SOUTH FLORIDA WATER MANAGEMENT DISTRICT

TECHNICAL PUBLICATION
WR-2020-002

Comparison of Outflow Total Phosphorus Concentrations from the Everglades Stormwater Treatment Areas Calculated with Autosampler vs. Grab Sample Data

Prepared by:
Michael J. Chimney Ph.D.

Water Quality Treatment Technologies Section
Applied Sciences Bureau, Water Resources Division
South Florida Water Management District
3301 Gun Club Road, West Palm Beach, FL 33406

October 2020

sfwmd.gov

INTRODUCTION

Treatment performance of the South Florida Water Management District's (District) Everglades Stormwater Treatment Areas (hereafter STAs) is evaluated based on flow-weighted mean (FWM) total phosphorus (TP) concentrations measured at the outflow structure(s) of each wetland[1]. A *Restoration Strategies Science Plan* (SFWMD, 2013) study that assessed the comparability of water samples obtained by different collection methods (autosamplers versus grab samples) concluded that:

> *"In many instances, all* [collection] *methods can be expected to produce very similar long-term data. However, significant short-term deviations in data from grabs and autosamplers have been documented, and these have the potential to impact estimates of concentrations, associated flows, and water quality performance"* (Rawlik, 2017).

The Rawlik study was based on water quality samples collected from two STA structures: The G-310 outflow pump station located at STA-1W and G-390B, a gated culvert within STA-3/4. Rawlik recommended that his results be validated with data collected at other District structures. The analysis presented in this report was conducted in response to that recommendation.

The District calculates outflow FWM TP concentrations for the STAs using its web-based Nutrient Load application (Germain, 2014) and autosampler data from each permitted structure; companion grab sample data collected at these structures are used only as a back-up[2]. The Rawlik study's conclusion about sample collection method affecting concentration estimates raised interesting questions for the STAs. How comparable are outflow FWM TP concentrations calculated with autosampler versus grab sample data (hereafter TP_{auto} and TP_{grab}), i.e., do FWM TP_{grab} concentrations reliably replicate FWM TP_{auto} concentrations? Are there any long- or short-term temporal differences between outflow TP_{auto} and TP_{grab} concentrations in these wetlands and, if so, do these differences conform to the collection-method pattern noted by Rawlik? The objective of this analysis is to address these questions by quantifying differences between estimates for outflow FWM TP_{auto} and TP_{grab} concentrations from each STA, and all STAs pooled together, over their respective periods-of-record (POR). It is beyond the scope of this study to evaluate why specific outflow TP_{grab} concentrations differed from corresponding TP_{auto} concentrations nor was it possible to identify the environmental and/or operational factors responsible for these differences. In addition, this report does not address any aspect of STA compliance with treatment performance goals mandated by the District's STA operating permit (State of Florida 2017).

---

[1] The District's STA operating permit requires that water samples be collected at permitted structures with autosamplers and grabs (State of Florida, 2017). Autosamplers are operated in flow-proportioned mode where sample aliquots are composited into a single collection bottle that is retrieved weekly and analyzed for TP provided there was enough flow at a structure to trigger its autosampler. Back-up grab samples also are collected weekly and analyzed for TP. Grab and autosampler samples are always paired, i.e., grab samples are collected from the same locations where autosamplers are deployed and at the same time when autosamplers are serviced.

[2] The District sets the Nutrient Load application to Computation Mode 2 when making these calculations where data from autosamplers are used preferentially while grab sample data are used only on those infrequent occasions when autosampler data are missing and flow occurred on the day when the grab sample was collected.

METHODS

As described above, the focus of this study was to compare outflow FWM TP concentrations calculated with autosampler versus grab sample data. The District's Nutrient Load application was used to calculate monthly outflow water volumes, TP loads and FWM TP concentrations for each STA[3]. Monthly water volumes and TP loads were then summed by District water year[4] for each STA. Estimates of outflow FWM TP concentrations for each water year were calculated as:

$$TP_{auto[i]}, TP_{grab[i]} = \frac{\sum M_{auto[i]} \times 10^9, \sum M_{grab[i]} \times 10^9}{\sum V_i \times 10^9} \quad (1)$$

