#### Deliverable A-5-B: Water Quality Report: Quantifying Operational Boundaries Inter-Agency Agreement to Conduct Scientific Studies Relevant to the Stormwater Treatment Areas

# Agreement No. 4600003125

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### Introduction

There are potential benefits to shallow water depths in PSTA systems, including increased light penetration to the benthic surface. However, because shallow depths may be difficult to establish and maintain in full-scale STA flow paths, particularly under pulse loading conditions, the effects of water depth on PSTA performance must be better defined. Prior research at 30 or 60 cm water depths showed no difference in P performance, though static depth treatments outperformed variable depth treatments (CH2M-Hill 2003). The best performing experimental PSTA platforms were operated at 30 cm (0.2 ha test cell and mesocosms) and 9 cm (DB Raceways, DeBusk et al. 2004). The STA-3/4 PSTA Cell typically has operated at a depth of 30-45 cm, with simulated high flow events increasing water depths to just over 60 cm.

The ability of these prior PSTA research efforts to define suitable water depth ranges has been limited in some cases by a lack of replication, and in other instances by the inability to produce ultra-low outflow TP concentrations, as well as short periods of operation (< 2 yrs). To overcome these limitations and provide insights into the effects of water depth on surface water TP concentrations, periphyton communities and P removal mechanisms in PSTA systems, we currently are operating a replicated outdoor mesocosm study using periphyton and macrophytes from the STA 3/4 PSTA Cell.

### Methods

### **Experimental Design**

Operational requirements of a PSTA system are being investigated in mesocosms at the experimental facility near the outflow of STA-1W. Triplicate flow ways with a local limerock substrate were established under each of four water depth treatments. The first two treatments are static in depth. Shallow treatments (23 cm) and deeper treatments (46 cm) consist of 4 tanks (each 1.8 m<sup>2</sup>) plumbed in series. These tanks were initially established in September 2013, under

constant flows that provide a hydraulic retention time (HRT) of 5 and 10 days for the shallow (23 cm) and deep (46 cm) flow ways, respectively. Delivery of a constant flow rate to both shallow and deep tanks insures equal P mass loading rate (PLR) to those treatments on an area basis.

In January 2014, additional mesocosms were established to test PSTA performance at greater water depths. Six new flow ways were constructed using larger tanks (2.8 m<sup>2</sup> per tank) plumbed two in series (Figure 1). These systems were initially established at 46 cm depth, and flows are being delivered to provide equivalent HRT and PLR conditions to the existing mesocosms operating with 4 tanks-in-series at 46 cm depth. The first tanks in series of the new flow ways receive an equivalent PLR to the first half (first 2 tanks) of the 4-in-series systems. This approach enables a comparison of "midpoint" and "outflow" positions with equivalent HLR and P loading across static and variable-depth treatments. Key operational parameters of these systems are outlined in Table 1.



**Figure 1.** Mesocosms established at a range of water depths to explore the effects of operating conditions on P removal effectiveness and biological community response. The shorter tanks (to the lower left) were plumbed 4 in-series at depths of 23 or 46 cm, while the larger mesocosms were established 2 in-series at 46 cm before transitioning to 69 cm or 92 cm water depths.

Static Depth Treatments						
	Tank					
	А	В	С	D		
HLR (m/day)	0.182	0.091	0.061	0.046		
PLR at 20 ppb (g P/m <sup>2</sup> /yr)	1.33	0.67	0.44	0.33		
	-					
Water Depth		HRT (	(days)			
23 cm	1.3	2.5	3.8	5.0		
46 cm	2.5	5.0	7.5	10.0		
Variable Depth Treatments						
	First Tank	Last Tank				
HLR (m/day)	0.091	0.046				
PLR at 20 ppb (g P/m <sup>2</sup> /yr)	0.67	0.33				
Water Depth	HRT (days)					
46 cm	5	10				
69 cm	7.5	15				
92 cm	10	20				

Table 1. Operational targets for experimental flow ways assigned to one of four depth treatments.

