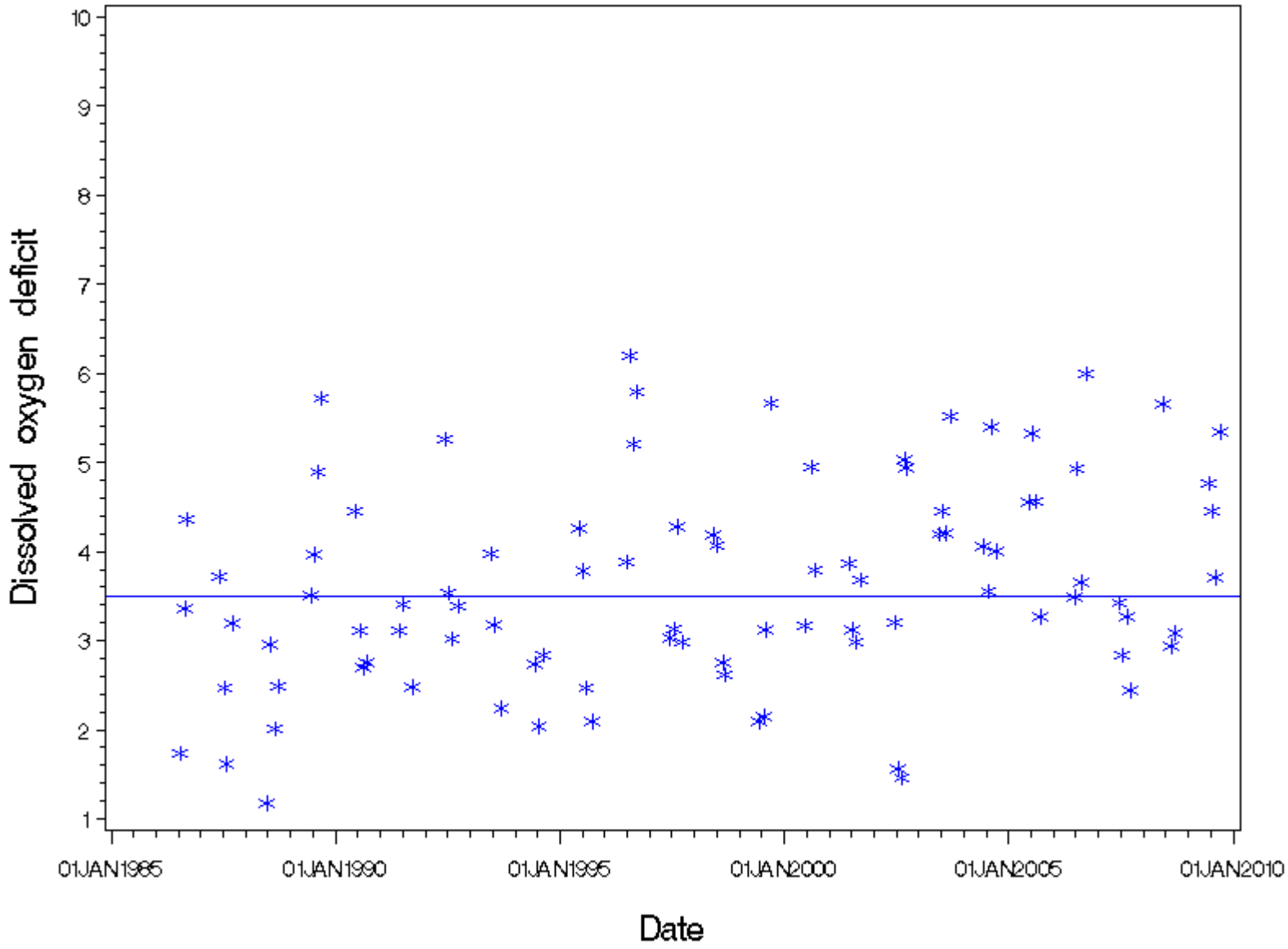

Figure 5. Station ET10.1 in POCTF June through September surface dissolved oxygen deficit (mg/L), with mean (blue line).