where $TP_{auto[i]}$, $TP_{grab[i]}$ = outflow FWM TP concentration for the i^{th} STA and water year calculated with autosampler or grab sample data (µg L^{-1}), $\Sigma M_{auto[i]}$, $\Sigma M_{grab[i]}$ = monthly outflow TP loads based on autosampler or grab sample data summed for the i^{th} STA and water year (kg) and V_i = monthly outflow water volumes summed for the i^{th} STA and water year (hm^3). The 10^9 multiplication factors in the numerator and denominator convert kg to µg and hm^3 to L, respectively. Calculations were performed separately for the Everglades Nutrient Removal Project (ENRP) during the years (1994 to 1999) before it was incorporated into the footprint of STA-1W. Similarly, separate calculations were performed for STA-5 and STA-6 during the years (2000 to 2012 and 1997 to 2012, respectively) before these two wetlands were combined into STA-5/6. Annual TP_{auto} and TP_{grab} concentrations for all STAs pooled together were calculated by summing outflow TP loads and water volumes across all STAs within water years. The difference between annual outflow TP concentrations calculated with autosampler vs. grab sample data (ΔTP_{annual}) was computed for each STA, and all STAs pooled together, by water year as:

$$\Delta TP_{annual} = TP_{grab} - TP_{auto} \quad (2)$$

where ΔTP_{annual} (µg L^{-1}) is positive when annual TP_{grab} is greater than annual TP_{auto} and negative when the reverse is true. Summary statistics for ΔTP_{annual}, a linear regression of annual TP_{auto} against annual TP_{grab} and one-sample Wilcoxon Signed Rank tests to determine if ΔTP_{annual} medians differed from zero were calculated with the R functions *numSummary*, *lm* and *wilcox.test*, respectively (R v3.5.3; R Core Team, 2019). The critical level of statistical significance (α) was set at 0.05 in all cases. Monthly TP_{grab} and TP_{auto} concentrations were used to calculate individual monthly ΔTP values (ΔTP_{month}), which were used to evaluate the intra-annual variation for each

[3] I followed the District's procedure and set the Nutrient Load application to Computation Mode 2 to calculate monthly water volumes and TP Loads using autosampler data. Computation Mode 5, which uses grab samples regardless of flow, was used to calculate the same monthly values using only grab sample data. Rawlik (pers. comm.) found virtually no differences when annual TP concentrations were calculated with grab samples collected only on days when flow occurred at the structure (Mode 0) versus all grab samples regardless of flow (Mode 5). My preference was to use Mode 5. Note that the Nutrient Load application automatically screens out data with fatal flags before calculations are made. I did not perform any additional data screening as part of my analyses. Appendix 1 summarizes the Nutrient Load application workspaces and output Excel workbooks that were generated for this study along with the outflow structures at each STA and the start and end dates specified in each workspace.

[4] A District water year runs from May 1 through April 30 of the following calendar year.

STA. All graphics were prepared with the R packages *ggplot2* (v3.2.0; Wickham, 2016) and *cow-plot* (v1.1.0; Wilke, 2020).

RESULTS

Annual TP_{auto} and TP_{grab} concentrations for the STAs were highly correlated (R^2 = 0.97), although a scatterplot indicated that a number of data points deviated from falling directly along the 1:1 line where TP_{auto} equaled TP_{grab} (**Figure 1**). There was a tendency for larger deviations from a 1:1 relationship to occur when annual TP_{auto} and TP_{grab} exceeded 75 µg L^{-1}, which happened most often in STA-5.