After an initial phase of comparable operations, the newer mesocosms were assigned to two new variable water depth treatments (46-69 cm and 46-92 cm). The transition to deeper conditions began after the water sampling on 5/29/2014 (Figure 2). On 9/15/2014, water depths were lowered to 46 cm in the variable depth treatments, and the "shallow" conditions continued until January 15, 2015. Since January, water depths have been maintained at 69 and 92 cm in the respective variable-depth treatments to examine the P removal performance and periphyton community response to longer-duration deep water conditions.



**Figure 2.** Water depths in each of four depth treatments during the monitoring period (December 12, 2013 – April 1, 2015).

#### Water Quality Monitoring

Inflow and outflow surface water quality sampling began December 18, 2013 with weekly TP and enzyme activity, pH and temperature measurements. From March 5 to May 28, 2014 additional samples were collected on a bi-weekly basis from the midpoint and outflows of each flow way (Figure 3), and analyzed for P species (TSP, SRP). On a monthly basis beginning in February 2014, nitrogen species (TKN, NO<sub>x</sub>, NH<sub>4</sub>), DOC and UV absorbance properties were evaluated in inflow, midpoint and outflow samples from each flow way. In July 2014, surface water sampling frequency for TP and enzyme activity was reduced to twice per month. The analytical methods and detection limits for each parameter are provided in Table 2.

The data presented in this report are limited to water quality from the period between December 18, 2013 and April 1, 2015. The chemical measurements described above examined the response in PSTA performance to differences in water depth. However, it will also be important to determine the mechanisms causing such performance differences. Periphyton and macrophyte sampling was also performed, and will be presented in a future report.



Figure 3. Sampling locations in the static depth and variable depth mesocosms

Table 2.	Analytical	methods	and	method	detection	limits	(MDLs)	for	inflow	and	outflow
waters co	ollected from	n the mes	ocosi	ns.							

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
Alkaline Phosphatase Activity	DBE SOP	0.01 µM/hr
Ammonia	EPA 350.1 (1978)/ SM4500-NH3 (18 <sup>th</sup> ed.)	0.020 mg/L
Nitrate + Nitrite (NO <sub>x</sub> )	SM4500NO3 H-2000	0.016 mg/L
Total Kjeldahl Nitrogen	EPA 351.2	0.033 mg/L
Dissolved Organic Carbon	SM 5310B	1.0 mg/L
S <sub>275-295</sub>	Helms et al. 2008	n/a
UV <sub>254</sub>	SM5910B	0.005 cm <sup>-1</sup>

### Results

During the initial phase (December 12, 2013 to April 1, 2015) of this on-going study, the PLR to these systems varied with inflow P concentration and ranged from 0.15 to 0.62 g P/m<sup>2</sup>/yr, with an average 0.36 ± 0.02 g P/m<sup>2</sup>/yr for the period (Figure 4). Inflow TP concentrations averaged 21 ± 1  $\mu$ g/L. These loading rates and inflow concentrations fall within the range of annual values for the STA-3/4 PSTA Cell.



**Figure 4.** Inflow phosphorus (P) loading rate to each flow way during the period of record (December 18, 2013 – April 1, 2015).

#### Effect of shallow depth on TP removal performance

Total phosphorus concentrations were similar in the outflow waters of 23 cm and 46 cm static water depth conditions (Figure 5). Mean inflow concentrations of  $21\pm1 \mu g/L$  were reduced to 8  $\pm 0 \mu g/L$  in both 23 cm and 46 cm treatments over the period from December 12, 2013 through April 1, 2015. After July 2014, the inflow TP concentrations became very low for several weeks. However, P export was not observed from any of these periphyton-dominated mesocosms on a limerock substrate.



