Inter-Agency Agreement to Conduct Scientific Studies Relevant to the Stormwater Treatment Areas

Agreement No. 4600003125

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PREPARED FOR: South Florida Water Management District, and
Everglades Agricultural Area Environmental Protection District

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Introduction

Among the Everglades Stormwater Treatment Areas (STAs) constructed on previously-farmed lands, the STA-3/4 Periphyton-based STA (hereafter, the PSTA Cell) appears uniquely capable of consistently producing low outflow total phosphorus (TP) concentrations. The PSTA technology ultimately may prove useful for incorporation into new STA treatment areas, or as part of a retrofit to improve the performance of existing STA facilities. From a design standpoint, however, it is important to understand how much of the PSTA Cell's footprint is required to achieve target outflow TP levels under a range of hydraulic and P loading conditions. To better understand where P reductions are occurring within the PSTA cell, and to characterize potential transformations in P species in the system, DB Environmental Inc. (DBE) is performing periodic internal assessments of surface water chemistry.

For the period October 2014 – September 2015, three internal water quality surveys were performed. The first of these surveys was conducted on November 5, 2014 and the second was performed on February 25, 2015. To provide context for the comparisons to earlier sampling events, a brief description of recent PSTA cell hydrology precedes the water quality results. Additionally, results are compared to wet season water quality surveys in STA-3/4 Cells 2B and 3B, which were performed on July 28, 2015.

Methods

Surface water samples were obtained on June 23, 2015, by collecting grab samples from stations along internal transects established in the PSTA Cell. Phosphorus species, ammonia nitrogen, chlorophyll *a* and dissolved organic carbon (DOC) concentrations were analyzed using the methods described in **Table 1**. Chlorophyll was corrected for pheophytin. Ultraviolet (UV) radiation absorbance properties of (0.45 μm) filtered water samples were used to characterize

the relative size and recalcitrance of the constituents that comprise the dissolved organic matter (Helms et al 2008).

Enzyme activities were measured to determine the role of microbial activity in P cycling. The phosphatase activities of surface waters within the PSTA Cell were assayed by fluorometry using methylumbelliferyl (MUF) substrates. Enzyme activity was measured over a 1-hr period with readings at 5-min intervals. The rate of fluorescence increase over time was converted to MUF concentration using a standard curve, and adjusted for quenching by each sample.

Additional supporting flow, stage and TP data were retrieved from the District's on-line database (SFWMD.gov/DBHydro).

Table 1. Analytical methods and method detection limits (MDLs) for surface waters collected on June 23, 2015.

Parameter	Method	MDL
Total Phosphorus	SM4500-P F	3 µg/L
Total Soluble Phosphorus	SM4500-P F	3 µg/L
Soluble Reactive Phosphorus	SM4500-P F	2 µg/L
Ammonia	EPA 350.1 (1978)/ SM4500-NH3 (18th ed.)	0.020 mg/L
Dissolved Organic Carbon	SM 5310B	1.0 mg/L
Chlorophyll a	SM 10200H	0.1 µg/L

PSTA Cell Results

Hydrology and Antecedent TP Concentrations

The most recent PSTA Cell internal water quality sampling event in June 2015 took place early in the wet season, with flows into the cell averaging 11 cfs over the 14-day period prior to sampling (**Table 2**). Water depths have been stable within the PSTA Cell during all three sampling events this past year, and P loading rate during the 3-month period prior to June 23, 2015 was also comparable to other recent sampling events. The nominal hydraulic retention time within the PSTA Cell was ~12 days, based on the flow rate at the inflow structure on the day of sampling. Declining flows leading up to the day of sampling resulted in minimal discharge from the cell the day of the sampling event (**Figure 1**). Water stages and inflow and outflow TP concentrations also were quite stable up for the two week period prior to the internal monitoring event (**Figure 1**).

Table 2. Hydrologic parameters during and prior to 19 surface water sampling events along transects within the PSTA Cell.

Monitoring Event	Sample Date	3-month	14-day Period Prior to Sampling			Day of Sampling					TP In	TP Out
		P Load	P Load	Inflow	Outflow	Inflow	Outflow	HRT Based on Inflow	HRT Based on Outflow	Depth		
		g P/m^2/yr	g P/m^2/yr	cfs	cfs	cfs	cfs	days	days	m	µg/L	µg/L
Dry Season - No Inflow	5/2/2012	0.41	0.00	0	7	0	3	no flow	16	0.34	13	12
Flows Resumed to Cell	7/12/2012	0.06	0.36	8	10	9	10	6	6	0.36	24	15
Pulse #1 monitoring	7/25/2012	0.16	0.47	10	11	11	12	5	5	0.36	17	12
	8/2/2012	0.25	0.85	20	22	58	61	1	1	0.44	11	11
	8/8/2012	0.31	0.82	25	29	20	25	3	2	0.38	11	8
	8/22/2012	0.45	0.62	20	26	17	28	4	2	0.40	9	8
Pulse #2 monitoring	10/18/2012	0.51	0.35	22	30	19	28	3	2	0.38	10	8
	10/25/2012	0.48	0.44	27	29	56	55	2	2	0.57	6	6
	11/1/2012	0.46	0.41	27	31	17	21	4	3	0.38	6	7
Dry Season - No Outflow	4/24/2013	0.61	0.45	6	0	5	0	17	no flow	0.49	19	12
Wet Season monitoring	9/10/2013	0.25	0.13	3	3	7	8	12	10	0.49	20	9
Wet Season monitoring	10/21/2013	0.25	0.21	5	5	6	9	13	9	0.50	16	9
Dry Season	2/12/2014	0.35	0.85	19	24	12	14	6.9	5.8	0.49	18	9
Pulse #3 monitoring	6/19/2014	0.26	0.39	7	12	20	28	4.2	3.0	0.50	20	10
	6/26/2014	0.35	1.44	27	31	75	73	1.2	1.2	0.53	15	10
	7/7/2014	0.35	1.07	23	24	5	7	16	11	0.49	19	10
Dry Season - No Outflow	11/5/2014	0.33	0.15	5	3	3	0	33	no flow	0.51	11	5
Dry Season - Low Flow	2/25/2015	0.29	0.40	13	14	12	15	7	5	0.51	12	8
Wet Season monitoring	6/23/2015	0.35	0.34	11	11	7	1	12	95	0.51	15	9