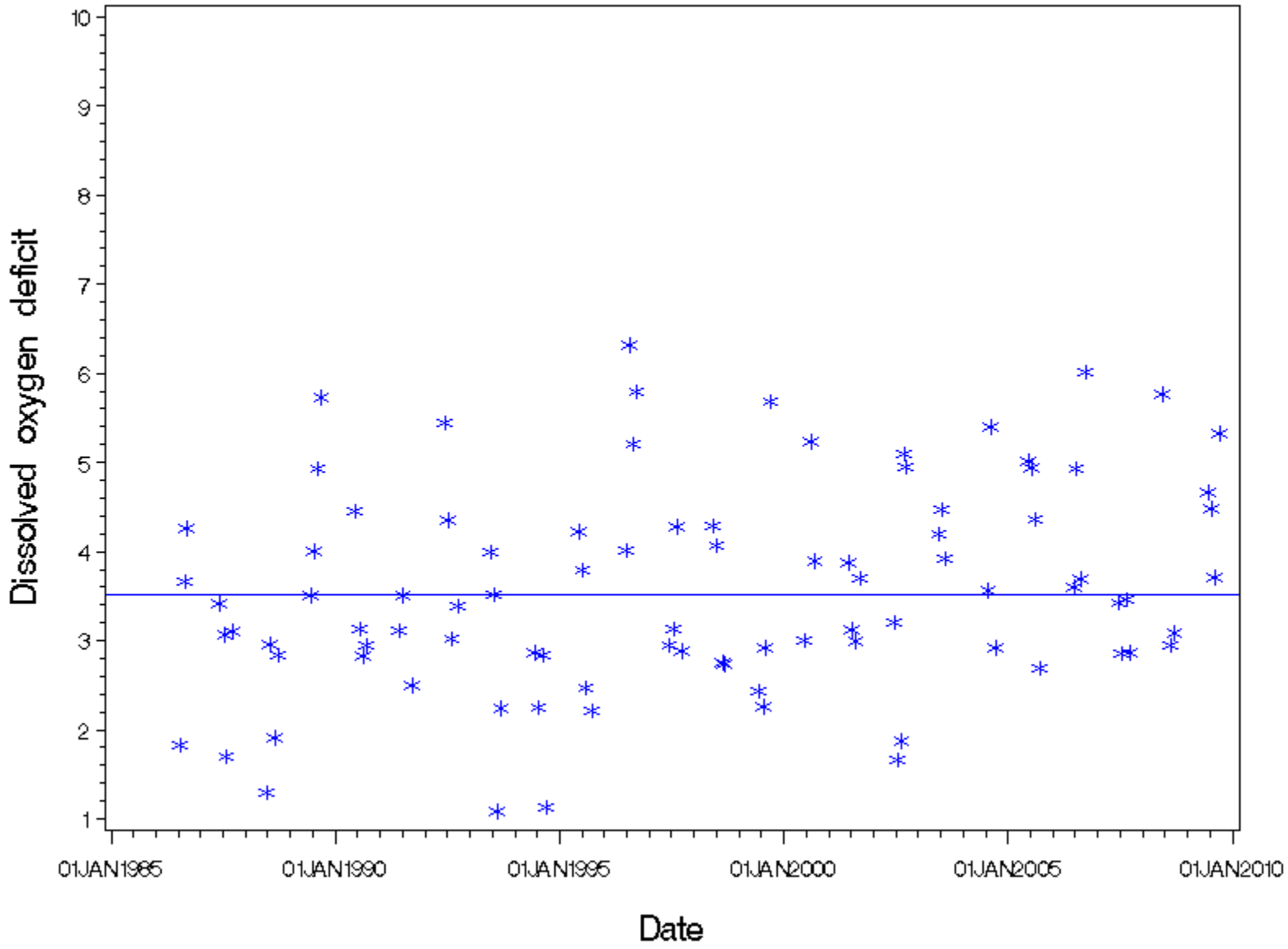

Figure 6. Station ET10.1 in POCTF June through September bottom dissolved oxygen deficit (mg/L), with mean (blue line).

