DELIVERABLE A-4-B: PSTA CORE AND MESOCOSM STUDIES

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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1 Introduction

A field-scale periphyton-based stormwater treatment area (PSTA) was constructed from 2004 to 2005 for the purpose of addressing uncertainties associated with large-scale implementation of periphyton-based treatment technology. The PSTA Cell in STA-3/4 is unique among STA treatment cells in that the extant peat was scraped to expose the underlying rock.

A key aspect of the PSTA concept is that the removal of muck soils to expose underlying limerock substrate is thought to be necessary for optimal P removal. This is based on the premise that successful removal of P to ultra-low levels depends on limiting internal P loading sources.

However, removal of muck may be cost-prohibitive, particularly in areas where a deep layer of muck exists above the underlying limerock. It therefore is important to understand whether or not “capping” of the muck, with a thin layer of limerock, can provide conditions conducive to effective, long-term low-level P removal. Further, the actual role played by limerock in PSTA systems remains unclear: it is unknown whether presence of a limerock surface is important to the development of desired biota (e.g., calcareous periphyton), or whether the limerock is simply providing a “cap” to impede diffusion and/or macrophyte mining of P.

2 Approach

Two investigations, pertaining to the above questions, are described in this report.

1) A long-term, outdoor mesocosm study to assess P removal performance by submerged macrophytes/periphyton on unfarmed, low-P muck soils, with and without a limerock cap.
2) A short-term core incubation study to measure the effectiveness of a limerock cap on

reducing P flux from farmed muck soils under aerobic and anaerobic conditions.

3 Investigations with Low-P Muck Soils and a Limerock Cap

3.1 Background

Due to past exceptional P removal performance of STA-2 Cell 1, it recently has been assumed that "unfarmed" muck soils exhibit chemical or physical attributes that minimize P flux, or in some other fashion contribute to low P levels in the overlying waters. We therefore established a mesocosm study, using muck soils obtained from an unfarmed parcel of land adjacent to STA-1W (beneath the eastern FPL power lines), to investigate this phenomenon. As a second treatment, we employed a "cap" of limerock over this same muck, to assess whether the presence of $CaCO_3$ or some other constituent would enhance development of a desirable benthic community, which in turn would lead to reduced outflow P levels. This approach is similar to the concepts investigated in the pilot-scale PSTA trials performed previously in the STA-1E eastern flow path, in which three separate types of calcitic substrates were deployed. The results from the STA-1E investigation, however, were inconclusive.

3.2 Methods

The outdoor mesocosm study was established in April 2011. Limerock "gravel" (6 – 10 mm diameter nominal size, #89 stone from SFWMD Lake Okeechobee Division) was applied as a 3-cm thick "cap" over 15 cm muck soils in triplicate mesocosms, while three mesocosms with un-amended muck soils served as controls (Figure 1).

The mesocosms were operated with water from the discharge canal of STA-1W; with additional pre-treatment as necessary during periods when the STA performance was not adequate to provide inflow water TP levels < 40 µg/L. A water column was maintained at constant depth of 45 cm, and the hydraulic loading rate of 9 cm/day resulted in a 5-day nominal hydraulic retention time within each mesocosm.

The initial period of operation was characterized by ultra-low inflow TP concentrations. On January 29, 2013, the pre-treatment system was bypassed, which enabled us to deliver higher P water to the study. During a 2-week transition period, hydraulic loads were also increased, which mimicked a large prolonged flow pulse. On February 13, 2013, flows were returned to normal and a nominal 5-day HRT was resumed.

After water, vegetation and soil sampling was completed on April 9, 2014 (described below), the mesocosms were subjected to a drawdown of water levels. The surface waters were drained to within a few cm of the sediment surface. This exposed the remaining SAV to drying out above the sediment. On May 22, 2014, inflow water was reintroduced to the mesocosms, ending the 42-day dry down period.

This report presents the data for the entire period of record (April 2011 – February 2015), but focuses on the effects of dryout and a subsequent 8-month period of operations after the dryout/reflood event. Water quality data from the pre-drawdown period was presented in an earlier report (PSTA Interim Report October 2014). Additional solids characterization data will be presented in a later report.

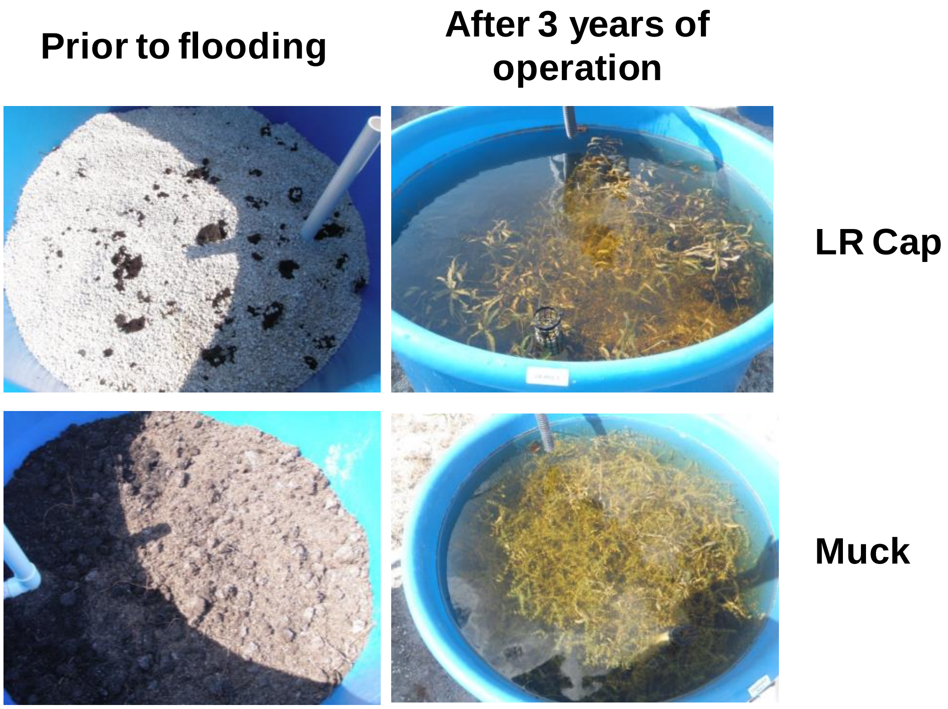


Figure 1. Mesocosms were established on unfarmed low-phosphorus muck soils with and without a "cap" of limerock gravel placed onto the sediment surface prior to flooding.

3.2.1 Water sampling and analyses

Routine water monitoring consisted of biweekly sampling for TP from April 2011 through April 2014. Beginning in November 2011, samples were collected bi-weekly for analyses of TSP, SRP, dissolved Ca, DOC and UV absorbance. Calcium monitoring was discontinued on January 17, 2012. DOC and UV absorbance monitoring was reduced to monthly from September 2012 through July 2013, and then discontinued. Enzyme activity in the surface water was measured monthly from July 2013 through April 2014.

After the dryout/reflood period, surface water sampling resumed on a biweekly basis for P species and enzyme activities until the conclusion of the monitoring period on February 2, 2015.

3.2.2 Vegetation sampling and analyses

Aliquots of the originally stocked macrophyte vegetation were analyzed for TP and TCa contents. Plant tissue grab samples were collected April 27, 2012, May 2, 2013, April 9, 2014, and February 2, 2015, and analyzed for TP, TN, TC, TOC, and Total Ca. Biomass standing crop was sampled April 9, 2014, by harvesting all the SAV biomass from a 0.5m x 0.5 m quadrat placed generally in the center of each tank. At the conclusion of the study, plants from the entire tank were collected (aboveground biomass only) and separated by genera (*Potamogeton* or *Chara*). A wet weight was obtained in the field, and the entire sample was retained for dry weight analysis. Total dry weights of the biomass were determined at the lab to estimate standing crop biomass as plant dry weight per unit area. Observations on SAV species and periphyton coverage within each mesocosm were recorded periodically throughout the study.

3.2.3 Sediment sampling and analyses

Sediments were collected with a 2-inch diameter push corer in October 2013 and sectioned into an accrued layer (when present), 0-5 cm, 5-10 cm, and 10-15 cm layers. All layers were analyzed for bulk density, TP, TN, TC, TOC. Enzyme activity and pH were determined on the accrued and 0-5 cm layers.

Sediments were again collected on April 9, prior to the initiation of the drawdown. These cores were sectioned into accrued layer, 0-5, 5-10, and 10-15 cm depths. Bulk density, TP and pH were analyzed on all samples.

3.2.4 Additional Monitoring during the Dryout/Reflood Period

Distance from the sediment surface to a fixed benchmark in each mesocosm was used to monitor the change in soil thickness during desiccation. Sediment redox was measured *in situ* (5 cm below surface) several times prior to and subsequent to reflooding.

Reflooding of each mesocosm was initiated at same hydraulic loading rate used prior to the dryout. (9 cm/day, 5 day HRT @ 40 cm depth). Surface waters and porewaters were sampled during reflooding (~24 hours after flows turned on), when ~ 2 inches surface water had accumulated above the sediment surface. Porewaters were collected from each mesocosm using a sipper that targeted 5 cm depth into soil profile. Samples were retained for dissolved Ca, DOC, TSP and SRP.

Surface waters were sampled again once the water column was re-established at 40 cm deep (nominal operational depth during the experiment). The above surface water samples were analyzed for temp and pH in the field, and preserved as appropriate for TP, TSP, SRP, and dissolved Ca analyses.

3.3 Results

3.3.1 Water column constituents

Surface water (outflow) TP concentrations ranged from 6-20 µg/L during the POR, while inflow waters ranged from 6-35 µg/L (Figure 2). Long-term outflow TP concentrations in the LR Cap and Muck treatments were identical for both the low-P period (9 ± 0.3 µg/L) and the high-P period (13 ± 0.3 µg/L). Mean inflow TP concentrations for the two periods were 11 and 21 µg/L, respectively (Figure 3).