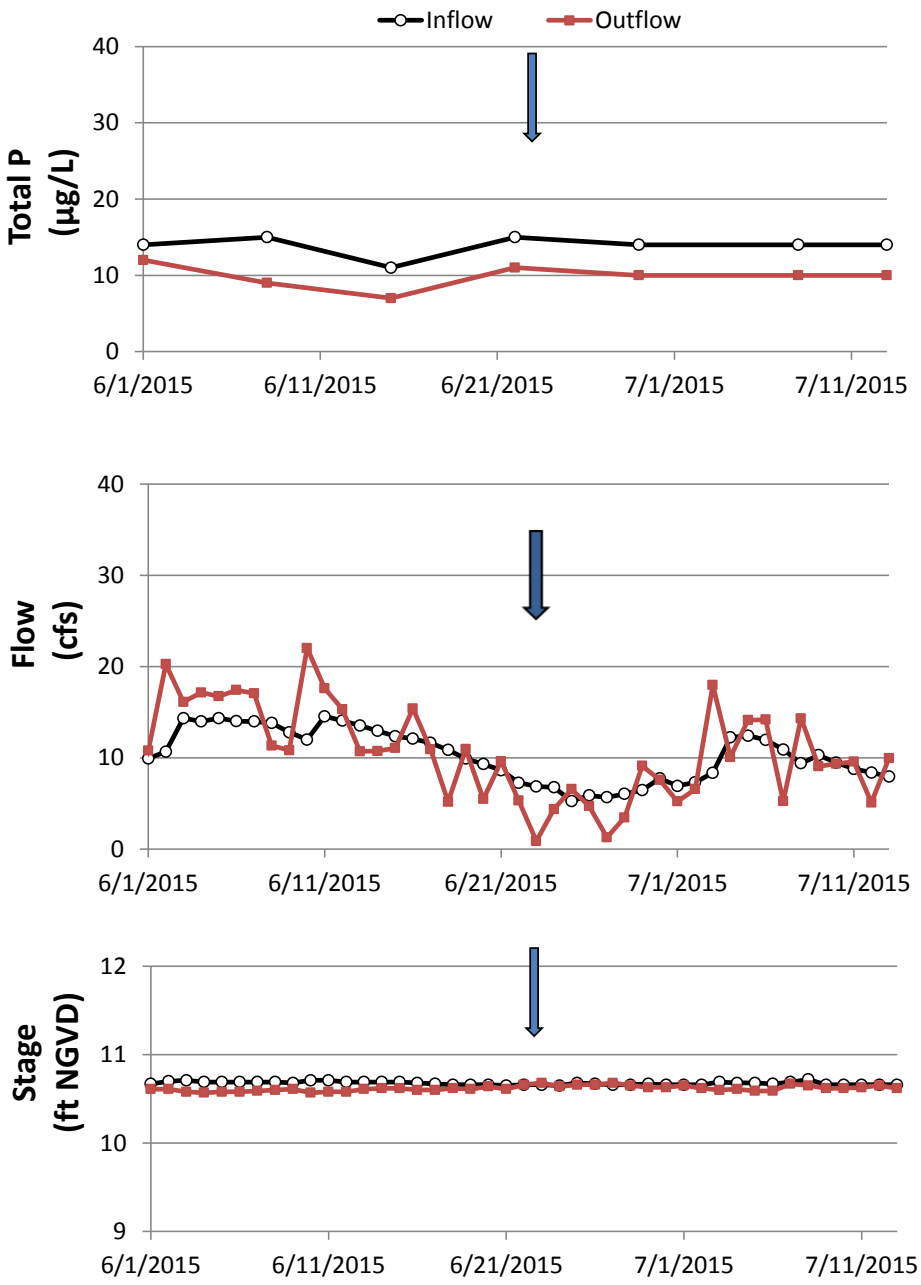

Figure 1. Flow and stage at the PSTA Cell inflow and outflow structures, and the surface water TP concentration at each structure during the period from June 1 – July 13, 2015. The arrow denotes internal water quality sampling event on June 23, 2015. Macrophytes were collected on June 24, 2015.

Total Phosphorus and Enzyme Activity under Flowing Conditions

On June 23, 2015, surface water entering the Central flow path of STA-3/4 contained 54 µg/L TP, and that concentration was reduced by 69% at the Cell 2A outflow (**Figure 2**). Thus, the

water entering the PSTA project Upper SAV Cell exhibited a fairly low TP concentration (17 µg/L). At the G390A structure, water flowing from the Upper SAV Cell into the PSTA Cell contained 15 µg TP/L, indicating that minimal TP reduction was observed within that cell. By contrast, TP concentration showed a steady decline through the PSTA Cell cell along the five transects monitored, and waters discharged from the cell at the G388 outflow structure contained a TP concentration of 9 µg/L (**Figure 2**).

Phosphatase enzyme activity in the surface water indicated different processes occurring in the upper SAV Cell and the PSTA Cell. A small increase in alkaline phosphatase activity (APA) was observed between the inflow to the Central flow way at G377 and the Cell 2A outflow structure (G378E), with little additional increase occurring upstream of the PSTA Cell inflow (**Figure 3**). At the first internal transect sampled (B transect, second "compartment" downstream of the inflow), APA rates increased to 0.76 µM MUF released/hr, and reached a peak activity along the L transect (2.13 µM/hr), before declining slightly at the G388 outflow structure. Phosphodiesterase (PDE) activity showed a similar trend to APA, though PDE rates were lower than APA in the PSTA Cell (**Figure 3**).

Phosphorus compounds in the PSTA Cell inflow water (**Figure 4**) were dominated by particulate forms, with an average PP concentration of 7.5 µg/L for the duplicate samples collected at G390B. DOP and SRP forms were equivalent at 3.5 µg/L in the inflow water. Through the cell, SRP concentrations declined to below detectable levels (depicted in **Figure 4** as one-half the MDL). By contrast, DOP concentrations persisted in the surface waters throughout the cell essentially unchanged. The PP concentration reductions occurred within ~150 m of the inflow levee (i.e., the distance to transect B).

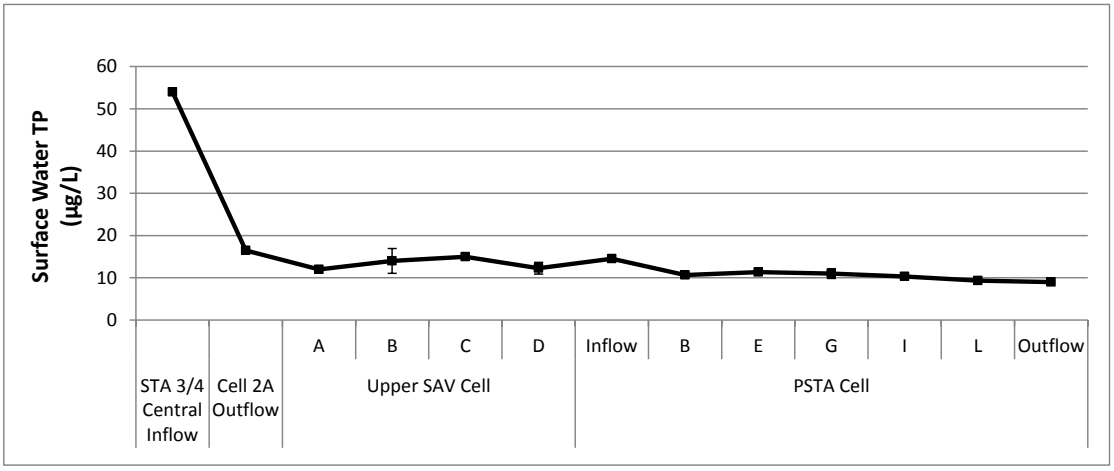

Figure 2. Longitudinal profile of total phosphorus concentrations through the PSTA Cell, as well as within the upstream Upper SAV Cell and Cell 2A, in the central flow way of STA-3/4 on June 23, 2015. Error bars denote ± standard error (SE) around the mean of three stations per transect in the PSTA Cell, and four stations along the B and D transects of the Upper SAV Cell.