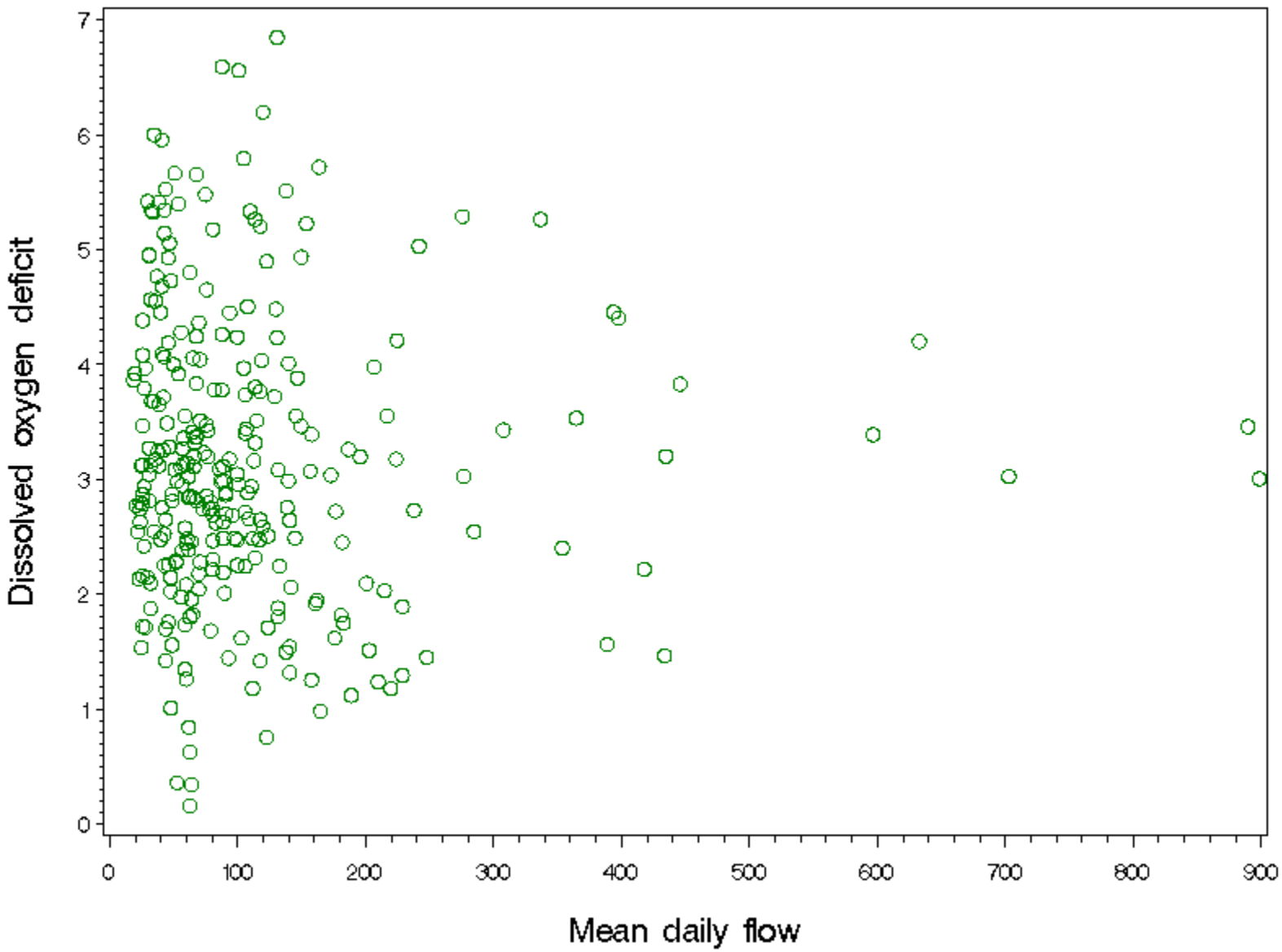

Figure 7. Dissolved oxygen deficit (mg/L) at ET10.1 in POCTF versus Pocomoke River flow (cubic feet per second) measured near Willards, MD.