The ΔTP_{annual} medians for individual STAs represent relatively small concentration differences that were negative in all but one STA (-3.0 to 0.5 µg L^{-1}; **Table 1**). Negative medians indicate that annual TP_{grab} was less than annual TP_{auto} in 50%, or more, of water years in these STAs; only the ENRP had a small positive median ΔTP_{annual} (0.5 µg L^{-1}). The median ΔTP_{annual} for all STAs pooled together was -1.0 µg L^{-1}. One-sample Wilcoxon Signed Rank tests detected statistically significant differences between ΔTP_{annual} medians and a value of zero in STA-1E, STA-2, STA-3/4, STA-6 and STA-5/6 but not for the ENRP, STA-1W, STA-5 and all STAs pooled together. Note that ΔTP_{annual} medians are comparable in magnitude to the District Chemistry Laboratory's method detection limit (MDL) for TP and within the TP practical quantitation limit (PQL)[5]. The other summary statistics in **Table 1** and boxplots (**Figure 2**) revealed greater variability in the data distribution of ΔTP_{annual} in STA-1E, STA-1W, STA-5 and STA-6 compared to the other STAs. STA-5 had both the smallest minimum and greatest maximum ΔTP_{annual} values: -25.2 and 36.9 µg L^{-1}, respectively. Annual TP_{grab} at STA outflows generally was slightly lower than corresponding annual TP_{auto}, resulting in mostly negative ΔTP_{annual} values, although this relationship was not true in all water years, particularly in STA-1W and STA-5 (**Figure 3**). Inspection of intra-annual variation in ΔTP_{month} values found that variability in ΔTP_{month} decreased towards the end of the POR in STA-1W, STA-2, and STA-3/4, but not in the other STAs (**Figure 4**). Interestingly, there was greater variability in ΔTP_{annual} and ΔTP_{month} in STA-5 and STA-6 when these STAs were operated independently compared to the variability in STA-5/6. Variability in ΔTP_{month} in STA-2 also declined after new cells were added to this facility. Operational changes in the STAs associated with events such as increasing treatment area may alter the relationship between grab and autosampler samples (P. Rawlik, Pers. Comm.).

CONCLUSIONS

The relatively small ΔTP_{annual} medians for individual STAs indicated that the autosampler and grab sample collection methods produced comparable outflow FWM TP concentrations on a

[5] The District Chemistry Laboratory's MDL for TP was 4 µg L^{-1} up through September 2002 after which time it was lowered to 2 µg L^{-1} (R. Walker, Pers. Comm.). The PQL for TP historically had been set at 4-times the MDL, but in recent years was established at 4 µg L^{-1} (R. Walker, Pers. Comm.). A MDL is defined as the smallest concentration of an analyte of interest that can be measured with 99% confidence that the analyte concentration is greater than zero, whereas the PQL is the smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence (SFWMD, 2020).

long-term basis, such as over a STA POR. However, summary statistics and data plots revealed considerable disagreement (≥ 10 µg L^{-1}) between outflow FWM TP concentrations calculated with autosampler versus grab sample data at shorter time scales (monthly and annual) in some STAs, e.g., STA-1W, STA-5 and STA-6. Results from this analysis support Rawlik's conclusion regarding long- and short-term computation differences related to the sample collection method; short-term differences in autosampler and grab data have the potential to impact concentration estimates generated with these data.

District scientists working in the Everglades STAs need to be aware of the potential affect that the sample collection method can have on the computation of FWM TP concentrations, especially on a short-term basis.

ACKNOWLEDGEMENTS

I would like to thank Cassondra Armstrong, Jacob Dombrowski , R. Tom James, Susan Mason, and Matt Powers for their review and constructive comments on drafts of this document. I also would like to thank the District Chemistry Laboratory's field and laboratory personnel for their dedication in collecting and analyzing TP samples from the STAs over the past 24 years.

DATA ARCHIVE

All computer files used in the preparation of this document (i.e., Microsoft Word and Excel files, graphic files, R scripts, data analysis output, etc.) are achieved in the Morpho data package: *Stormwater Treatment Area (STAs)_Comparison of Outflow TP*, which is available on the District's internal computer network.

REFERENCES

Germain, G. 2014. Nutrient Load User's Guide. Water Quality Bureau, South Florida Water Management District, West Palm Beach, FL. April 2014.

R Core Team. 2019. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. *https://www.R-project.org/*.

Rawlik, P.S. 2017. Results from Project REST: Remote Environmental Sampling Test. Evaluation of Sampling Methodologies. Technical Publication WR-2017-002. South Florida Water Management District, West Palm Beach, FL.

South Florida Water Management District [SFWMD]. 2013. Science Plan for the Everglades Stormwater Treatment Areas. South Florida Water Management District, West Palm Beach, FL. June 2013.

South Florida Water Management District [SFWMD]. 2020. Chemistry Laboratory Quality Manual. SFWMD-LAB-QM-2020-001. Prepared and maintained by the Analytical Services Section, Water Quality Bureau, Water Resources Division, South Florida Water Management District, West Palm Beach, FL. January 11, 2020.

State of Florida. 2017. State of Florida Industrial Wastewater Facility Permit # FL0778451 for STA-E, STA-1W, STA-2, STA-3/4 and STA-5/6 issued September 06, 2017 to the South Florida Water Management District, West Palm Beach, FL.