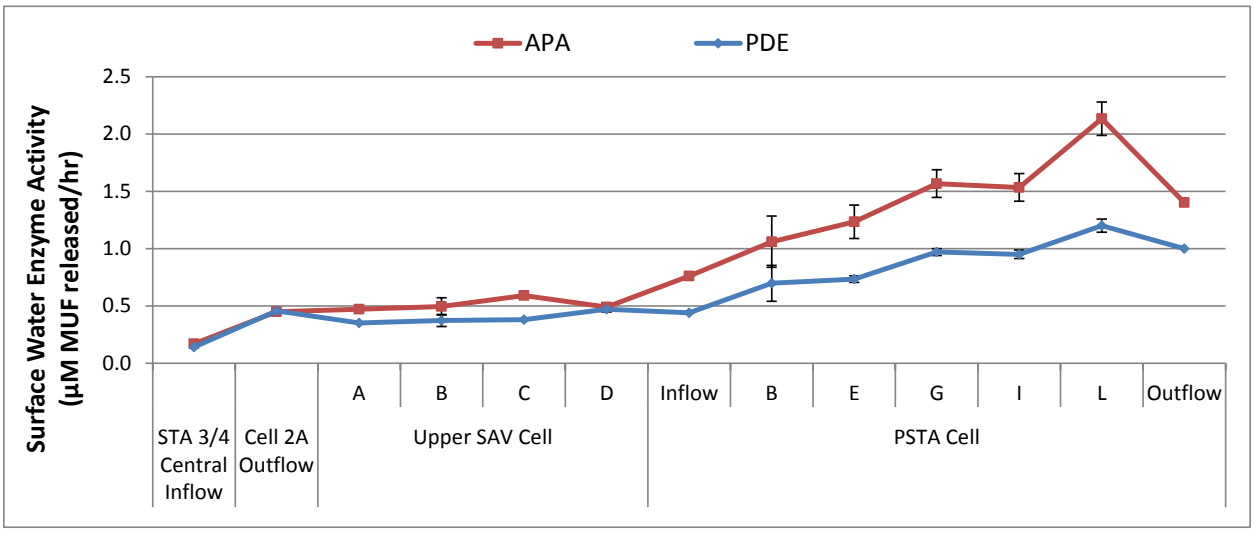

Figure 3. Enzyme activity in the surface waters along internal transects through the PSTA Cell and the upstream Upper SAV Cell, as well as at inflow and outflow structures, on June 23, 2015. Alkaline phosphatase activity (APA) for monoesterase and phosphodiesterase (PDE) were assayed fluorometrically using methylumbelliferyl (MUF)-P substrates, where the release rate of MUF is proportional to the rate of hydrolysis of phosphate from organic P compounds.

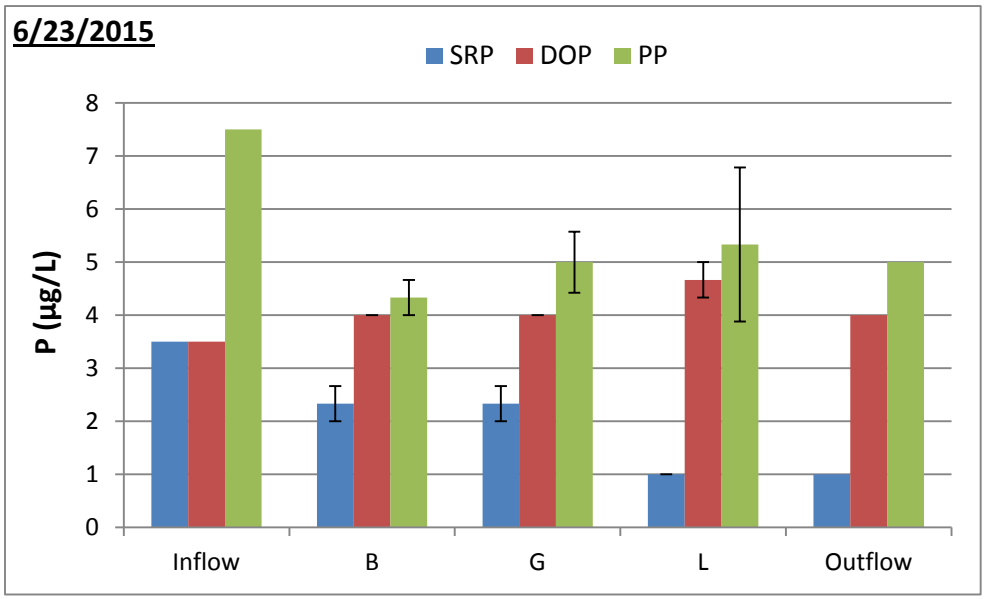

Figure 4. Phosphorus species concentrations in the surface water at inflow and outflow structures, and three internal transects within the PSTA Cell, on June 23, 2015. Error bars denote the standard error around the mean grab samples at three stations along the B, G and I transect.

Nitrogen Species

Ammonia nitrogen concentrations generally were quite low within the PSTA cell, with only modest spatial variation observed along the middle (G) transect (0.045 ± 0.005 mg/L). Overall, a slight reduction in ammonia-N concentrations was observed between inflow (0.064 mg/L) and outflow (0.053 mg/L) in June (**Figure 5**).

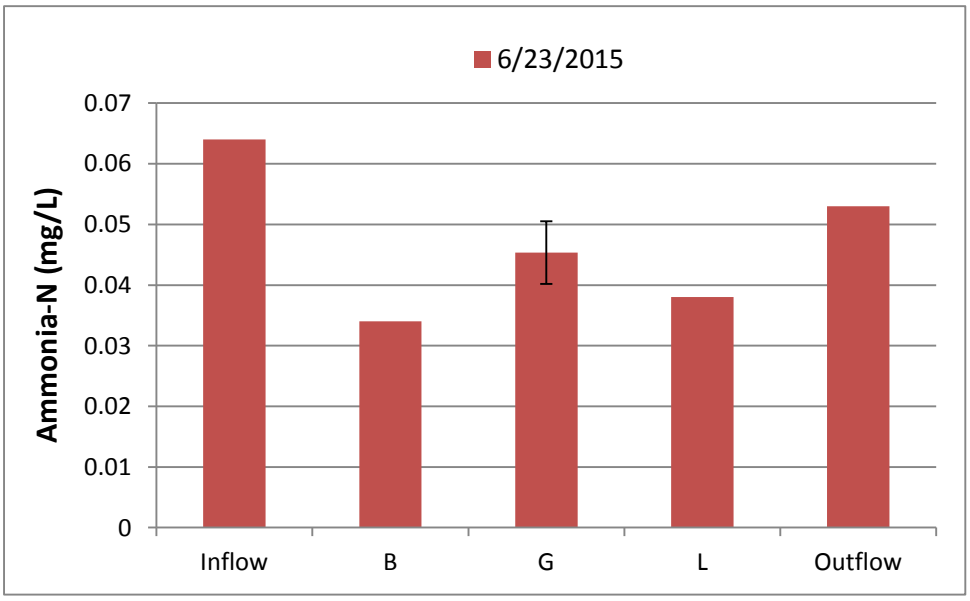

Figure 5. Ammonia nitrogen concentrations in the surface water at inflow and outflow structures, and three internal transects within the PSTA Cell, on June 23, 2015. Error bars denote the standard error around the mean of grab samples at three stations along the middle (G) transect.

Dissolved Organic Matter in the Surface Water of the PSTA Cell

Dissolved organic matter (DOM) was characterized by bulk DOC analysis (a measure of DOM quantity), as well as by the UV absorbance characteristics (spectral slope and $SUVA_{254}$) of filtered water samples (measures of DOM quality, relative size or aromaticity). Only a slight increase in DOC concentration from 28 to 31 mg/L was observed as waters passed through the PSTA Cell, occurring within the first half of the cell (**Figure 6**). In the outflow half of the PSTA Cell, DOC concentration was unchanged.