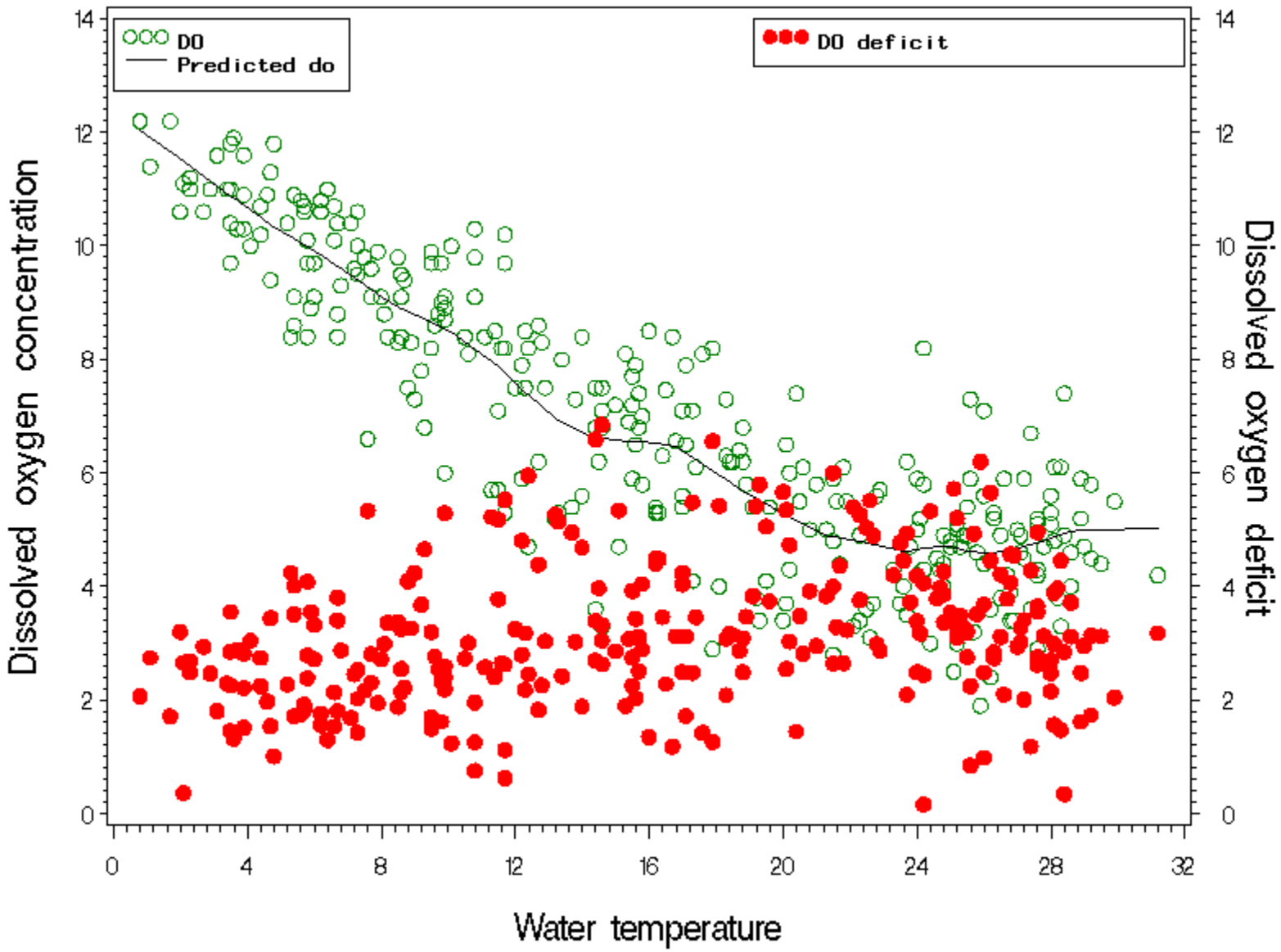

Figure 8. Dissolved oxygen (mg/L) and predicted dissolved oxygen (mg/L) fit with LOESS smooth, with dissolved oxygen deficit (mg/L) as a function of water temperature (^{o}C) at ET10.1 in POCTF.