Wickham, H. 2016. ggplot2: Elegant Graphics for Data Analysis. Springer-Verlag. New York, NY. *https://CRAN.R-project.org/package=ggplot*.

Wilke, C.O. 2020. Cowplot: Streamlined Plot Theme and Plot Annotations for 'ggplot2'. *https://CRAN.R-project.org/package=cowplot*.

Table 1. Summary statistics for ΔTP_{annual}, the difference between annual FMW outflow TP concentrations for each STA, and all STAs pooled together, calculated with grab sample (TP_{grab}) and autosampler (TP_{auto}) data as $\Delta TP_{annual} = TP_{grab} - TP_{auto}$.

	Mean	Min	1st Quartile	Median	3rd Quartile	Max	IQR	POR
ENRP	0.6	-0.7	0.0	0.5	1.1	2.2	1.1	4
STA-1E	-3.1	-12.2	-5.1	-3.0	-1.1	6.1	4.0	13
STA-1W	-0.6	-7.7	-3.9	-2.2	2.4	12.5	6.3	20
STA-2	-1.6	-4.2	-2.8	-1.5	-0.1	1.7	2.7	17
STA-3/4	-1.7	-4.4	-1.6	-1.5	-1.0	-0.7	0.6	14
STA-5	0.9	-25.2	-6.0	-3.0	4.1	36.9	10.0	12
STA-6	-2.5	-10.8	-4.0	-0.8	-0.3	0.5	3.8	14
STA-5/6	-1.4	-2.7	-1.6	-1.3	-1.1	-0.6	0.5	6
All STAs	-1.0	-11.2	-1.8	-1.0	0.0	5.2	1.9	24

Notes: Units of measure for all statistics = µg L^{-1}; the 1st quartile, median and 3rd quartile correspond to the 25%, 50% and 75% percentiles of the data distribution, respectively; IQR = interquartile range = 3rd – 1st quartiles; POR = # water years analyzed; positive values indicate TP_{grab} concentration > TP_{auto} concentration, whereas negative values indicate TP_{grab} concentration < TP_{auto} concentration.