Surface water $SUVA_{254}$ values decreased slightly from 3.1 to 2.9 L/mg DOC/m in the first half of the cell, and remained unchanged in the latter half of the cell (**Figure 7**). Spectral slope in the 275-295 nm range showed a slight increase within the inflow region of the PSTA Cell on June 23, 2015, followed a decline at the middle transect (**Figure 8**). The back half of the cell exhibited an increasing trend more typical for this parameter in the PSTA Cell. A comparison of inflow and outflow data across 14 sampling events in the PSTA Cell between May 2012 and June 2015 shows that the outflow water is typically higher in $S_{275\text{-}295}$ than the inflow water (**Figure 9**). This indicates that the DOM compounds remaining in the PSTA outflow water are, on average,

smaller and more labile than inflow DOM compounds. The magnitude of change in $S_{275\text{-}295}$ within the PSTA Cell is smaller, however, relative to seasonal changes in the inflow water (**Figure 9**).

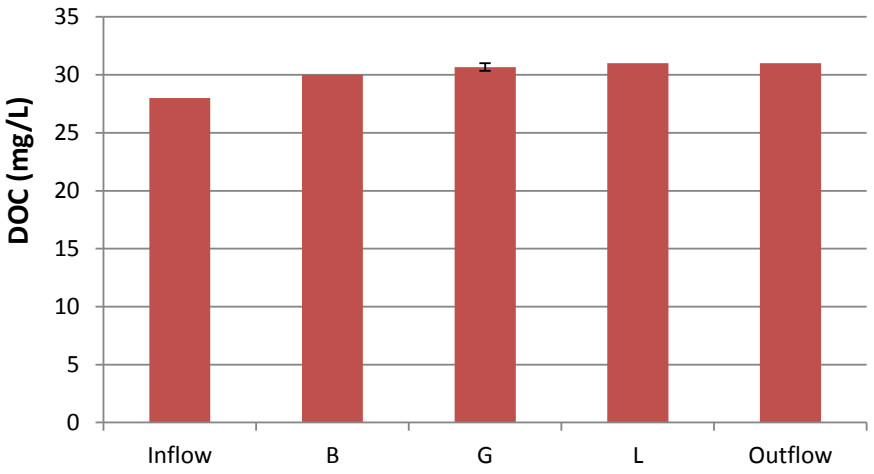

Figure 6. Dissolved organic carbon concentrations in the surface water at inflow and outflow structures, and three internal transects within the PSTA Cell, on June 23, 2015. Error bars denote the standard error around the mean of grab samples at three stations along the middle (G) transect.

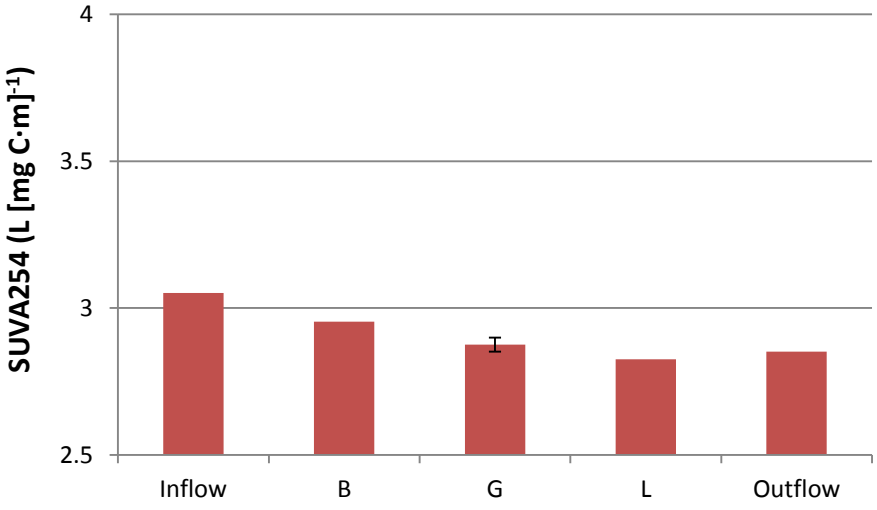

Figure 7. Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) in the surface water at inflow and outflow structures, and three internal transects within the PSTA Cell, on June 23, 2015. Error bars denote the standard error around the mean of grab samples at three stations along the middle (G) transect.

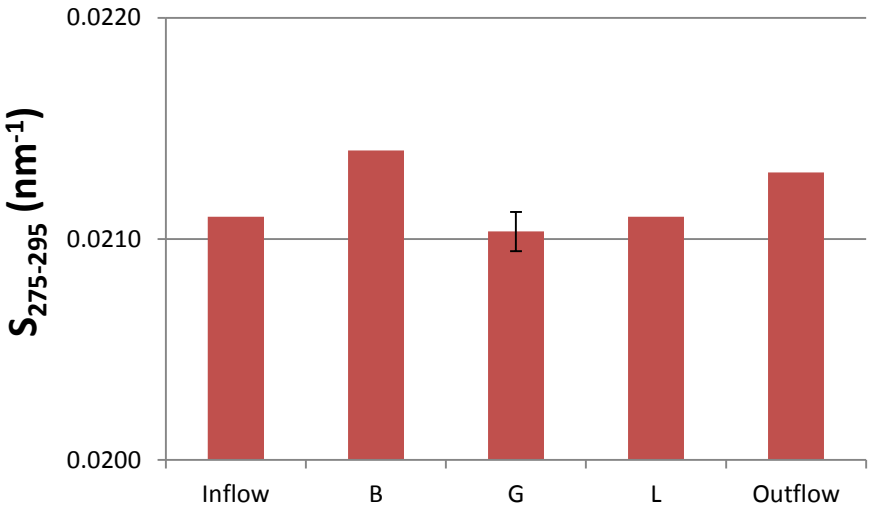

Figure 8. Spectral slope, $S_{275-295}$, in the surface water at inflow and outflow structures, and three internal transects within the PSTA Cell, on June 23, 2015. Spectral slope, determined as the change in absorbance across a range of ultraviolet radiation wavelengths (275-295 nm), indicates smaller, more labile dissolved organic matter compounds when values increase. Error bars denote the standard error around the mean of grab samples at three stations along the middle (G) transect.