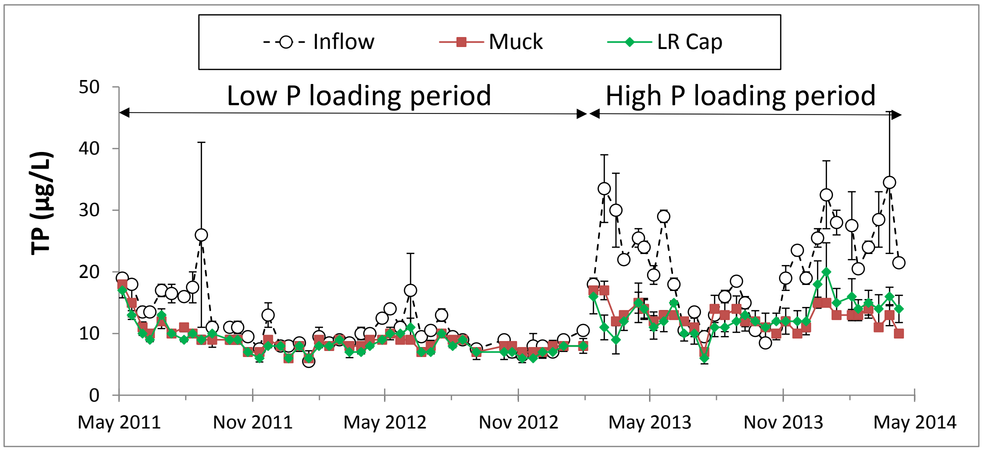
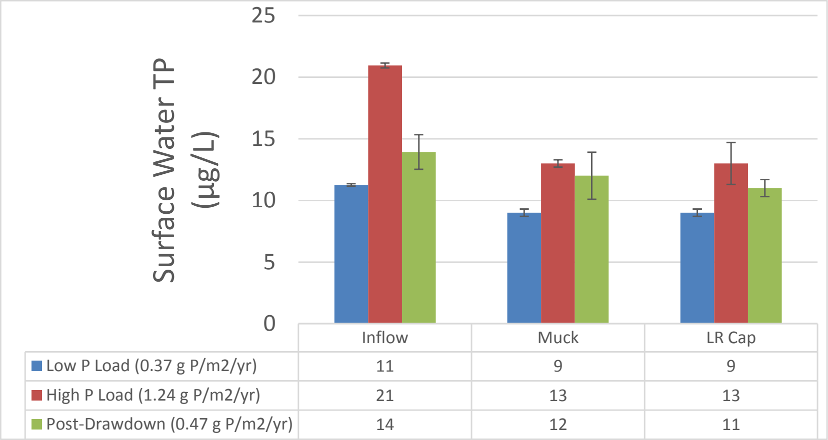


Figure 2. Daily mean total phosphorus (TP) concentrations in the inflow waters and outflow waters of triplicate mesocosms established with or without limerock added as a cap over muck soils, for the period of operation prior to draw-down (May 2011 – April 2014).



	Inflow	Muck	LR Cap
🟦 Low P Load (0.37 g P/m2/yr)	11	9	9
🟥 High P Load (1.24 g P/m2/yr)	21	13	13
🟩 Post-Drawdown (0.47 g P/m2/yr)	14	12	11

Figure 3. Long-term mean total phosphorus (TP) inflow and outflow concentrations from mesocosms for three periods of operation: an initial period of low P loading (May 2011 – January 2013), higher P loading (February 2013 – April 2014), and a post-drawdown period (June 2014 – February 2015). The error bars denote the standard error between triplicates of each treatment, or duplicate measures of the inflow.

Similar to TP concentrations, there was no difference in the long-term average SRP (data not shown), or DOP and PP concentrations between Muck soil and LR Cap treatments (Figure 4). The observed reductions in the inflow TP were the result of slight decreases in both DOP and PP fractions.

Enzyme hydrolysis rates were elevated under both treatments (Muck and LR Cap), compared to the inflow waters (Figure 5). Long-term average monoesterase hydrolysis rates increased from 0.12 ±0.01µM MUF released/hr in the inflow, to 0.40 ± 0.19 and 0.69 ± 0.39 µM/hr for the outflows from Muck and LR Cap treatments, respectively. Diesterase rates increased as well, from an inflow average of 0.08 ± 0.00 µM/hr, to 0.38 ± 0.15 and 0.39 ± 0.11 µM/hr in the Muck and LR Cap treatment outflows, respectively.

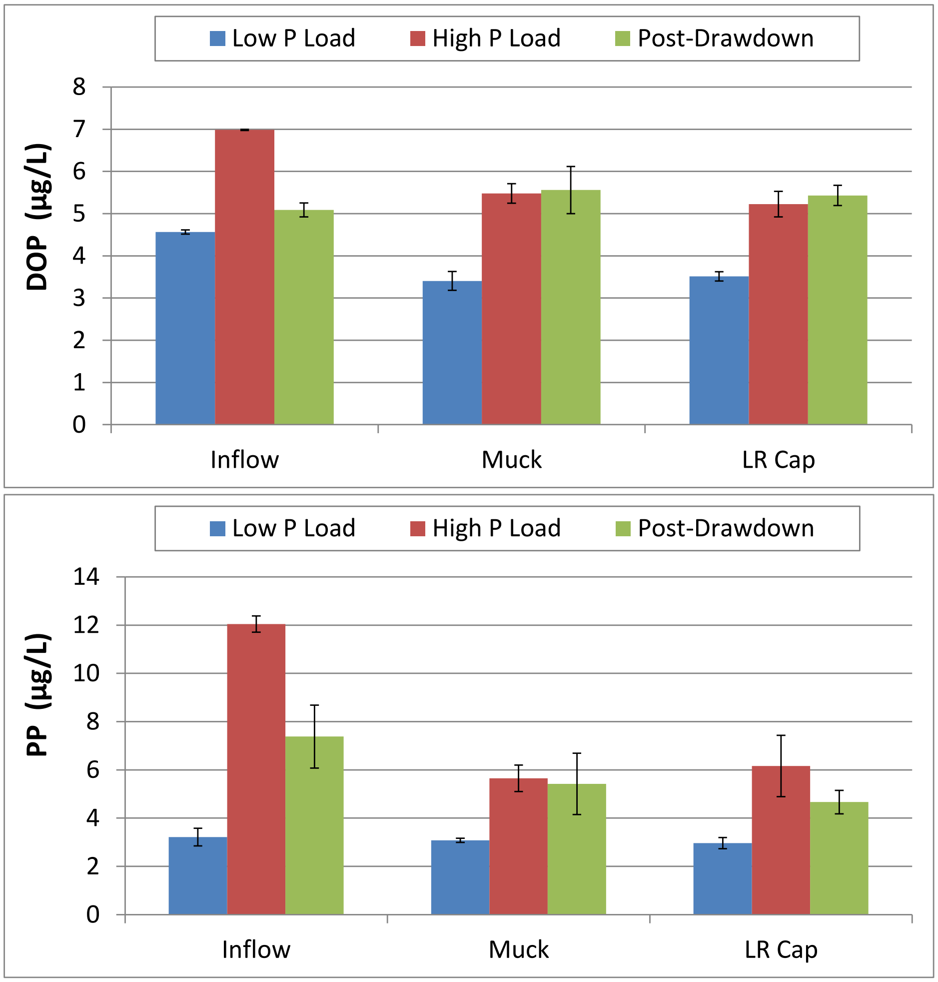


Figure 4. Mean surface water outflow dissolved organic phosphorus (DOP) and particulate phosphorus (PP) concentration for mesocosms established with limerock added as a cap to muck soils.

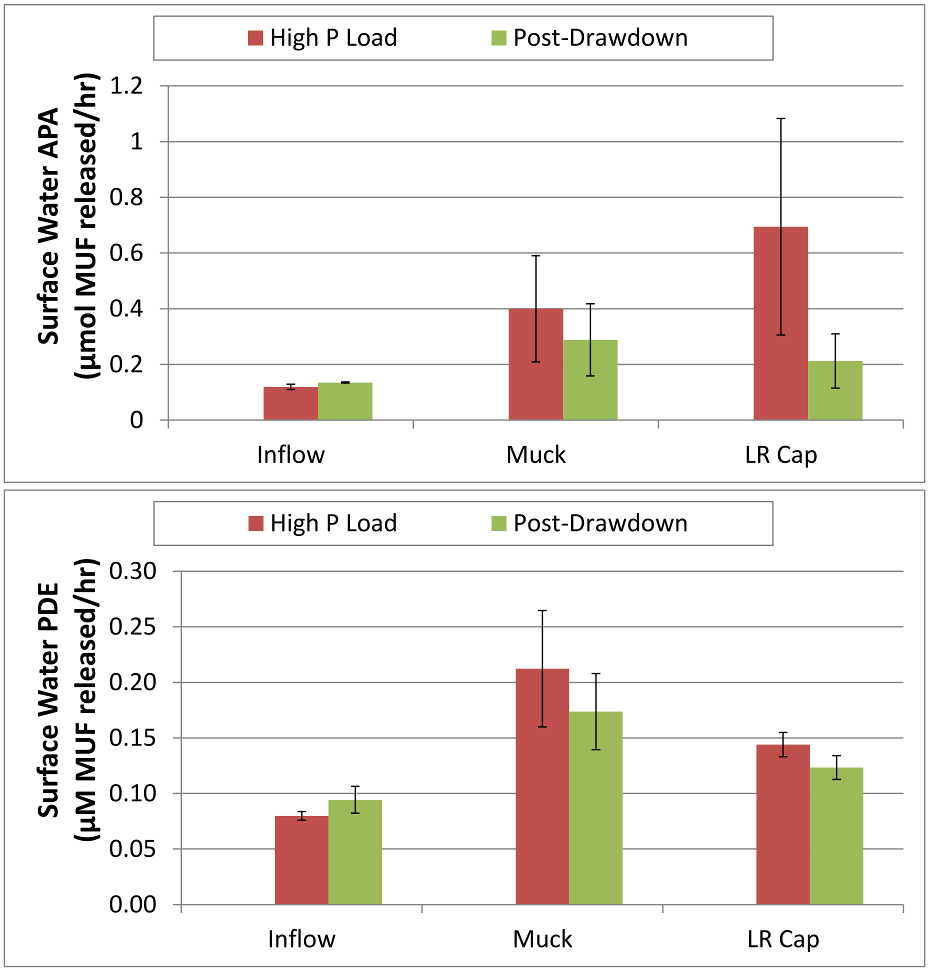


Figure 5. Average enzyme hydrolysis rates for monoesterase (APA) and diesterase (PDE) in the inflow and outflow waters of mesocosms with or without limerock added as a cap over muck soils. Error bars denote ± SE around the average of long-term means for triplicate mesocosms under each soil treatment, or for two inflow monitoring locations.