**Figure 5.** Surface water total phosphorus (TP) concentrations and alkaline phosphatase activity (APA) for inflow and outflow waters (D = fourth tank in series) from mesocosms operated at static depths of 23 and 46 cm.

Enzyme activity was typically low in the inflow water ( $0.20 \pm 0.01 \mu$ M MUF released/hr), with the highest values ( $0.85 \mu$ M/hr) measured on April 23, 2014 (Figure 5). Activity in the outflow waters was always higher than the inflow waters, with period of record average values of  $0.92 \pm 0.03 \mu$ M/hr and  $0.73 \pm 0.11 \mu$ M/hr, for the 23 cm and 46 cm depth treatments, respectively. The shallow (23 cm) mesocosms exhibited the greatest activity during the period up to July 2014. After that time, there was no difference between 23 cm and 46 cm treatments at the outflow.

Nitrogen compounds in the inflow waters were dominated by the organic fraction, with 1-3 mg/L (mean concentrations:  $2.11 \pm 0.03$  mg TN/L;  $1.82 \pm 0.024$  mg Org-N/L), compared to

maximum NO<sub>x</sub> and ammonia-N concentrations of 0.085 mg/L and 0.72 mg/L, respectively (Figure 6). Inorganic N forms were routinely removed to near the limits of detection (0.020 mg/L for ammonia, and 0.016 mg/L for NOx) (Figure 6).



**Figure 6.** Concentrations of three forms of nitrogen in the inflow and outflow waters from mesocosms operated at static water depths of 23 cm and 46 cm. Error bars denote the standard error around the mean from triplicate process trains under each depth condition.

A further examination of the organic matter in the water column revealed temporal changes in inflow quality and, at times, some reduction in DOC from inflow to outflow. Inflow DOC concentrations ranged from 16.0 to 41.5 mg/L (mean  $28.9 \pm 0.0 \text{ mg/L}$ ) over the period from February 19, 2014 through April 1, 2015. Outflow concentrations from the 23 and 46 cm treatments averaged 28.3 and 26.9 mg/L, respectively, indicating slightly greater DOC removal in the deeper treatment. No DOC removal has been observed in the last several months (since

January 2014) for either 23 cm or 46 cm treatments. The period of greatest DOC concentration reductions by the 46 cm treatment (October – December 2014) was coincident with org-N removal, low enzyme activity and low concentrations of TP and inorganic N in the inflow waters (Figure 6 and Figure 7). It appears from these data that the longer residence time of water in the deeper mesocosms (46 cm depth) may have been a more important factor for breaking down organic compounds than either shallow water depths or high enzyme activity.

The absorbance characteristics showed more consistent effects of water depth throughout the monitoring period. UV<sub>254</sub>, a measure of absorbance of ultraviolet light (at a wavelength of 254 nm) by the dissolved constituents of the surface waters, showed lower values in the outflows from flow ways at 46 cm depth than at 23 cm depth. Spectral slope (S<sub>275-295</sub>) and SUVA<sub>254</sub> are two parameters that describe the relative size and recalcitrance of the dissolved organic matter pool. These metrics showed greater changes from inflow to outflow in the 46 cm treatments, as compared to the shallower 23 cm deep flow ways. These metrics (UV<sub>254</sub>, SUVA<sub>254</sub>, and S<sub>275-295</sub>) also continued to show consistent differences between treatments during the recent months of little to no change in DOC concentration.



**Figure 7.** Dissolved organic matter characterization of the outflow waters from mesocosms operated at 23 cm and 46 cm water depths.

#### Effect of variable water depth

Mesocosms operated at variable water depths (up to 92 cm) showed higher TP concentrations at the first half ("midpoint") sampling location than the mesocosms operated at a static depth of 46 cm over the entire period of record (Figure 8 and Figure 9). At the outflow, however, mean TP concentrations were similar between static and variable depth treatments. Phosphorus removal performance by the midpoint of the variable depth treatments appeared to diverge from that of the static depth treatments during the first deep water phase that began in June 2014. Midpoint TP concentrations of the variable depth treatments remained elevated for several months, as compared to the static depth treatment, even after the depths returned to 46 cm in the variable depth tanks.