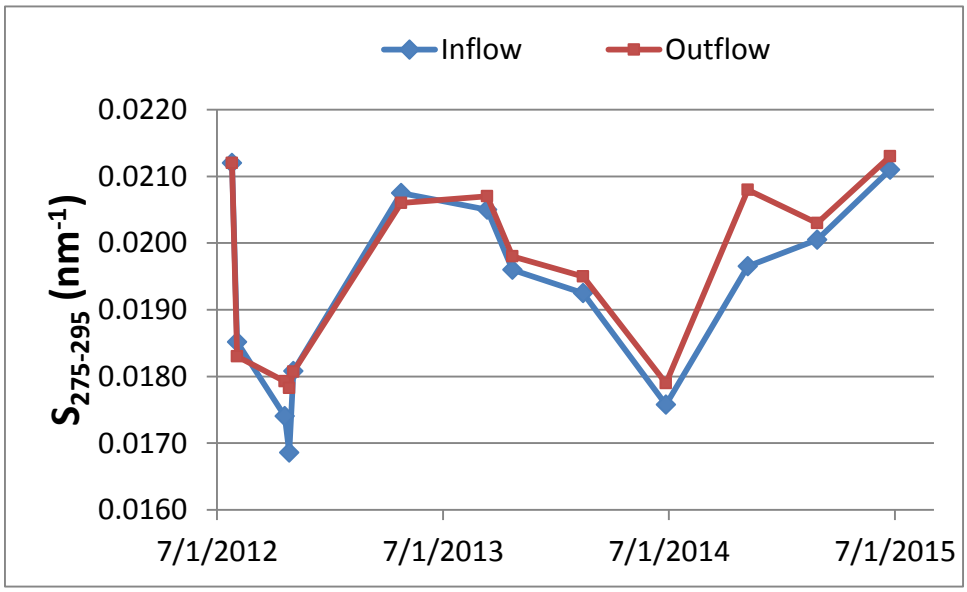

Figure 9. Spectral slope ($S_{275-295}$) values for inflow and outflow waters of the PSTA Cell for 14 sampling events between May 2012 and June 2015.

Chlorophyll concentrations in the inflow region were elevated during our June 2015 sampling event, as compared to the long-term average (N=14 events). On this date, the PSTA Cell reduced chlorophyll concentrations from 4.75 to 2.5 µg/L between inflow and outflow locations (**Figure 10**).

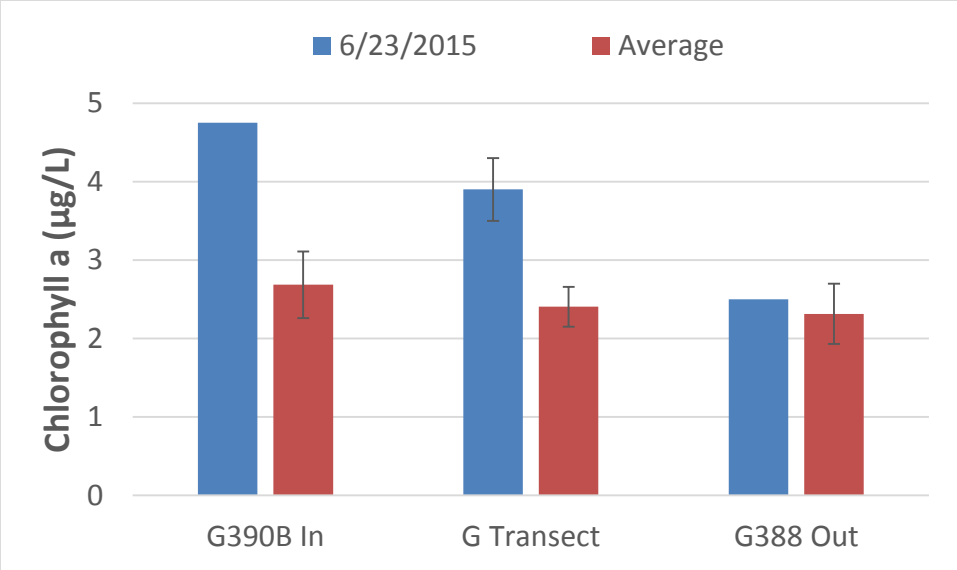

Figure 10. Concentrations of chlorophyll a (corrected for pheophytin) in the inflow and outflow waters of the PSTA Cell on June 23, 2015, and along an internal (G) transect within the middle of the cell. Error bars for June 23 indicate the standard error around the mean of three stations along the G transect. Error bars for average concentrations indicate the temporal SE for 14 sampling events in the cell between July 2012 and June 2015.

Comparison to Muck-based Flow-ways in STA-3/4

To facilitate comparisons between the PSTA Cell and muck-based systems, the adjacent muck-based cells (Cells 2B and 3B of STA-3/4) were sampled on July 28, 2015. These cells represent the back half of the Central and Western flow ways in STA-3/4, respectively, and are functionally equivalent to the Upper SAV Cell → PSTA Cell flow path. Cells 2B and 3B received little to no flow during part of July, but were flowing at the time of sampling (**Figures 11 and 12**).

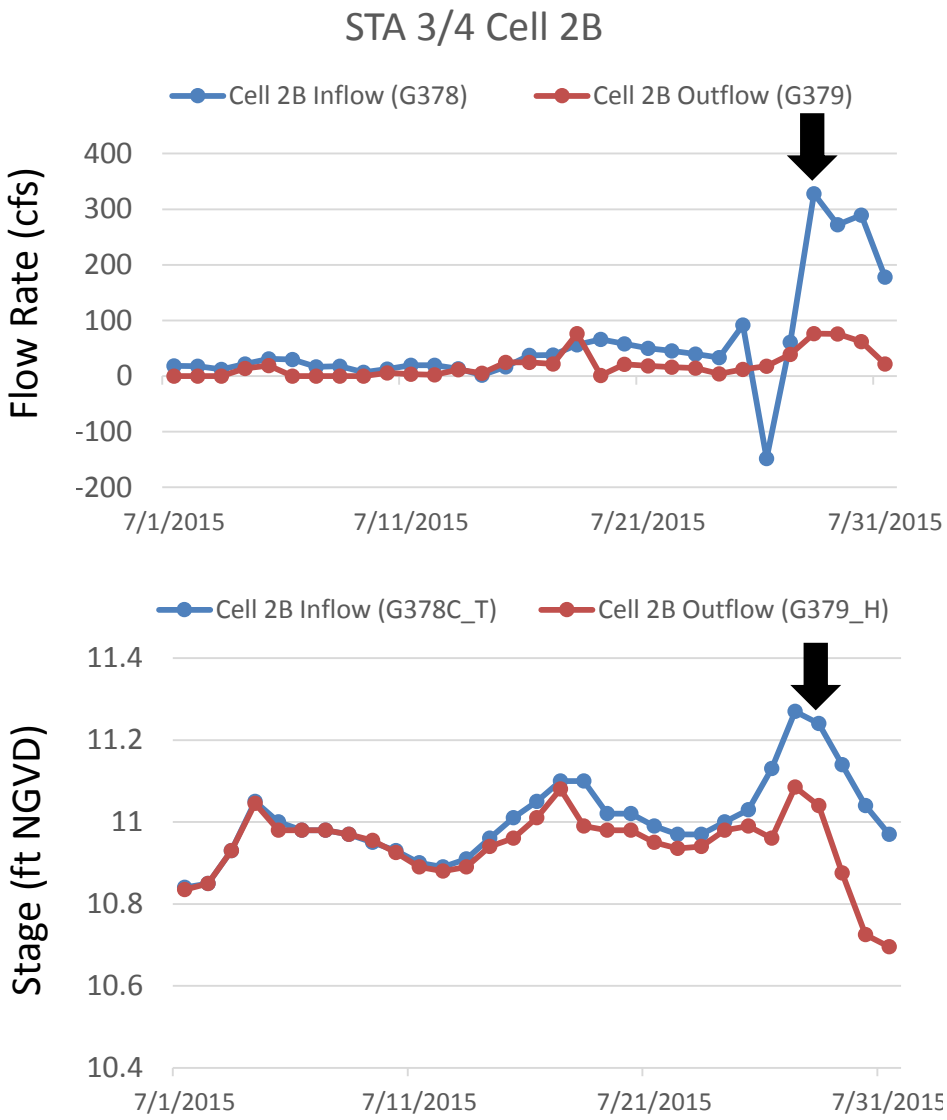

Figure 11. Mean daily flow and stage values for the inflow and outflow structures of STA-3/4 Cell 2B during July 2015. The arrow denotes the water sampling event along internal transects.