Dissolved organic carbon (DOC) concentrations were conservative through both substrate treatments, with an average concentration of 29 mg/L in both inflow and outflow waters, for the period November 2011 through July 2013 (Figure 6). Spectral slopes were lower, on average, in inflow waters than in surface waters within either treatment (Data not shown).

Dissolved calcium content in the surface water was, on average, 59 ± 0.3 mg/L and 58 ± 2.0 mg/L for the Muck and LR Cap treatments, respectively. These concentrations were slightly lower than the long-term average concentration (62 ± 0.3 mg/L) in the inflow waters (Figure 7).

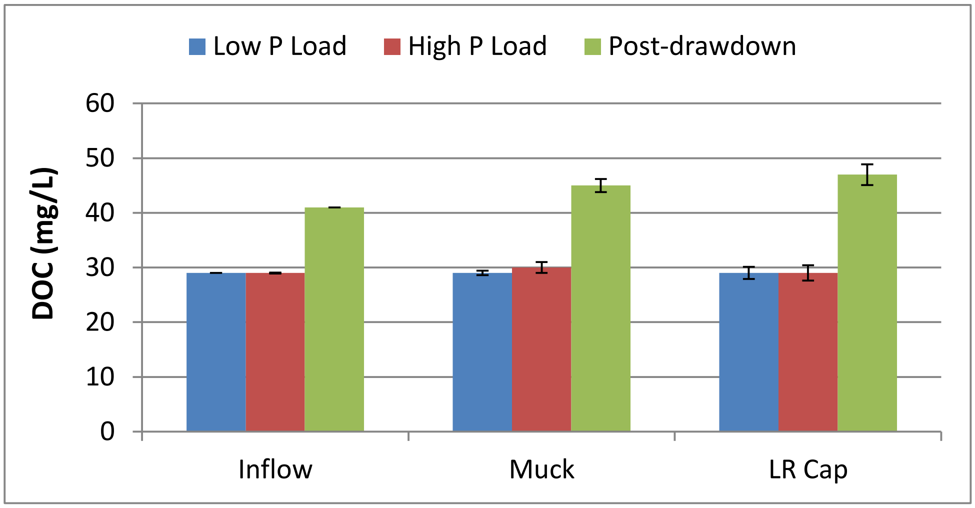


Figure 6. Average dissolved organic carbon (DOC) concentrations in the inflow and outflow waters of mesocosms with or without limerock added as a cap over muck soils. Error bars denote ± SE around the average of long-term means for triplicate mesocosms under each soil treatment, or for two inflow monitoring locations. The period of record represents November 2011 through July 2013.

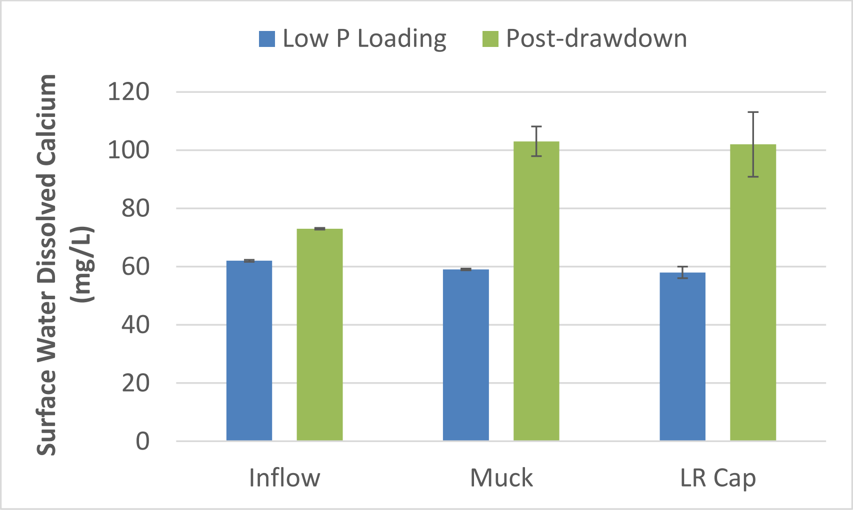


Figure 7. Average dissolved calcium concentrations in the inflow and outflow waters of mesocosms with or without limerock added as a cap over muck soils. Error bars denote ± SE around the average of long-term means for triplicate mesocosms under each soil treatment, or two inflow monitoring locations. The period of record for calcium was 11/10/2011 through 1/17/2012 (N = 6 bi-weekly sampling events) under the low P loading conditions, and 5/22/14-5/29/2014 (N = 3 events during the first week after reflooding).

3.3.2 Effect of Drawdown and Reflooding on water column P

The break in the time series in Figure 8 indicates a drawdown period that temporarily suspended water sampling. Higher than average concentrations of both DOP and PP were observed immediately following the reflooding of mesocosms. Senescent plant tissues and desiccated soils likely both contributed to the release of stored nutrients during this period. What is remarkable is the short duration of the effect of the drawdown. Within weeks, the concentrations of TP and P species returned to pre-drawdown levels. For the nine-month period following reflooding, as well as the prior periods of low and high P loading, the LR cap did not affect DOP or PP removal rates (Figure 4).

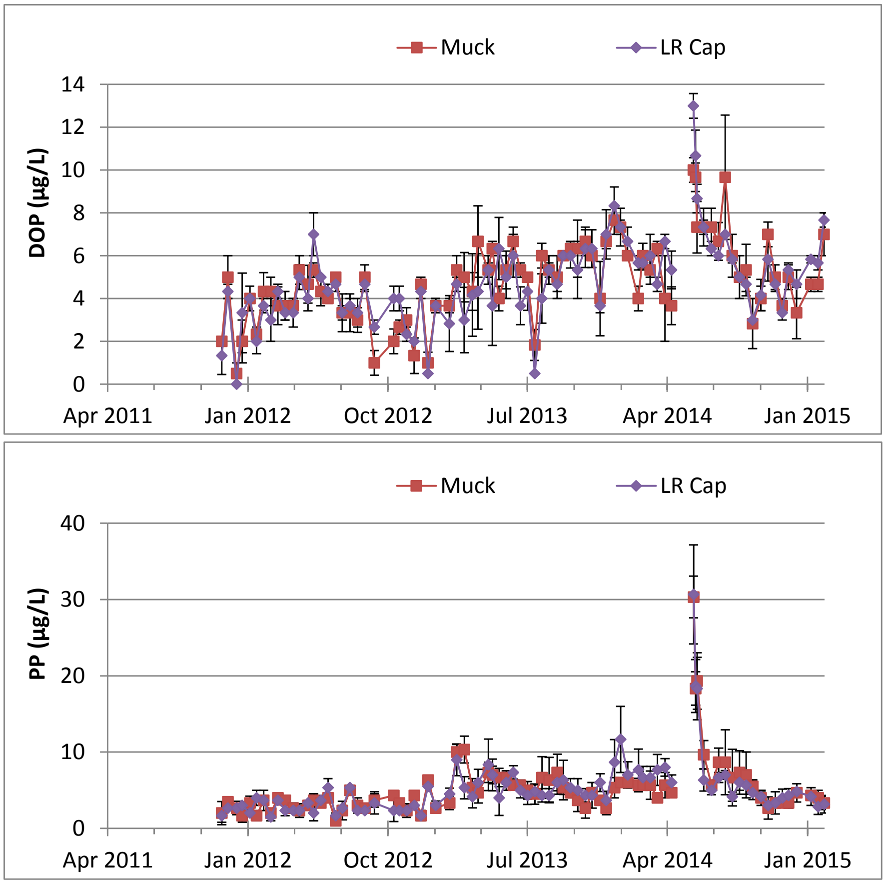


Figure 8. Dissolved organic phosphorus (DOP) and particulate phosphorus (PP) concentrations in the surface waters of muck-based mesocosms with or without a limerock cap, during a 3.8-year period of operations.

Enzyme activities in unfiltered surface water samples were variable in the LR-Cap treatment (Figure 5). The high APA rates observed in one replicate mesocosm were coincident with a benthic periphyton mat that developed during the first year and then subsequently was replaced by macrophytes. APA levels declined after the transition to macrophyte dominance in that LR-capped tank. Overall, the average APA in LR Cap and muck treatments were similar, and higher than in inflow waters. After the drawdown/reflood event, the increase in enzyme activity from inflow to outflow was reduced, with no difference between mesocosms with or without the added LR.

DOC concentrations were temporally variable, averaging between 20 and 38 mg/L among inflow samples collected between November 2011 and July 2013. Average concentrations were unchanged between inflow and outflow during the pre-drawdown periods, thus monitoring was suspended until after the reflood event. An increase in DOC was observed during post-drawdown monitoring, for both the muck and LR Cap treatments 45 ± 1 and 47 ± 2 mg/L, respectively, despite higher than previous inflow concentrations (41 ± 0 mg/L) during and immediately following mesocosm reflooding (Figure 6). It should be noted, however, that DOC monitoring occurred only the day of reflooding (5/22/2014) and four days later (5/26/2014).

3.3.3 Soil Characteristics

Soil characteristics in October 2013 were similar for both Muck and LR Cap treatments (Figure 9). Total P concentrations were elevated in the newly-accrued sediment layer (266 and 360 ± 60 mg/kg, for Muck and LR Cap treatments, respectively), as compared to the muck soil layers (134 – 180 mg/kg) from either treatment (Figure 9). Calcium enrichment of the newly-accrued layer (23 and 22 % for Muck and LR Cap, respectively), relative to underlying muck soil layers (2 – 5 % Ca), was evident in both muck and LR Cap treatments. Calcium enrichment can effectively dilute the P content of soils, but in the present study calcium contents in the accrued layer were similar between treatments and may have provided additional P sorption capacity to this new soil material. Total N and organic C contents were reduced in the accrued sediment layer, likely the result of dilution by Ca enrichment of that surficial layer.