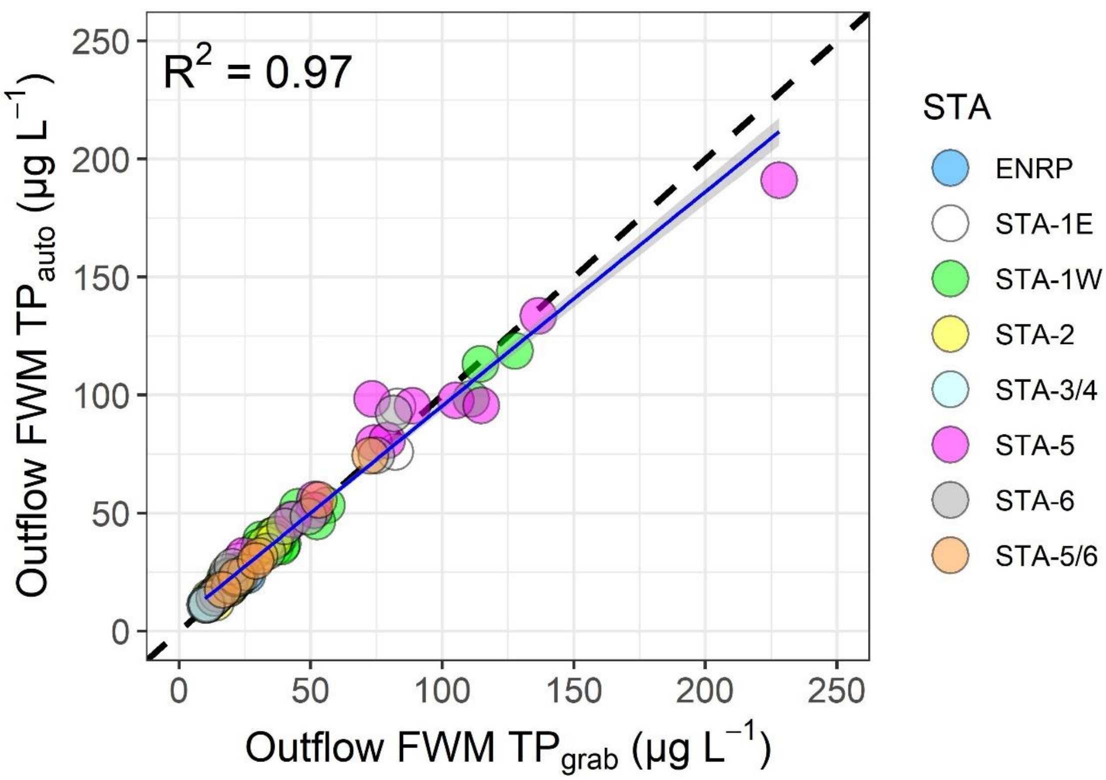

Figure 1. Scatterplot of STA annual FWM outflow TP concentrations calculated with grab sample (TP_{grab}) and autosampler (TP_{auto}) data. The dashed black line is the 1:1 line where $TP_{grab} = TP_{auto}$. The solid blue line is the line of best fit from a linear regression of TP_{auto} against TP_{grab} (R^2 = 0.97). The gray shading indicates the upper and lower 95% confidence bands around the regression line.