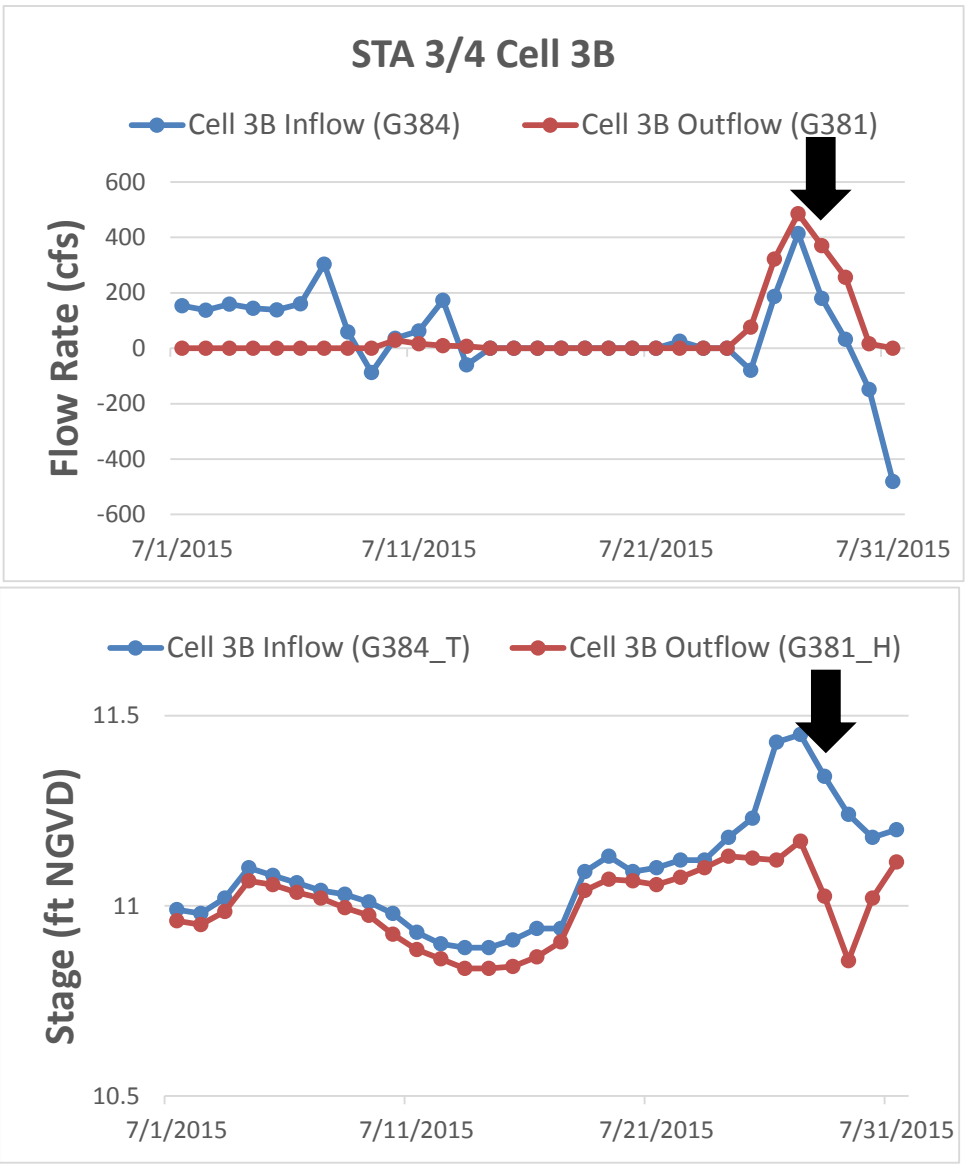

Figure 12. Mean daily flow and stage values for the inflow and outflow structures of STA-3/4 Cell 3B during July 2015. The arrow denotes the water sampling event along internal transects.

Phosphorus and Enzyme Gradients in Cells 2B and 3B

Total P concentrations in the inflow waters to Central (G377) and Western (G380) flow-ways on July 28, 2015 were 32 and 35 µg/L respectively (**Figure 13**). These concentrations are quite low for STA inflow waters. The inflow waters to Cell 2B were very low in TP, with concentrations of 9, 8, and 8 µg/L at the A C and D culverts along the G378 levee. The upstream Cell 2A therefore was providing very effective P removal performance, although it should be noted these low concentrations occurred at a time of minimal flow through the cell. Because of the low inflow concentrations, Cell 2B appeared to export P in July, with concentrations rising to 14 µg/L near

the outflow region (E transect) before discharging from the cell through G379 at 15 µg/L. By contrast, the P reductions in the Western flow way primarily occurred in 3B, with TP concentrations dropping from 31 µg/L at the G384 inflow levee to 12 µg/L at the G381 outflow structures (**Figure 13**).