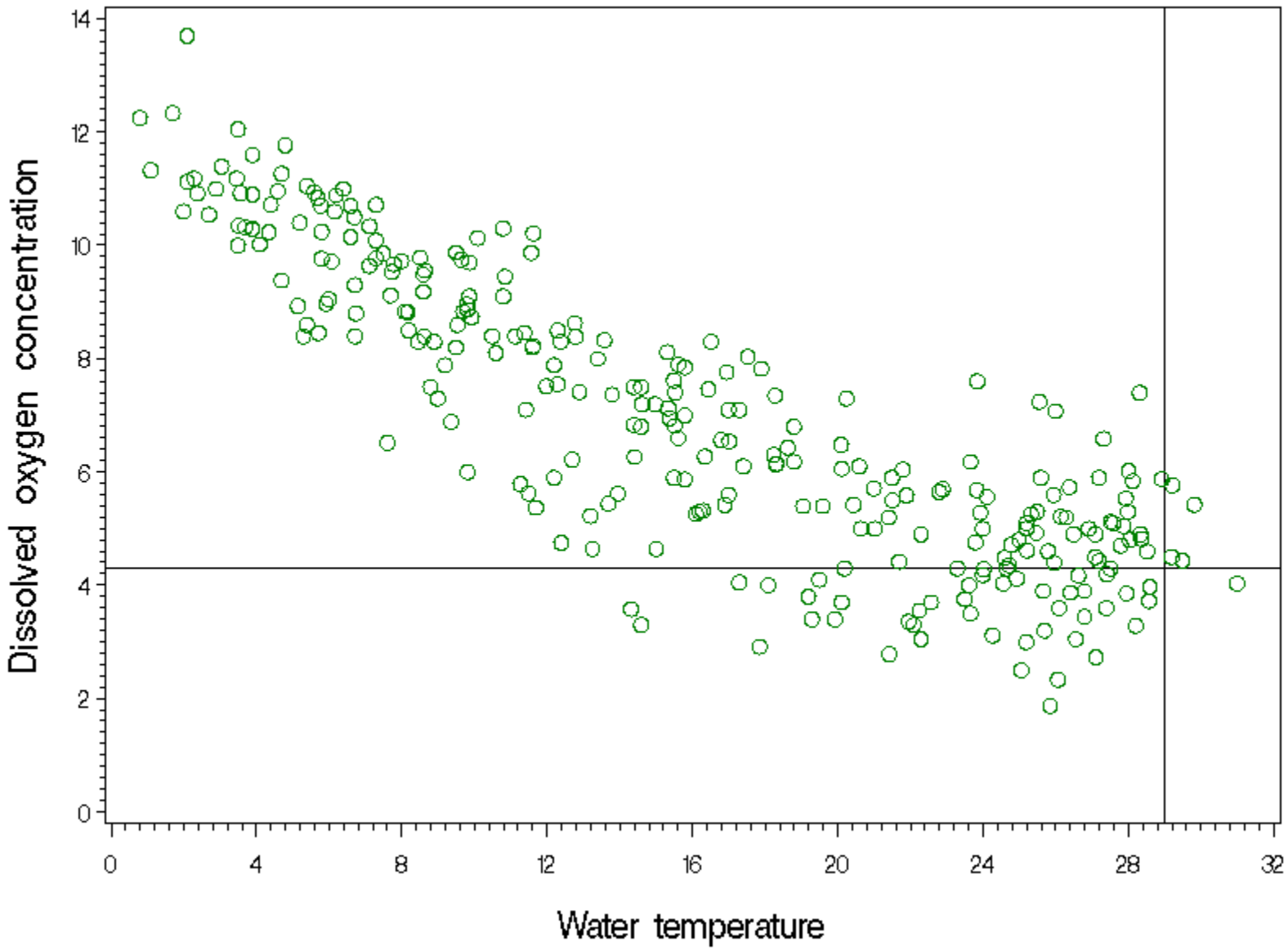

Figure 9. Dissolved oxygen concentrations (mg/L) less than 4.3 at water temperatures exceeding 29 ^{o}C using water column averaged data for station ET10.1 in POCTF.