Enzyme activity in the sediment increased in the accrued layer, relative to the upper (0-5 cm) muck layer. Muck-based mesocosms without limerock exhibited consistently higher potential for both APA and PDE than did the LR Cap soils within respective soil layers (Figure 10). Soil pH, by contrast, was similar between treatments and between accrued and 0-5 cm muck layers.

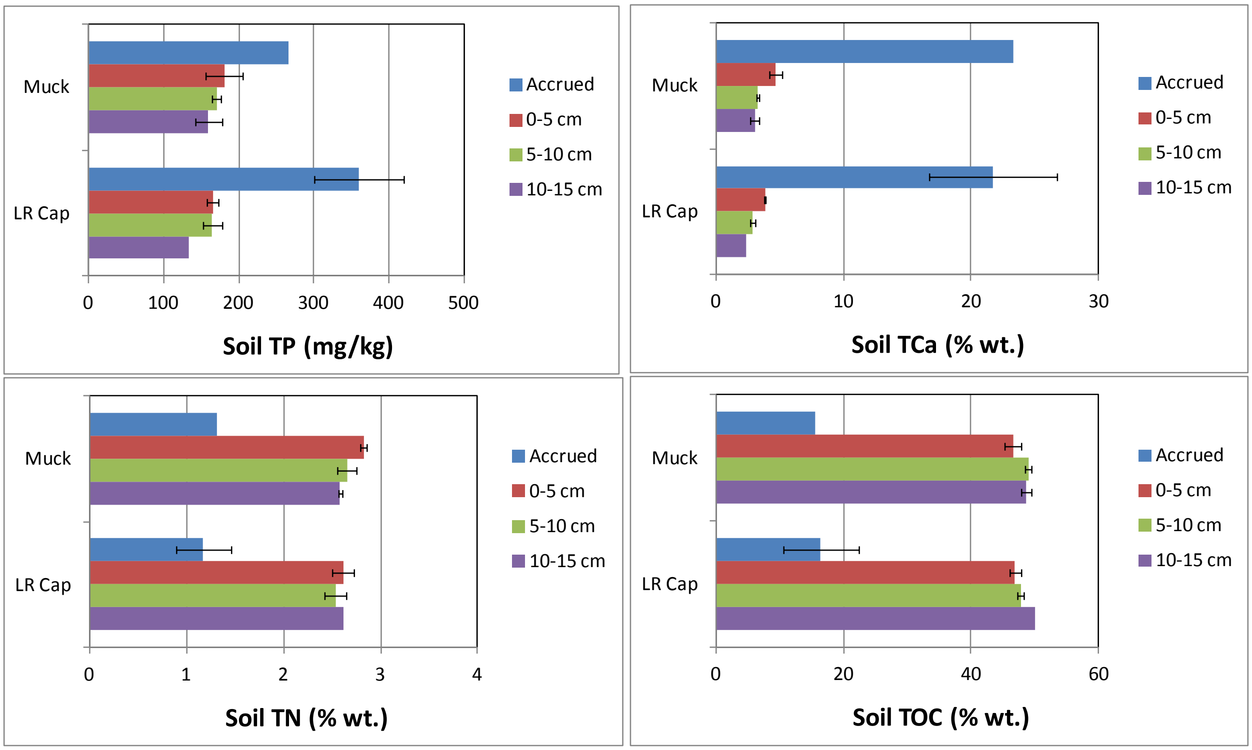


Figure 9. Soil characteristics in the accrued layer and at discrete depth intervals for cores collected on October 22, 2013, from mesocosms where the P removal performance of un-amended muck soils was compared to treatments with a limerock (LR) cap. Error bars denote ± SE around the mean value from triplicate mesocosms for each soil treatment.

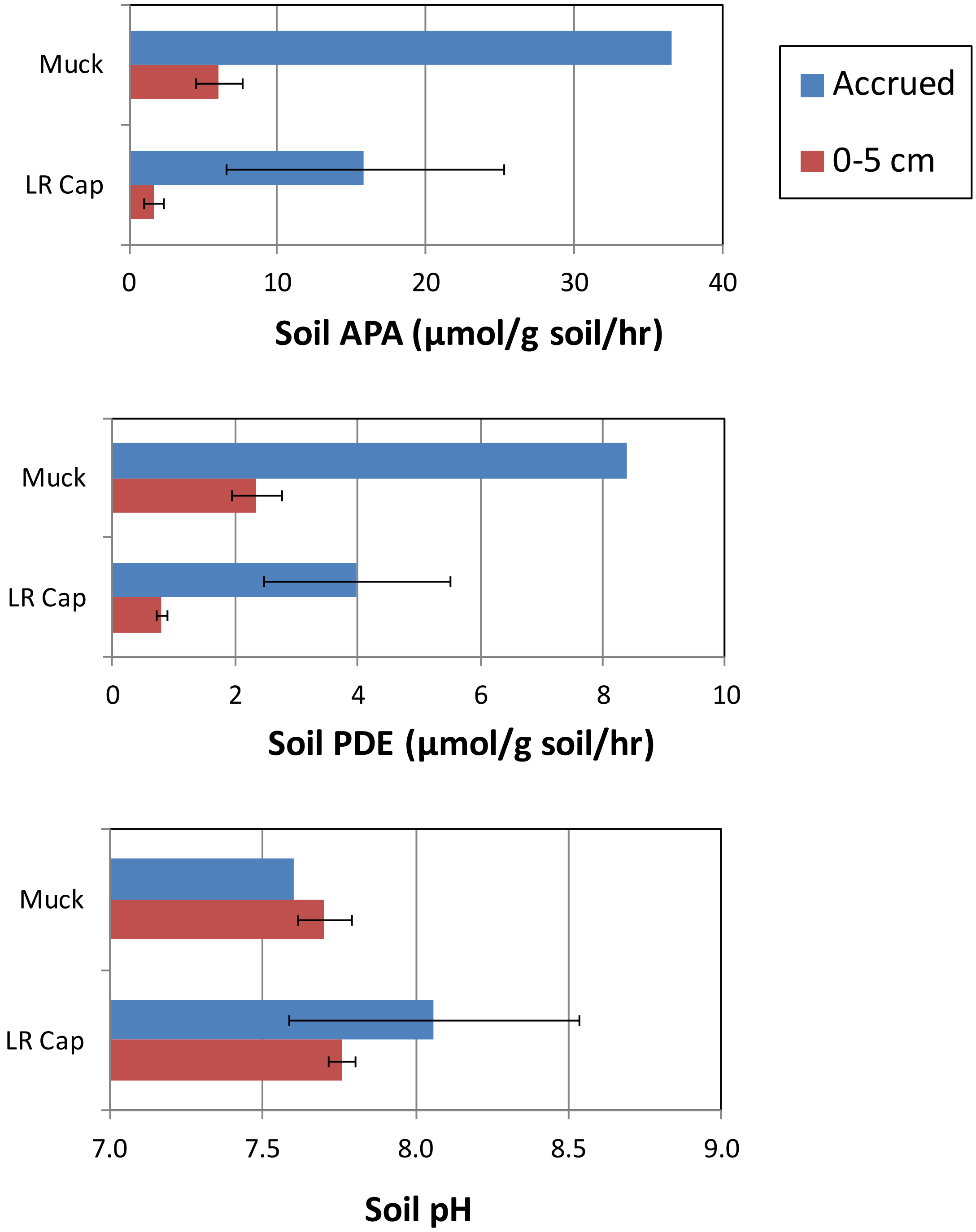


Figure 10. Alkaline phosphatase activity (APA), phosphodiesterase (PDE) activity and pH measured in the newly-accrued sediments and underlying muck soils collected from outdoor mesocosms on October 22, 2013, after 2.5 years of flow through operations. Drawdown Effects on Sediment Consolidation and P Stability

During the 42-day drawdown period, soil consolidation occurred in both limerock capped and unamended treatments. However, changes in soil thickness were small, < 2 cm from an original muck soil layer of 15 cm, or about 10% loss of soil volume. No difference was observed between LR cap and Muck treatments during the drawdown period. During rehydration of the soils, however, the muck treatments returned to near the original soil thickness, whereas limerock-capped muck soils maintained the consolidated soil depths achieved during the drawdown (Figure 11).

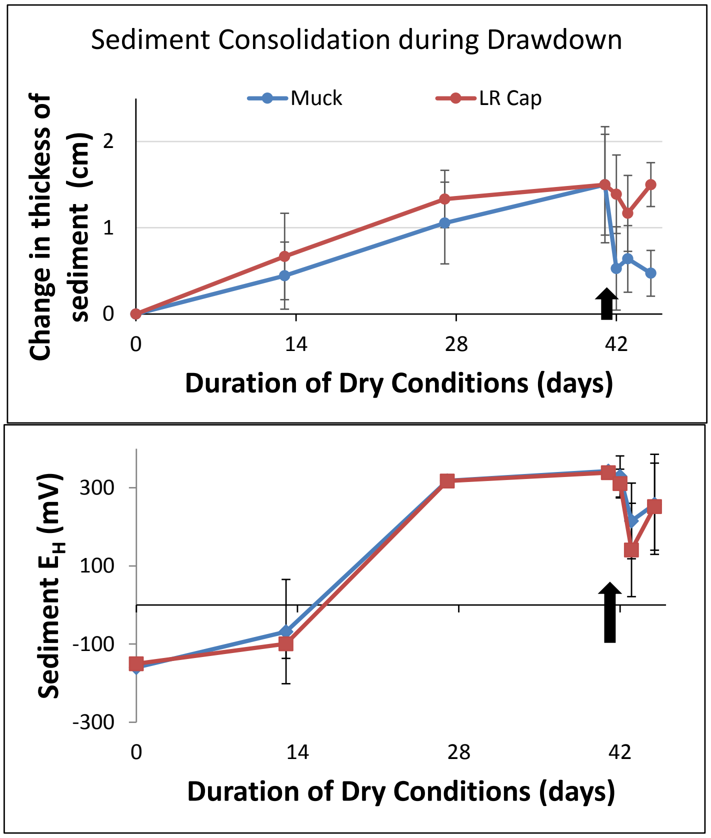


Figure 11. Change (amount of reduction) in sediment thickness (top panel) and sediment oxidation-reduction potential during a 42-day drawdown period. The arrow denotes when reflooding was initiated on May 22, 2014 (Day 42).