A summary of the TP concentrations in inflow and outflow waters during the initial establishment "shallow" phase, and subsequent phases of deep and shallow conditions, are shown in Figure 10. Characteristics of the dissolved organic matter and nitrogen concentrations are shown in Figure 11 and Figure 12. Dissolved organic carbon concentrations were typically stable between inflow and outflow, though slight reductions were seen in both static depth and variable depth treatments during the second shallow period (October 2014 – January 2015). Absorbance of UV radiation by the DOM pool indicated smaller, more labile compounds were associated with the static depth treatment than the variable depth treatments during second shallow period. This trend was less pronounced during the subsequent deep period. Statistical analysis of these treatment effects will be conducted at the conclusion of the study.

The light available at the sediment surface was measured in the outflow region of the last tank in each series, and indicates that light conditions are similar between the two variable depth treatments when both were operated at 46 cm depth (Figure 13).

For the entire period of record, TP concentrations at the midpoint locations were lowest for the two static depth treatments (11  $\mu$ g/L), and higher in the variable depth treatments (12-13  $\mu$ g/L). By the outflow, however, no effect of depth treatment could be observed from the TP concentration data (Figure 14). The differences in TP concentration between treatments at the midpoint were the result of higher PP concentrations in the variable depth mesocosms (Figure 15).



**Figure 8**. Response of surface water TP concentrations to increased water depths, measured at the midpoint and outflows from mesocosms operated at depths between 46 and 69 cm. The concentrations are also shown for mesocosms operated at a static depth of 46 cm throughout the study. Error bars denote  $\pm$  one standard error around the mean value from triplicate flow ways under each treatment.



**Figure 9.** Response of surface water TP concentrations to increased water depths, measured at the midpoint and outflows from mesocosms operated at depths between 46 and 92 cm. The concentrations are also shown for mesocosms operated at a static depth of 46 cm throughout the study. Error bars denote ± one standard error around the mean value from triplicate flow ways under each treatment.



□ Inflow ■ Static 46 cm ■ Variable 46-69 cm ■ Variable 46-92 cm

**Figure 10.** Average ( $\pm$  SE) inflow and midpoint surface water total phosphorus (TP) concentrations (top panel) and outflow concentrations (lower panel) from process trains operated at static depth (46 cm) or variable depths during the period between March 2014 and January 2015. Variable-depth treatments were changed from a water depth of 46 cm to either 69 cm or 92 cm after sampling on May 28, 2014. Water depths in variable-depth treatments were returned to 46 cm after sampling on September 15, 2014, then increased again on January 15, 2015. Error bars denote  $\pm$  1 SE around the mean of triplicate process trains under each treatment.



#### 🗆 Inflow 🔳 Static 46 cm 🔳 Variable 46-69 cm 🔳 Variable 46-92 cm

**Figure 11.** Characteristics of the dissolved organic matter in inflow and outflow waters from mesocosms operated at static or variable depths. Values reflect the average  $\pm$  SE across triplicate flow ways under each treatment for four periods of time where variable depth treatments were either "shallow" (46 cm) or "deep" (69 or 92 cm).



□ Inflow ■ Static 46 cm ■ Variable 46-69 cm ■ Variable 46-92 cm

**Figure 12.** Nitrogen concentrations in inflow and outflow waters from mesocosms operated at static or variable depths. Values reflect the average  $\pm$  SE across triplicate flow ways under each treatment for four periods of time where variable depth treatments were either "shallow" (46 cm) or "deep" (69 or 92 cm).

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**Figure 13.** Light remaining at the sediment surface, as a fraction of the ambient light available above the water column, in the outflow region of mesocosms operated under four depth treatments. Error bars denote  $\pm$  SE around period averages for triplicate flow ways under each treatment. Light was measured in the photosynthetically-active range (400-700 nm) during midday.