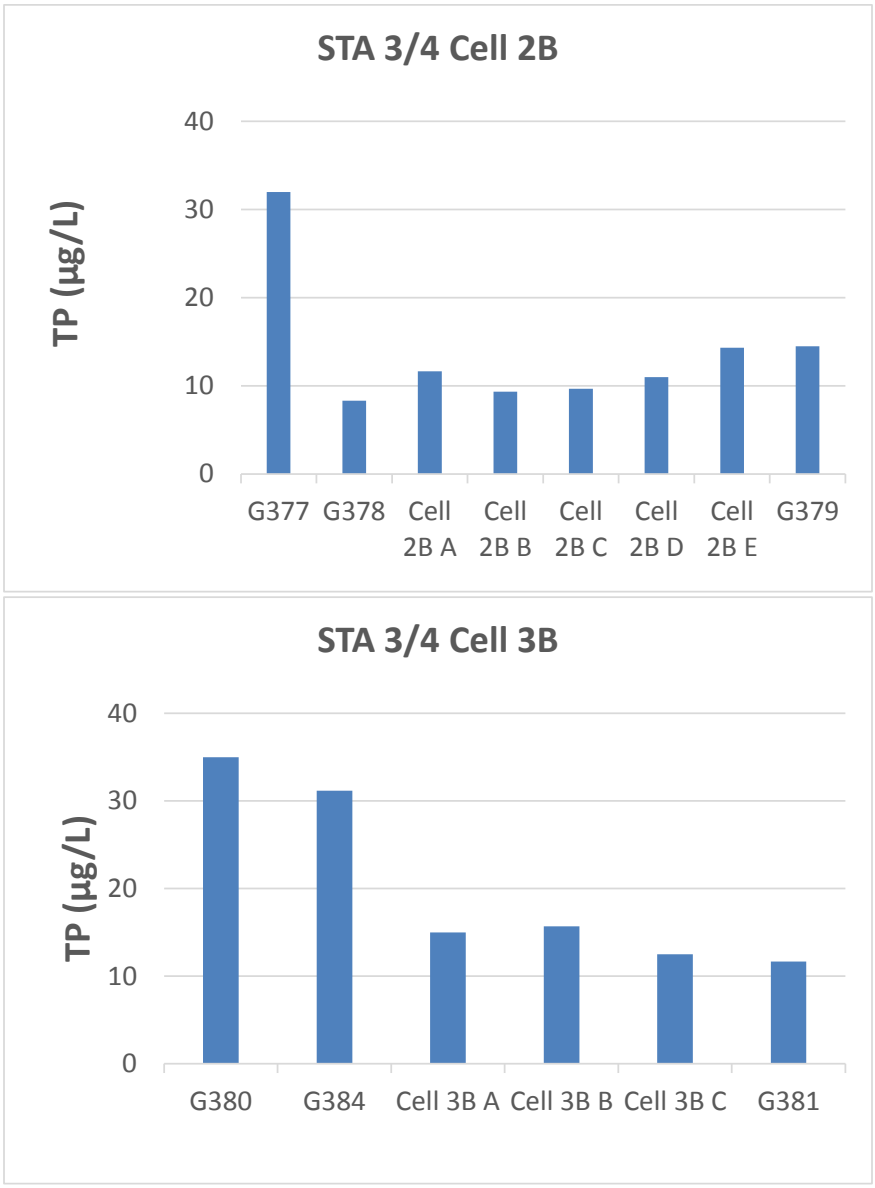

Figure 13. Total phosphorus (TP) concentrations along internal transects within Cell 2B (top) and Cell 3B (bottom) on July 28, 2015. Five transects were sampled in Cell 2B (A through E) and three transects were sampled within Cell 3B (A through C). Also shown are the concentrations measured at the inflow structures for the flow path (G377 and G380), inflows to each cell (G378 and G384), and outflow structures from each cell (G379 and G381, respectively) for the same date.

Our assessment of water column P speciation for the muck-based cells demonstrated that the increases in P observed within Cell 2B were the result of increases in DOP and PP fractions (**Figure 14**). By contrast, in Cell 3B, DOP concentrations were reduced from 12 µg/L to 5 µg/L in the outflow region of the cell, before increasing slightly to 6 µg/L at the outflow structure. Both 2B and 3B contained greater DOP concentrations during this survey (6 µg/L in each cell) than was observed in the PSTA Cell outflow waters on June 23, 2015 (4 µg/L). For outflow PP, Cell 2B concentrations (8 µg/L) were higher than in either Cell 3B or the PSTA Cell (5 µg/L in each cell). All cells exhibited SRP concentrations below the MDL (i.e., < 2 µg/L) in the outflow waters, despite Cell 3B inflow waters having elevated concentrations (15 µg/L) of this labile form during the survey.

Enzyme activity in the waters of Cells 2B and 3B exhibited increases from inflow to outflow (**Figure 14**), a trend similar to those observed for the PSTA Cell and Upper SAV Cell. However, the rates measured in the muck cell outflow waters were lower than for the PSTA Cell. The maximum APA observed value of 0.43 µM MUF released/hr was approximately 5-fold lower than the maximum rate observed for the PSTA Cell in June (2.13 µM MUF released/hr).

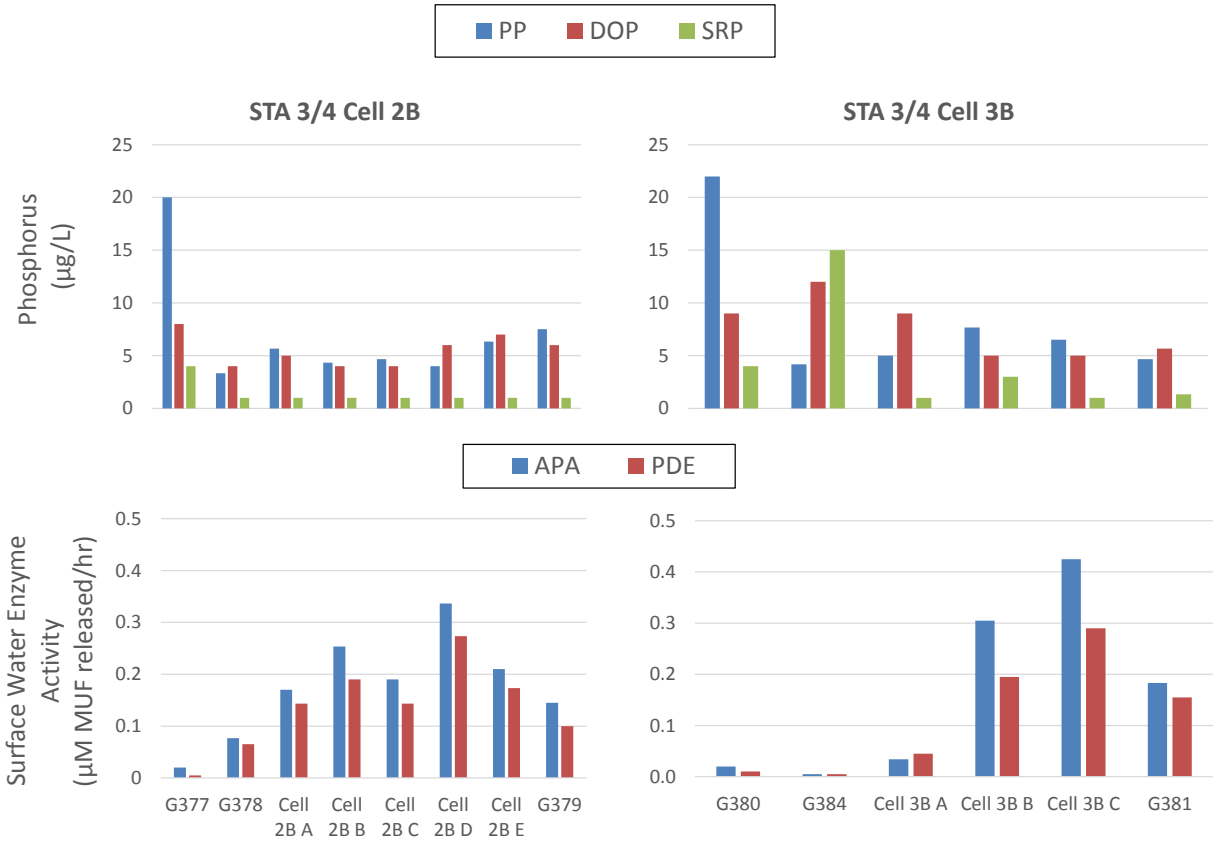

Figure 14. Phosphorus concentrations and phosphatase enzyme activities in two "back-end" cells of STA-3/4 on July 28, 2015.

Interestingly, the internal transects within Cells 2B and 3B, as well as in the Upper SAV Cell, all exhibited PDE rates similar to the APA rates, while in the PSTA Cell, APA exceeded PDE by ~60-70%. This class of enzyme (PDE) may be important in hydrolyzing diesters of organic P that are commonly associated with organic soils in wetlands (Turner and Newman 2005). In both PSTA and muck-based cells, the water at outflow structures showed slightly lower enzyme activities than the samples collected along internal transects in the outflow region of these cells.

Ammonia Nitrogen in the Surface Water of Cells 2B and 3B

Similar to observations in the PSTA Cell, ammonia nitrogen levels in Cells 2B and 3B were lower along the internal transects than at either the inflow or outflow structures (**Figure 15**). In Cell 2B, ammonia levels rose above the MDL along internal transects D and E in the outflow region before exiting the cell at 0.034 mg/L, while in Cell 3B, values at all internal stations were < MDL. In general, ammonia-N concentrations in the muck cells were as low, or lower than those in the PSTA cell waters (cf. Figure 5).