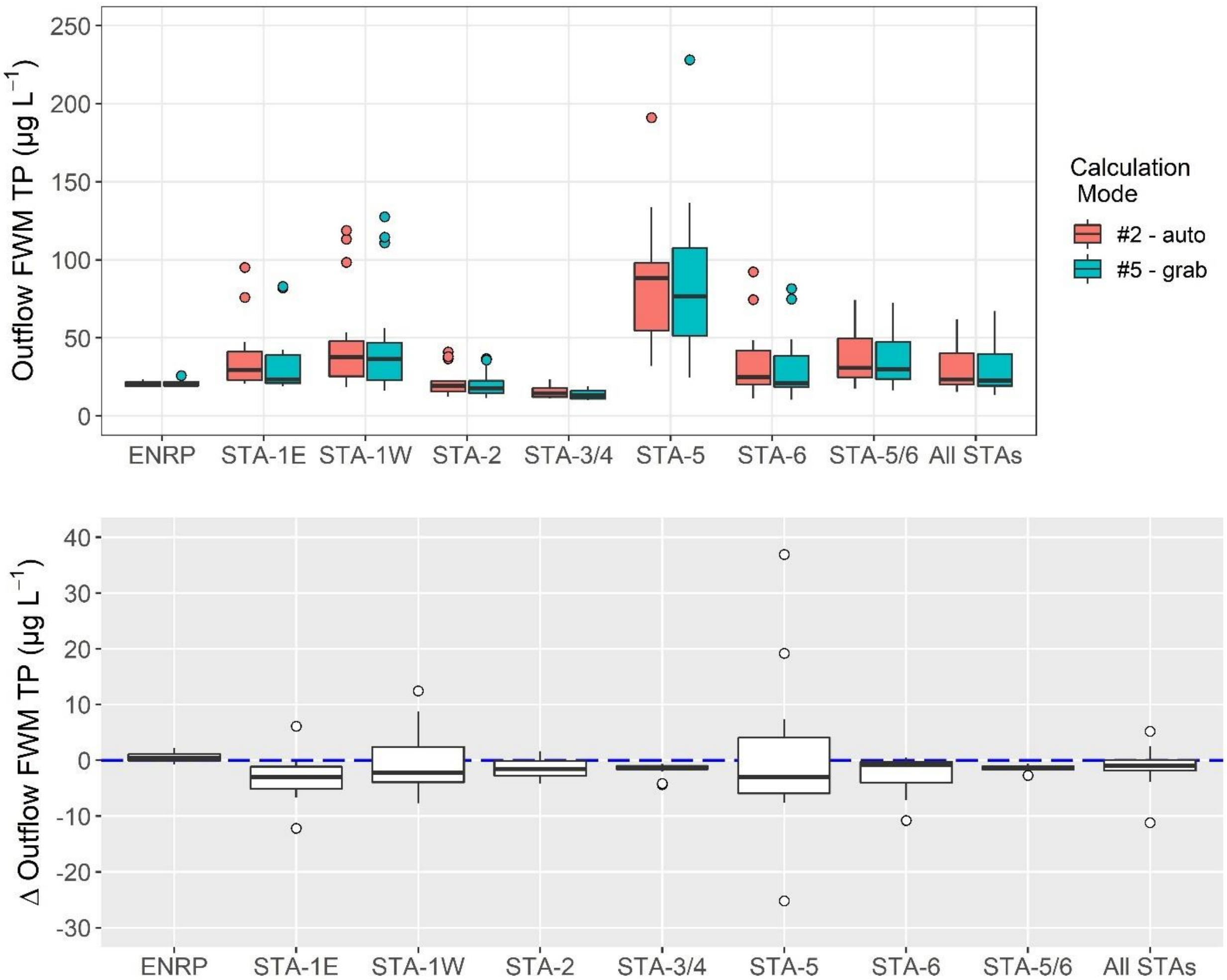

Figure 2. Boxplots of annual FWM outflow TP concentrations for each STA, and all STAS pooled together, calculated with both grab sample (TP_{grab}) and autosampler (TP_{auto}) data. **Top panel**: Comparison of annual outflow TP concentrations by calculation mode for each STA over its POR. **Bottom panel**: Differences between annual outflow TP concentrations for each STA where $\Delta TP_{annual} = TP_{grab} - TP_{auto}$. **Boxplot description**: thick horizontal black line = median of the data distribution; bottom and top of boxes = 25th and 75th percentiles of the data distribution (i.e., 1st and 3rd quartiles); lower and upper whiskers extend to 1.5x the interquartile range beyond the 1st and 3rd quartiles; open circles = outlier values. Positive ΔTP_{annual} values indicate $TP_{grab} > TP_{auto}$, whereas negative ΔTP_{annual} values indicate $TP_{grab} < TP_{auto}$.