3.3.4 Porewater during reflooding

Porewater concentrations of SRP and DOP were slightly higher in the LR Cap treatments than Muck treatments immediately upon reflooding (Table 1). However, neither treatment showed high P levels that might be expected to contribute to large P releases. DOC concentrations were slightly higher in the porewater after reflooding than the average surface water concentrations during the rest of the study. However, the concentrations in the reflood waters were also elevated (41 mg/L), indicating little to no additional DOC contribution from the soil porewater was expected. By contrast, porewater calcium concentrations were high in both LR capped and uncapped muck treatments, relative to surface water concentrations.

Table 1. Porewater constituents on May 23, 2014, one day after reflooding of the dried soils in mesocosms containing low-P soils with or without a limerock cap. Also shown are the surface water concentrations for each treatment, as measured during reflooding on May 22, 2014. Values represent the mean ± SE of triplicate mesocosms for each treatment.

		Porewater		Surface Water	
Parameter	**Units**	**Muck**	**LR Cap**	**Muck**	**LR Cap**
SRP	µg/L	11 ± 2	15 ± 5	5 ± 1	7 ± 2
DOP	µg/L	17 ± 1	20 ± 3	10 ± 1	13 ± 1
DOC	mg/L	43 ± 1	45 ± 1	45 ± 2	48 ± 2
Dissolved Ca	mg/L	127 ± 7	121 ± 17	134 ± 5	115 ± 10

3.3.5 Water Column P Response to Drawdown-Reflood Event

Immediately following the reflooding of mesocosms the TP concentrations increased in both treatments to levels higher than the inflow waters (Figure 12). However, this phenomenon was temporary, and outflow TP concentrations returned to very low levels within a few weeks of reflooding. During the post-drawdown monitoring period, outflow TP concentrations remained low in both treatments, averaging 11 and 12 µg/L in mesocosms with and without a limerock cap, respectively (Figure 3). Inflow TP was also quite low (14 ± 1 µg/L) over the same period, but net P removal was maintained by these recently dried systems.

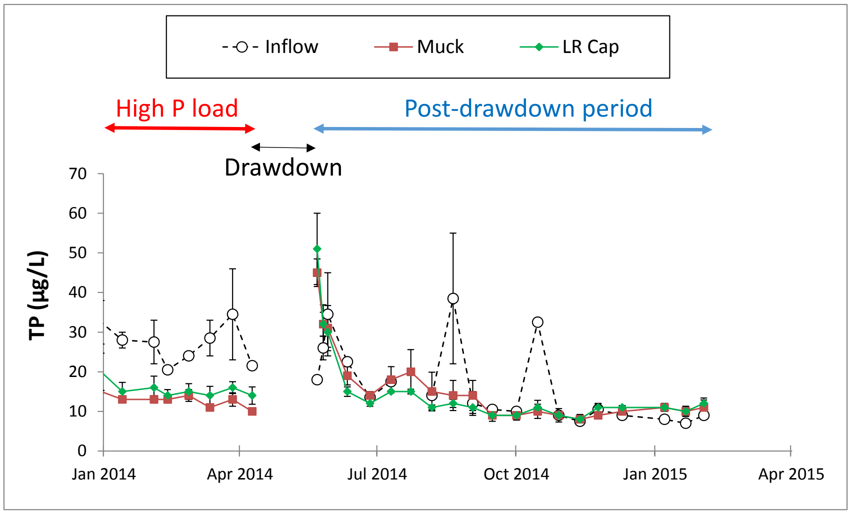


Figure 12. Average total phosphorus (TP) concentrations in the inflow and outflow waters of mesocosms established on low-P muck soils with and without a limerock cap, for the period prior to and following a drawdown of water levels in each mesocosm. Error bars denote the standard error around values for triplicate mesocosms under each soil treatment.

Phosphorus forms in the post-drawdown period were similar between treatments, with greater particulate P concentrations immediately after reflooding (Figure 8). Outflow concentrations of DOP immediately after reflooding were only slightly elevated from pre-drawdown levels. Average outflow DOP concentrations were equivalent during the post-drawdown and high loading periods and lowest during the low loading period at the beginning of the study (Figure 4). Particulate P concentrations in the mesocosm outflow waters were also lowest during the low loading periods and higher during the high load and post-drawdown periods. No difference in P species was observed between treatments (with or without the limerock cap) for any of the three evaluation periods.

Enzyme activity was generally higher in the outflow waters than inflow waters for both the high loading period and the post-drawdown period (Figure 5). Differences between treatments were not apparent in the monoesterase activity (APA), in part due to large variability in the LR capped treatments during the high loading phase. Phosphodiesterase (PDE) activity showed higher levels in the muck treatments than LR cap treatments for both the high loading period and the post-drawdown period. Diesters are common within organic P compounds derived from soil organic matter. The levels of PDE observed in the outflow waters were lower compared to APA, but high enough to suggest that the LR cap may have limited the supply of soil-derived DOP compounds to the water column.

Surface water Ca and DOC levels in the post-drawdown period were higher than previously observed in this study (Figure 6 and Figure 7). However, the monitoring period for these parameters was limited to the first week following reflooding of the mesocosms. The elevated concentrations were likely the result of DOC and Ca released from both desiccated soils and macrophyte biomass. Again, no difference was observed in DOC or calcium between treatments.

3.3.6 Vegetation Characteristics

Initial plant stocking materials were added in equal portions to all mesocosms, and contained 440, 841, and 1812 mg P/kg dry weight, for *Potamogeton*, *Chara* and *Najas* tissues, respectively. After one year of operation under low P-loading conditions, the macrophyte biomass was low in the LR Cap treatments, which precluded grab sampling for tissue nutrient analysis without compromising the potential for new growth. In the muck treatment, tissue P content was very low (200 ± 30 mg/kg), indicating a lack of available P for uptake. *Chara* and *Potamogeton* were co-dominants while *Najas* biomass declined during the first year, based on visual observations.

Over the next two years, P contents remained low in the macrophytes growing in both muck and LR Cap treatments (Figure 14). The N contents of macrophytes growing on muck increased slightly over time, from 0.70 ± 0.08 % N in April 2012 to 0.94 ± 0.01 % N in April 2014. Macrophytes in the LR-capped mesocosms were 1.00 ± 0.17 % N and 0.92 ± 0.10 % N, after 2 and 3 years of operation, respectively. Tissue C contents of macrophytes were slightly lower in the

Muck treatment than the LR Cap treatment for May 2013 and April 2014. This was likely due to greater calcification of tissues in the muck treatments, as compared to the LR cap treatment (Figure 14).

Throughout the study period, macrophyte biomass appeared lower in the LR Cap treatment than in Muck treatments. After 3 years of operation, measurements of the standing crop in April 2014, and again 9 months after a drawdown/reflood cycle (February 2015), confirmed this observation (Figure 15). Macrophyte biomass was largely *Chara* in both treatments, but a larger percentage of the total biomass was *Potamogeton* in the LR capped treatment (25 ± 10%) than in the unamended muck treatment (5 ± 3%)(Figure 16). Phosphorus contents were slightly higher in *Potamogeton* than in *Chara* tissues in February 2015 (Figure 17). This result was consistent with increased P supply from the soil to the rooted vascular species (*Potamogeton*) than to the rootless macroalga (*Chara*). Assays of epiphyte enzyme activity showed higher APA rates were associated with the *Chara* than with *Potamogeton*, supporting the notion that soil P supply to rooted SAV may become available to epiphytes and reduce the production of enzymes needed in P limited environments (Figure 18). However, there was no difference in the PDE rates between treatments or species at the end of the mesocosm study (Figure 18). This class of enzymes may be influenced more by soil-derived diesters of organic P than SAV or epiphyte-derived organic P.

Muck

Limerock Cap

Figure 13. Macrophyte biomass in muck-based mesocosms with and without a limerock cap, on April 7 2014, just prior to vegetation sampling and water level drawdown.

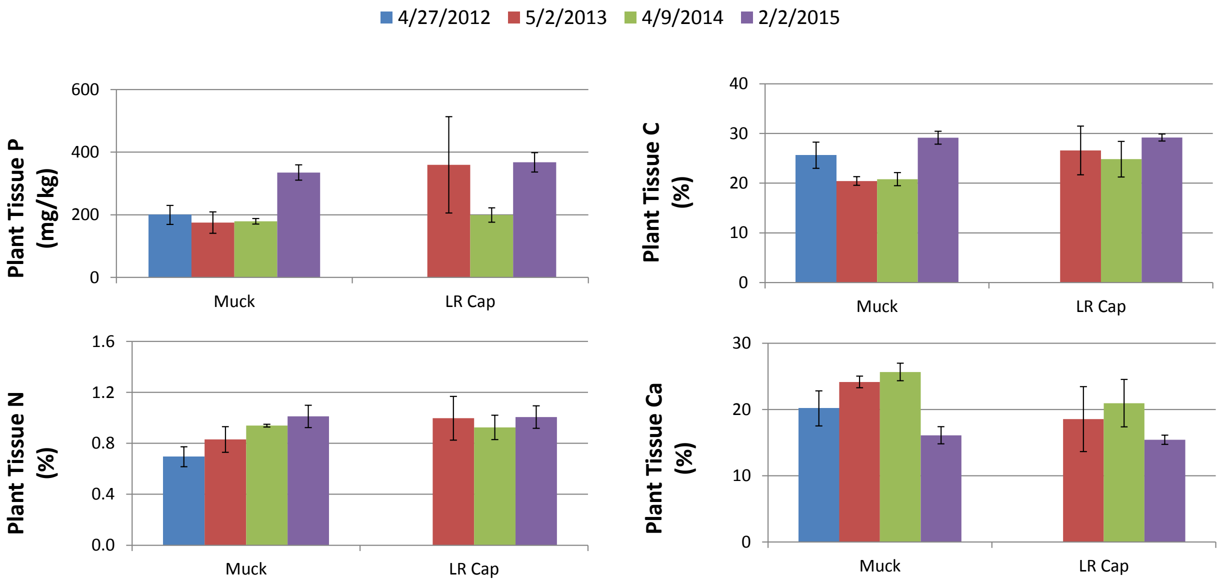


Figure 14. Plant tissue characteristics on four sampling dates. Values represent the average (± SE) of grab samples from triplicate mesocosms under each treatment. Macrophyte biomass in the LR Cap treatments was low during the April 2012 sampling, which precluded sampling tissues for nutrient analysis on that date.