**Figure 14.** Inflow, midpoint and outflow concentrations of total phosphorus (TP) for mesocosm flow ways operated at either static depths (23 cm or 46 cm) or variable depths (46-69 cm or 46-92 cm). Values represent the average ± standard error for triplicate flow ways under each depth treatment, for the period of record (December 2013 – April 2015).



**Figure 15.** Inflow concentrations of phosphorus species are compared to midpoint concentrations (upper panel) and outflow concentrations (lower panel) for mesocosm flow ways operated at either static depths (23 cm or 46 cm) or variable depths (46-69 cm or 46-92 cm). Values represent the average ± standard error for triplicate flow ways under each depth treatment, for the period of record (March 2014 – April 2015).

#### Phosphorus and enzyme gradients

Phosphorus gradients became established in all four treatments during the initial monitoring phase, with steadily declining TP concentrations from inflow to outflow (Figure 16 and Figure 17). These gradients indicate the greatest removals occurred in the first tank in series, but decreases in surface water TP concentrations continued to ultra-low levels (< 10  $\mu$ g/L). Enzyme activities were highest in the variable depth mesocosms, especially during the deep water phase between June and September 2014 (Figure 18). Activities were elevated in both midpoint and outflow samples during that time. In fact, APA was frequently higher at the midpoint location than in the outflow waters. There are several reasons why this could be occurring, including differences in periphyton communities or a limitation on enzyme production, such as nitrogen or a micronutrient.

Dissolved organic phosphorus was consistently reduced by the midpoint under all treatments, with further reductions in the second half of each flow way (Figure 19). Particulate phosphorus was also reduced between inflow and outflow in all treatments, but the midpoint PP concentrations indicated some increases occurred in the first tanks in series under of variable depth conditions (Figure 20). The back half of those flow ways was able to maintain low PP concentrations regardless of depth variation.



**Figure 16.** Average total phosphorus concentrations in the inflow waters and outflow-region surface waters of flow ways operated at either 23 cm or 46 cm depths, for the period December 2013 – April 1, 2015. Each flow way was comprised of four tanks in series (A, B, C, D). Error bars denote the standard error from triplicate flow ways under each depth treatment.





Figure 17. A comparison of total phosphorus concentrations in the inflow, midpoint, and outflows from the four treatments.

→ Inflow → Midpoint

---Outflow



**Figure 18.** Alkaline phosphatase activity (APA) in the surface waters of inflow, midpoint and outflow waters during the period of record between February 2014 and April 2015.



Figure 19. A comparison of dissolved organic phosphorus (DOP) concentrations in the inflow and outflows from the four treatments.



Figure 20. A comparison of particulate phosphorus (PP) concentrations in the inflow and outflows from the four treatments.

## **Synopsis of Initial Findings**

Gradients in surface water phosphorus concentrations have become established in these periphyton-dominated, limerock-based mesocosms. To date, water depth fluctuations between 46 and 92 cm have had little to no impact on P removal by the variable depth systems as a whole. Midpoint monitoring indicated compromised removal efficiency of particulate forms of phosphorus by the first half of the flow way during the deep water operations. Coincident with the lower PP reductions under deeper conditions, an increase in enzyme activity was observed, which may have contributed to the effective back-end performance that reduced overall phosphorus levels to comparable, ultra-low levels by the outflows under all treatments. Dissolved organic matter quality was affected as water passed through these periphyton systems, but this process was not strongly affected by water depth.

The 5-day hydraulic retention time of the shallowest systems (23 cm depth) was adequate to reduce TP from 21 to 8  $\mu$ g/L. The continued operation of the variable-depth flow ways under deep conditions may eventually result in a degradation in P removal performance, but during the first 1.3 years these systems have performed as well as systems that operated under static, shallow conditions.

### References

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