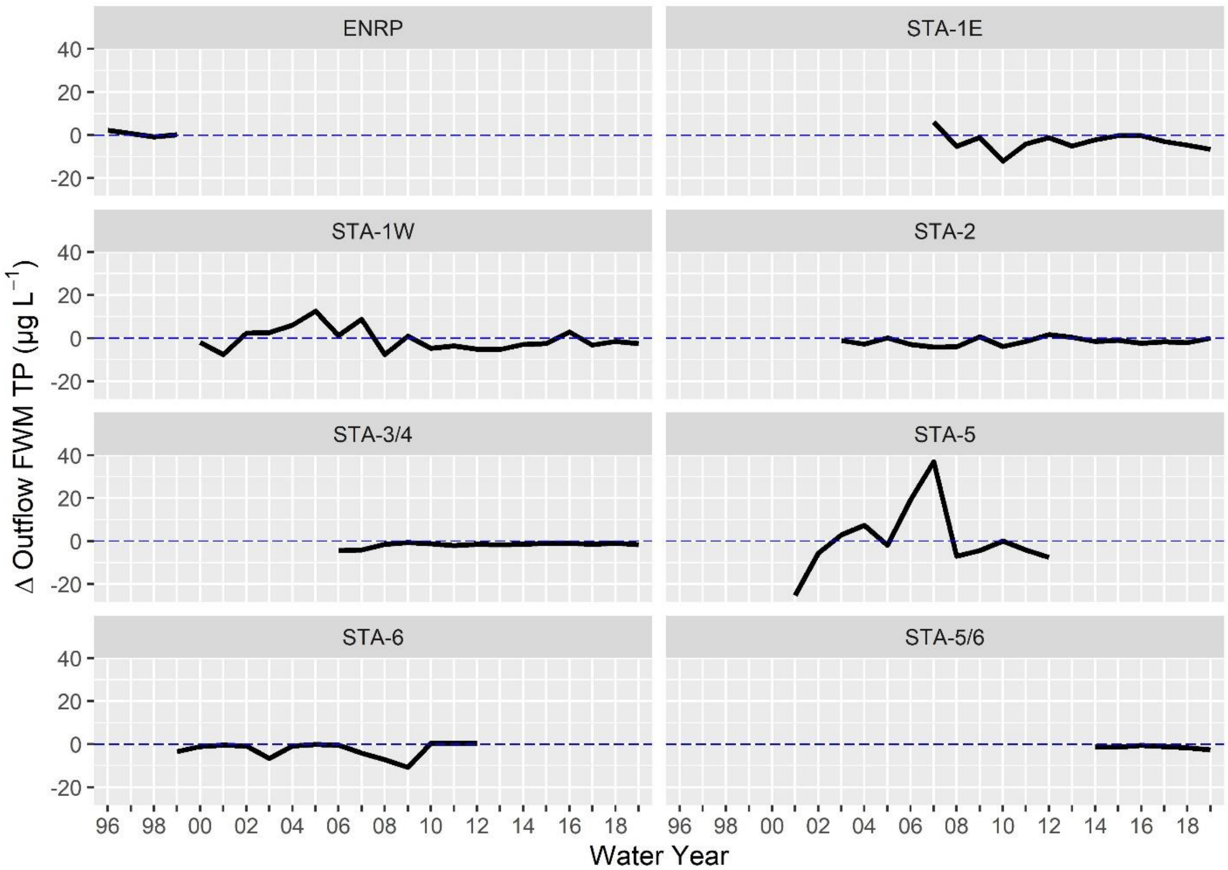

Figure 3. Time-series plots of ΔTP_{annual} - differences between annual FWM outflow TP concentrations calculated with grab sample (TP_{grab}) and autosampler (TP_{auto}) data over each STA's POR.

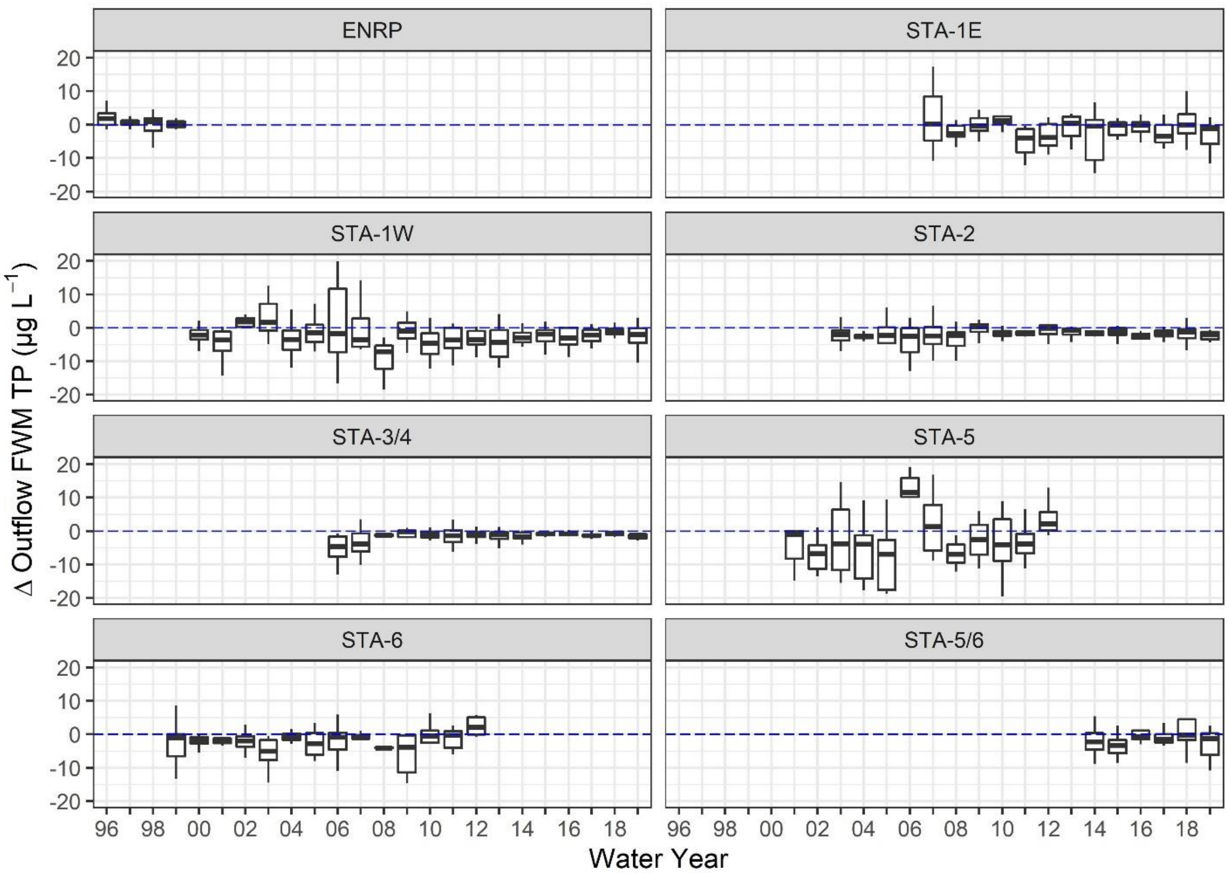

Figure 4. Boxplots of ΔTP_{month} - differences between monthly FWM outflow TP concentrations calculated with grab (TP_{grab}) and autosampler (TP_{auto}) data for each STA arranged by water year. See **Figure 2** for description of boxplots.