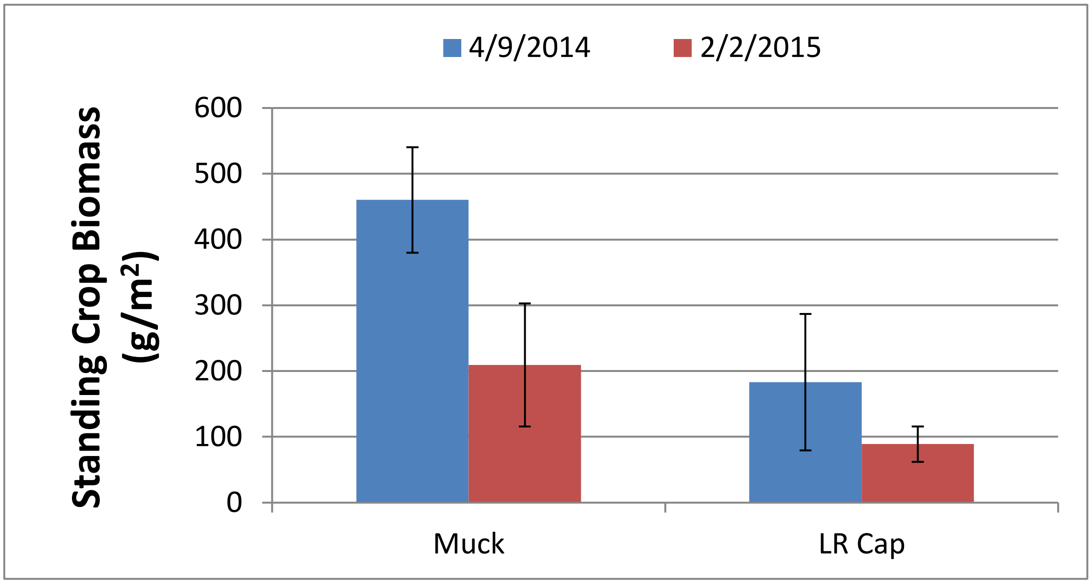


Figure 15. Average (± SE) standing crop biomass of submerged aquatic vegetation (primarily *Chara* and *Potamogeton*) in triplicate mesocosms with or without a limerock (LR) cap above muck soils, as determined on April 9, 2014 after three years of flow-through operations and on February 2, 2015.

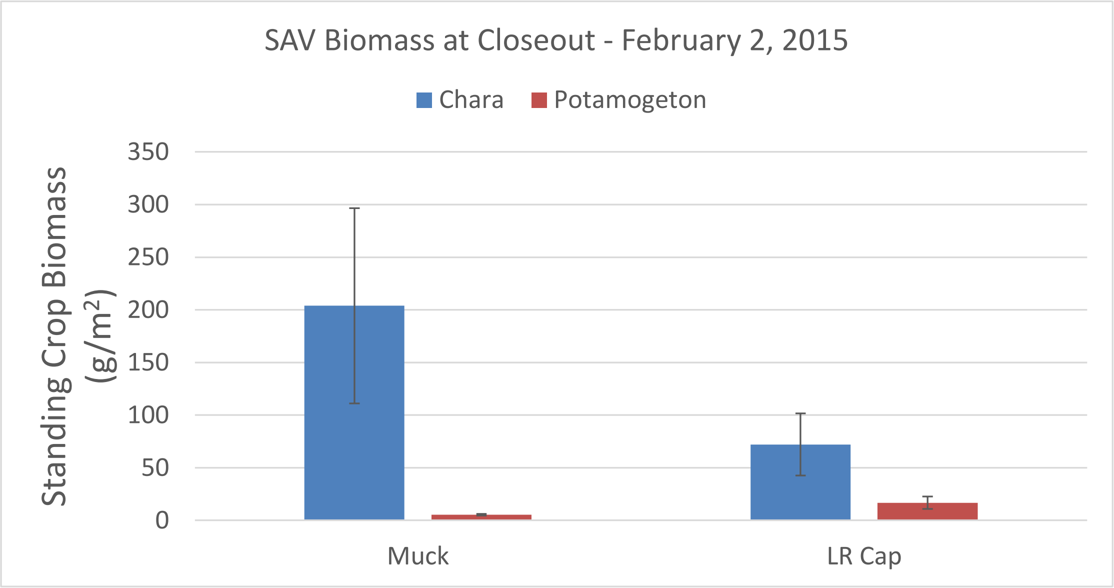


Figure 16. Standing crop biomass of the two dominant SAV species at the conclusion of the study on February 2, 2015. Error bars denote the standard error from triplicate mesocosms under each treatment.

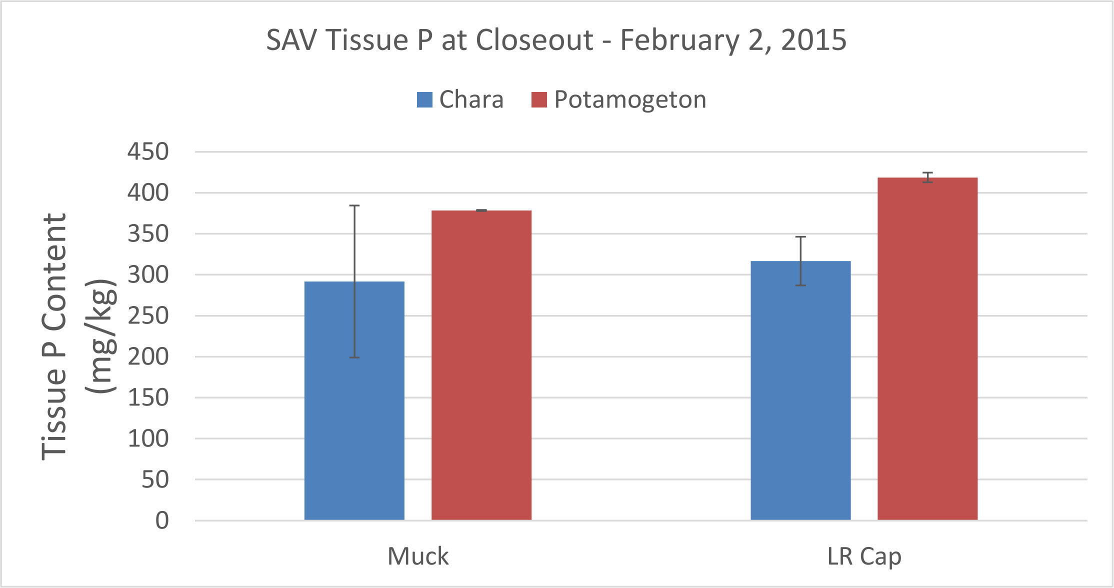


Figure 17. Standing crop biomass and total phosphorus content of submerged aquatic vegetation (SAV) tissues on February 2, 2015, at the end of the period of operations. Error bars denote ± SE around the mean value from triplicate mesocosms.