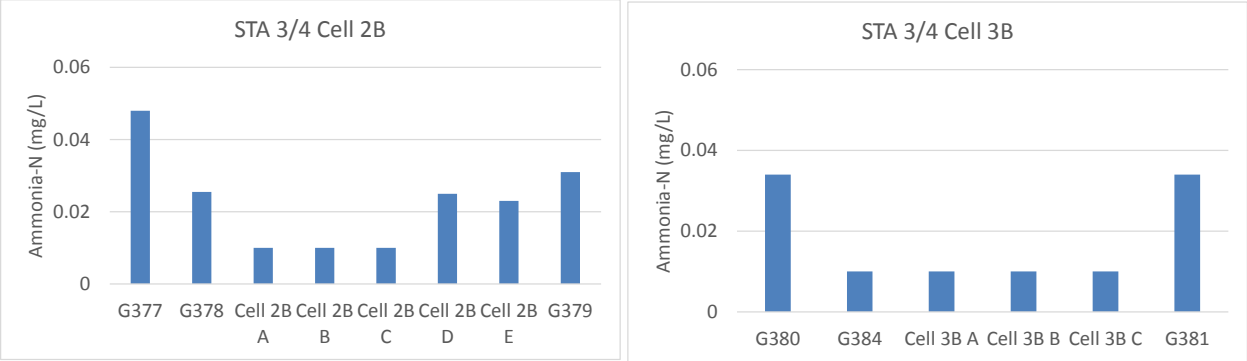

Figure 15. Ammonia nitrogen concentrations in the surface water of two cells in STA-3/4, on July 28, 2015. Values less than the method detection limit of 0.02 mg/L are depicted as one-half the MDL.

Dissolved Organic Matter in the Surface Water of Cells 2B and 3B

The DOM characterization of surface waters in Cells 2B and 3B showed increasing spectral slope and decreased $SUVA_{254}$ with distance through each flow way (**Figure 16**). The DOC concentration was somewhat variable in both muck-based cells, ending slightly higher in Cell 2B outflow waters, and lower in Cell 3B waters, as compared to the inflow waters to each STA flow way. The greatest observed change in DOC concentration was between 21 mg/L at the inflow to the Western flow way and 17 mg/L at the inflow to Cell 3B.

The overall inflow-outflow trends within the muck cells are similar to the PSTA Cell for DOC, $SUVA_{254}$ and spectral slope, however, the absolute values are different. DOC concentration is lower in the muck cells, ranging from 17 to 21 mg/L compared to the PSTA Cell ranging from 28 to 31 mg/L (cf. **Figures 6 and 16**). $SUVA_{254}$ concentrations are higher in the muck cells,

ranging from 3.3 to 3.7 L/mg DOC/m compared to ~2.7 to 3.1 L/mg DOC/m in the PSTA Cell (cf **Figures 7 and 16**). Lastly, the spectral slope was lower in the muck cells indicating larger DOM compounds than in the PSTA Cell (cf. **Figures 8 and 16**).

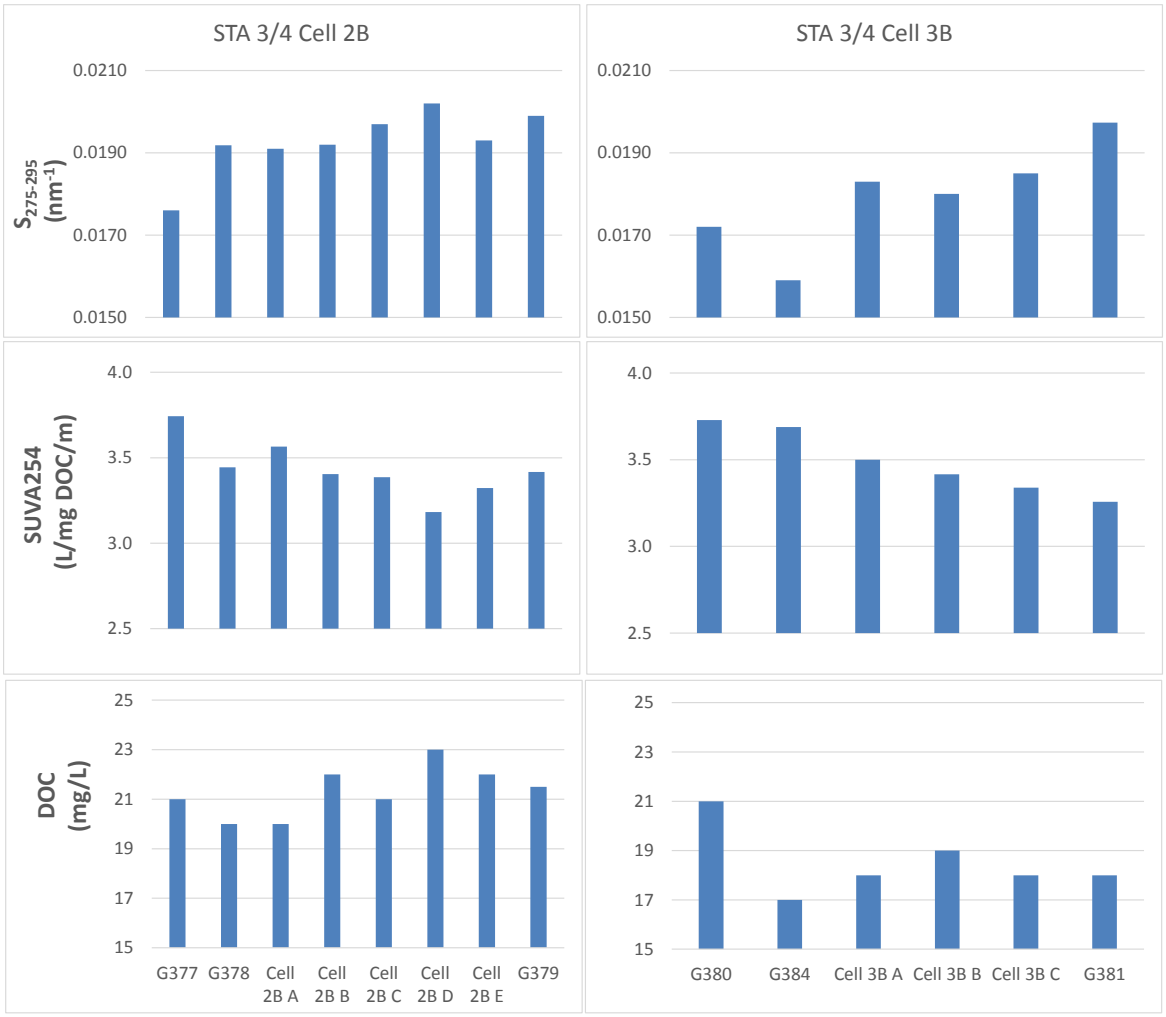

Figure 16. Characteristics of the dissolved organic matter ($S_{275-295}$, $SUVA_{254}$ and DOC concentration) in surface waters from two cells in STA-3/4 on July 28, 2015.

References

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Turner, B.L., and S. Newman. 2005. Phosphorus cycling in wetland soils. the importance of phosphate diesters. J. Environ. Qual. 34:1921-1929.