Appendix 1. Nutrient Load application workspaces, Excel workspace output, outflow sites and the start and end dates used in an analysis of STA outflow FWM TP concentrations calculated with autosampler vs. grab sample data*.

STA	Nutrient Load Workspace	Excel Workspace Output	Outflow Sites	Start Date	End Date
ENRP	P&N_Summary_ENRP_M2 P&N_Summary_ENRP_M5	ENRP_N+P_Mode.2.xls ENRP_N+P_Mode.5.xls	G251	05/01/1995	04/30/1999
STA-1E	P&N_Summary_STA-1E_M2 P&N_Summary_STA-1E_M5	STA-1E_N+P_Mode.2.xls STA-1E_N+P_Mode.5.xls	G311(neg. flow), S362	05/01/2006	04/30/2019
STA-1W	P&N_Summary_STA-1W_M2-a P&N_Summary_STA-1W_M2-b P&N_Summary_STA-1W_M5-a P&N_Summary_STA-1W_M5-b	STA-1W_N+P_Mode.2_#1.xls STA-1W_N+P_Mode.2_#2.xls STA-1W_N+P_Mode.5_#1.xls STA-1W_N+P_Mode.5_#2.xls	G310, G251	05/01/1999	04/30/2019
STA-2	P&N_Summary_STA-2_M2 P&N_Summary_STA-2_M5	STA-2_N+P_Mode.2.xls STA-2_N+P_Mode.5.xls	G335, G436	05/01/2002	04/30/2019
STA-3/4	P&N_Summary_STA-3/4_M2-2a P&N_Summary_STA-3/4_M2-2b P&N_Summary_STA-3/4_M5-2a P&N_Summary_STA-3/4_M5-2b	STA-3.4_N+P_#2a_Mode.2.xls STA-3.4_N+P_#2b_Mode.2.xls STA-3.4_N+P_#2a_Mode.5.xls STA-3.4_N+P_#2b_Mode.5.xls	G376A-F, G379A-E, G381A-F, G388	05/01/2005	04/30/2019
STA-5	P&N_Summary_STA-5_M2-1 P&N_Summary_STA-5_M2-2 P&N_Summary_STA-5_M5-1a P&N_Summary_STA-5_M5-1b P&N_Summary_STA-5_M5-2	STA-5_N+P_#1_Mode.2.xls STA-5_N+P_#2_Mode.2.xls STA-5_N+P_#1_Mode.5.xls STA-5_N+P_#2_Mode.5.xls	G344A-F	05/01/2000	04/30/2012
STA-6	P&N_Summary_STA-6_M2-1 P&N_Summary_STA-6_M2-2 P&N_Summary_STA-6_M2-3 P&N_Summary_STA-6_M5-1 P&N_Summary_STA-6_M5-2 P&N_Summary_STA-6_M5-3	STA-6_N+P_#1_Mode.2.xls STA-6_N+P_#2_Mode.2.xls STA-6_N+P_#3_Mode.2.xls STA-6_N+P_#1_Mode.5.xls STA-6_N+P_#2_Mode.5.xls STA-6_N+P_#3_Mode.5.xls	G606; G354A-C, G393A-C, G352A-C	05/01/1998	04/30/2012
STA-5/6	P&N_Summary_STA-5/6_M2-1 P&N_Summary_STA-5/6_M5-1a P&N_Summary_STA-5/6_M5-1aa	STA-5.6_N+P_#1_Mode.2.xls STA-5.6_N+P_#1_Mode.5.xls	G344A-K, G352A-C, G354A-C, G393A-C	05/01/2013	04/30/2019

*Multiple workspaces were created for STA-1W, STA-3/4, STA-5, STA-6 and STA-5/6 that 1) divided the number of parameters being analyzed among workspaces due to limitations on the number of worksheet columns in the output Excel workbooks, 2) subdivided the POR among workspaces due to computer memory restrictions or 3) both divided the number of parameters and subdivided the POR among workspaces.