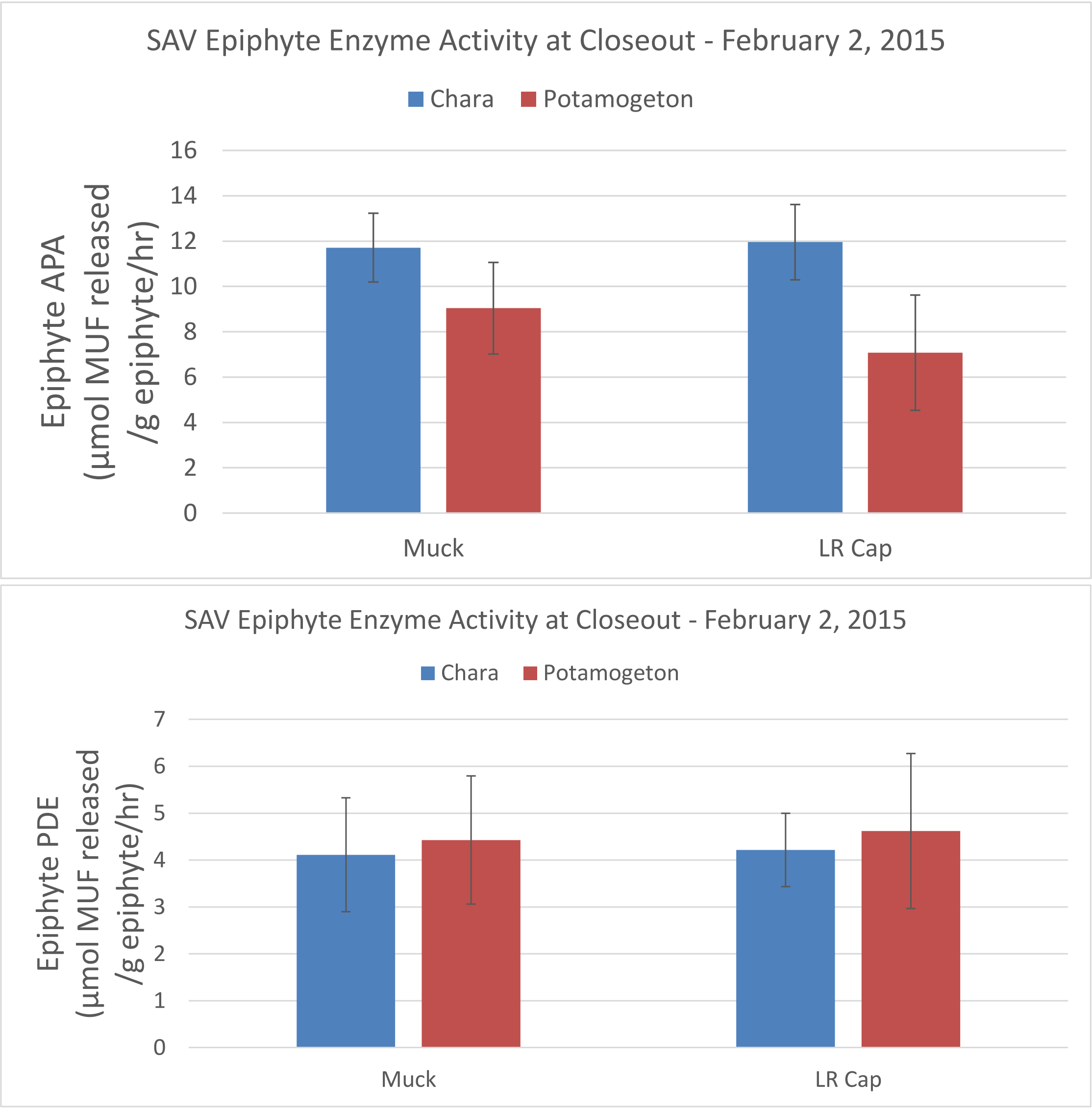


Figure 18. Enzyme activity of epiphytic algae on *Chara* and *Potamogeton* grown in outdoor mesocosms established on a low-phosphorus muck soil with or without a limerock (LR) cap. Alkaline phosphatase activity (APA) and phosphodiesterase (PDE) hydrolysis rates are shown in the top and bottom panels, respectively.

3.4 Synopsis of Findings

Long-term mean outflow TP concentrations from mesocosms operated with low-P muck with and without a limerock cap were identical between treatments for both the low-P period (9 ± 0.3 µg/L) and the high-P period (13 ± 0.3 µg/L). Mean inflow TP concentrations for the two periods were 11 and 21 µg/L, respectively.

Drawdown in a long-term (3.8 years), replicated outdoor mesocosm study resulted only in a short-term (a few weeks) period of elevated TP concentrations. Most of the released P was measured in PP form, likely indicating phytoplankton growth was occurring before macrophyte biomass recovered. No effect on long-term P removal performance was observed for either substrate; outflow TP concentrations were near 10 µg/L within several months of reflooding.

SAV biomass rebounded after reflooding within several months on the low-P muck soils with or without a LR cap. However, throughout the study, the LR cap maintained lower SAV biomass than muck soils without the cap.

4 Use of Limerock Cap to Reduce Flux from High P Soils

4.1 Background

It is generally thought that in order to achieve strict outflow P concentration targets, internal P loading in the outflow region of STAs should be minimized. Internal loading in wetlands can be direct, through advective and diffusive transfers of nutrients from soil porewater to the overlying water, or indirect, through plant uptake and senescence. One approach to limiting internal loads is to remove soils with moderate or high P release potential. Another approach is to add soil amendments that stabilize nutrients and provide a low-P substrate to limit flux into the water column. Either of these approaches could potentially be applied to outflow regions of existing STAs or to areas where farmed soils will be flooded to expand treatment areas.

The present study examined P flux from high-P muck soils to overlying water, and the effect of a limerock layer above muck soil, under unvegetated conditions.

4.2 Methods

On January 14, 2015, intact soil cores were collected from Roth Farm near STA-1W (hereafter, "Farm Muck") and the Lower SAV Cell in STA 3/4 (hereafter, "STA Muck"). The Farm muck was collected after removing vegetation from the soil surface. From the STA muck cores, the accrued layer was removed to expose the underlying muck soil. Target soil depth in each core was 10-15 cm. Cores with > 15 cm soil, large rocks or large roots were discarded and additional cores were collected until 12 uniform cores were obtained from each site.

The day after soil collection, the walls of each core were wiped clean. For each of the two muck soil types, a layer of limerock was placed above the muck soil in replicate cores. Treatments consist of 0, 5, 10, or 15 cm of added limerock above the soil (Figure 19). Phosphorus flux rates to the overlying water from the muck soils with and without these calcareous amendments were compared to P flux from PSTA sediments (Figure 20). This additional treatment was established using PSTA sediment collected from the back end of the PSTA Cell near station L1.

In each core designated for limerock amendment, a sampling well (clean 3/8" diam. rigid tubing) was installed. Each well was sealed at the bottom, but perforated just above the muck soil surface to allow water to be drained from the limerock layer during water exchanges. For +15 cm treatments, the sampling well also had holes drilled 7-8 cm above the muck, at the midpoint of the limerock layer.

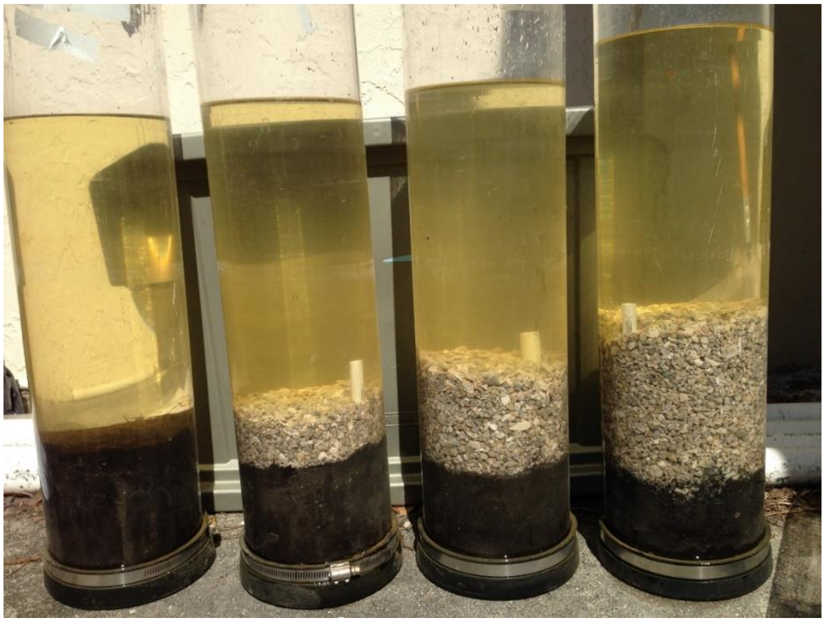


Figure 19. Four limerock treatments were applied to the muck soils: 0, +5, +10, +15 cm limerock gravel amendments.

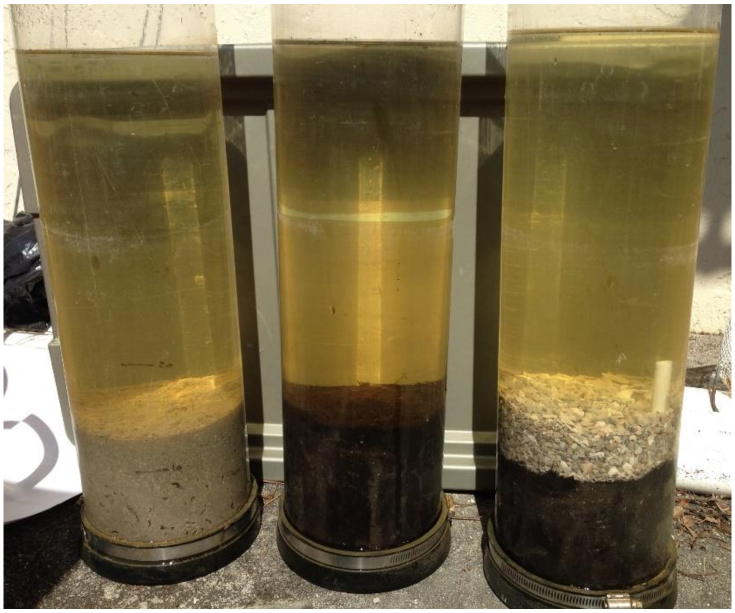


Figure 20. Soil incubation treatments (from left to right): PSTA sediments, STA muck soil without limerock, and STA soil with a 5-cm limerock cap.

4.3 Reflood Water

Outflow water from the PSTA Cell was used to reflood each core. Two samples of the reflood water were collected during each water exchange and measured for SRP, TP, and Ca. Reflood water was added to saturate the soil in Roth Farm treatments, while STA soils from the Lower SAV Cell and PSTA Cell were already saturated. The overlying water was drained from these later cores immediately prior to reflooding with fresh water at the start of the incubation. A total of 5 L was added to each core to establish a water column above the substrate. The cores remained unplanted, and stored in a dark water bath.

Aeration was provided to maintain aerobic conditions in all treatments during the first four cycles of the study. Dissolved oxygen was measured twice weekly and a minimum amount of bubbling was used to achieve DO concentrations of ~3-8 mg/L. Bubbles were released into the middle of the water column, ~15 cm above the sediment surface. Disturbance of surficial sediments was negligible. At the beginning of cycle 5, aeration was discontinued and the top of each core was sealed to minimize re-oxygenation of the water column. Nitrogen gas was sparged into each core to DO < 0.5 mg/L on two occasions during the final cycle.

4.4 Monitoring P flux

On a weekly basis, surface water SRP concentrations were determined, and pH and temperature were recorded during each sampling. Water was exchanged every two weeks.

Before each water exchange, DO was also measured. In control (no LR added) treatments and +15 cm LR treatments, dissolved calcium was also sampled in the surface water.

In the +15 cm LR treatments, porewater was also sampled for SRP, dCa, pH and temperature measurements at the middle of the LR layer (7-8 cm above the muck surface). This was accomplished by using a syringe and sample tubing placed within the sampling well.

This experiment continued for 12 weeks.

4.5 Results

4.5.1 Experimental conditions

Mean soil TP content of the farm muck was 971 ± 12 mg/kg, over twice the content of STA muck (456 ± 10 mg/kg) and three times higher than PSTA sediment (275 ± 7 mg/kg; Figure 21). During the incubation, DO concentrations were initially high (> 4 mg/L), but were lower in the final water exchange as a result of the nitrogen gas sparge of the water column (Figure 22).

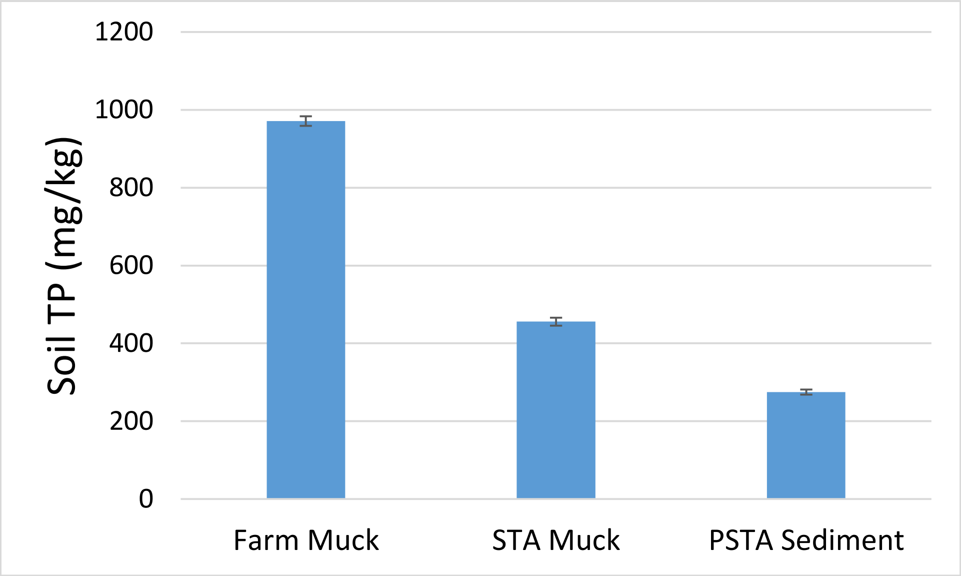


Figure 21. Mean soil total phosphorus (TP) content of three soils used in the incubation.

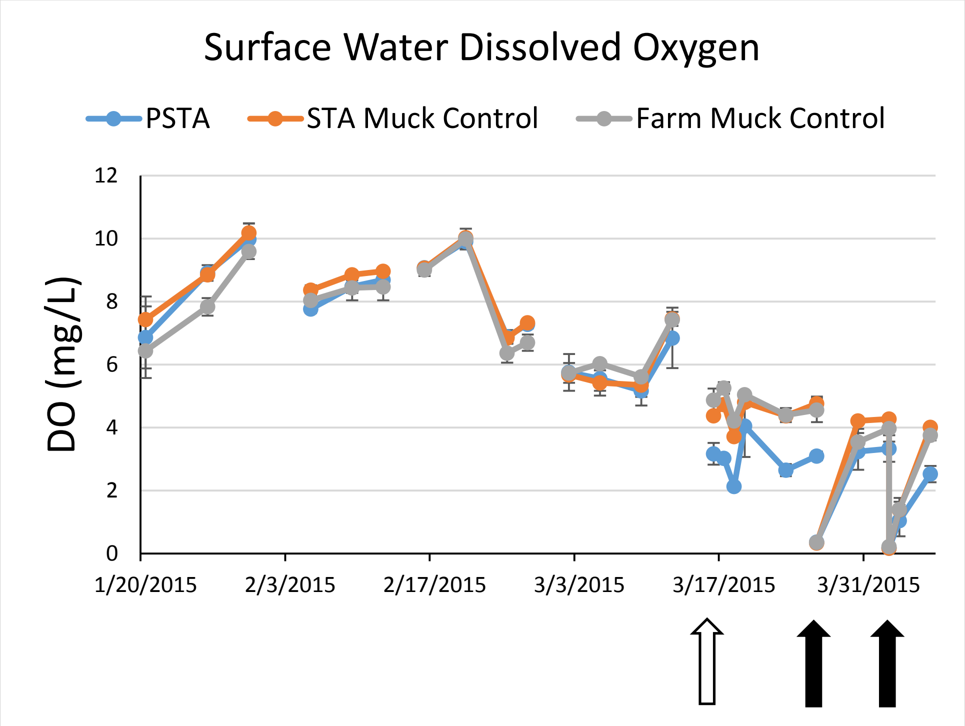


Figure 22. Mean dissolved oxygen (DO) concentrations in control cores containing muck soils or PSTA accrued sediments during the 12-week study. Breaks in the lines denote water exchanges between each of six cycles. The open arrow at the beginning of cycle 5 denotes when aeration ceased and the top of each core was sealed to minimize reaeration. Solid arrows denote N_2 sparge to DO < 0.5 mg/L on two occasions during the final cycle.

4.5.2 P Concentrations in the Water Column

Concentrations of SRP in the water column increased during each cycle for the cores with farm muck (no limerock), while STA muck (no limerock) and PSTA sediment treatments showed a decrease in SRP concentrations to the limits of detection (Figure 23). After the end of the first 14 days of incubation, the farm muck cores had SRP concentrations of 126 ± 21 µg/L in the overlying water. Subsequent cycles showed lower TP concentration increases (< 50 µg/L), until the 5th and 6th cycles. Elevated P accumulation in the water column above farm muck during the last cycle was likely due to the temporarily hypoxic conditions that resulted from the sparging with N_2 gas.

The same hypoxic conditions that affected the farm soils had no influence on P stability in the STA muck soils. The STA soils would have been exposed to anoxic conditions under flooded conditions typical of STA soils. Therefore, phosphorus forms that become unstable under anoxic conditions (such as Fe-hydroxide associated P compounds) were likely not a substantial part of the soil P in the STA muck soil or PSTA sediments, but may have been more prevalent in the farm muck soil.

Limerock thickness showed little effect on SRP in the water column for either soil type (Figure 24 and Figure 25).

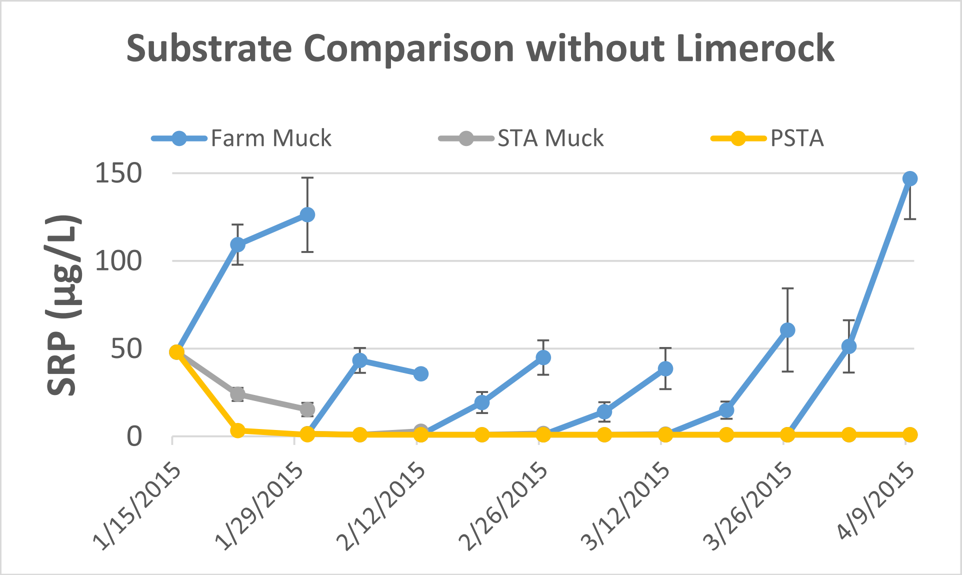


Figure 23. Soluble reactive phosphorus (SRP) concentrations in the overlying water above three soil types. Error bars denote the standard error around the mean of triplicate cores under each treatment**.**

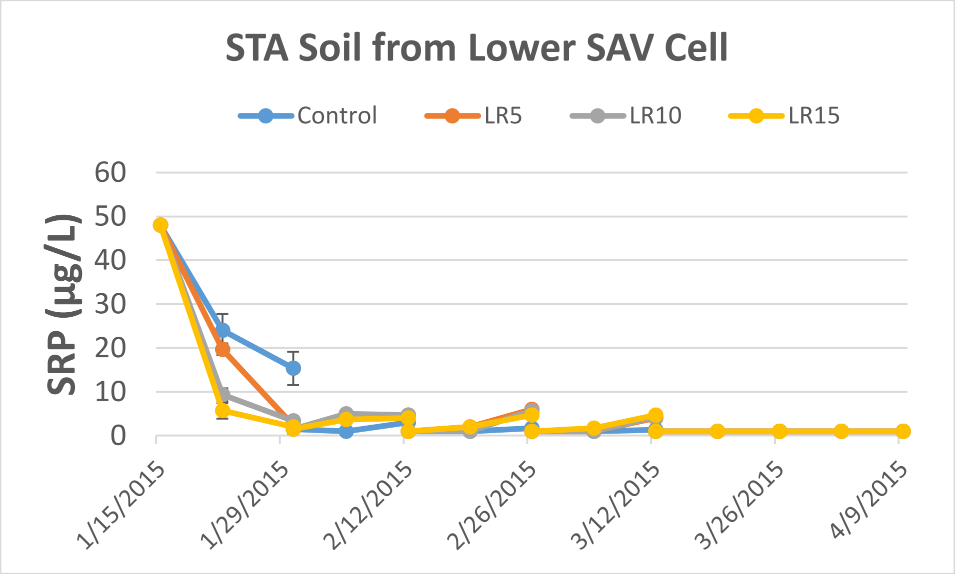


Figure 24. Soluble reactive phosphorus concentrations in the surface waters overlying STA muck soils during six consecutive batch cycles of 14 days each. Error bars denote the standard error around triplicate soil cores assigned to each of four limerock cap treatments (0, 5, 10 or 15 cm of limerock added).

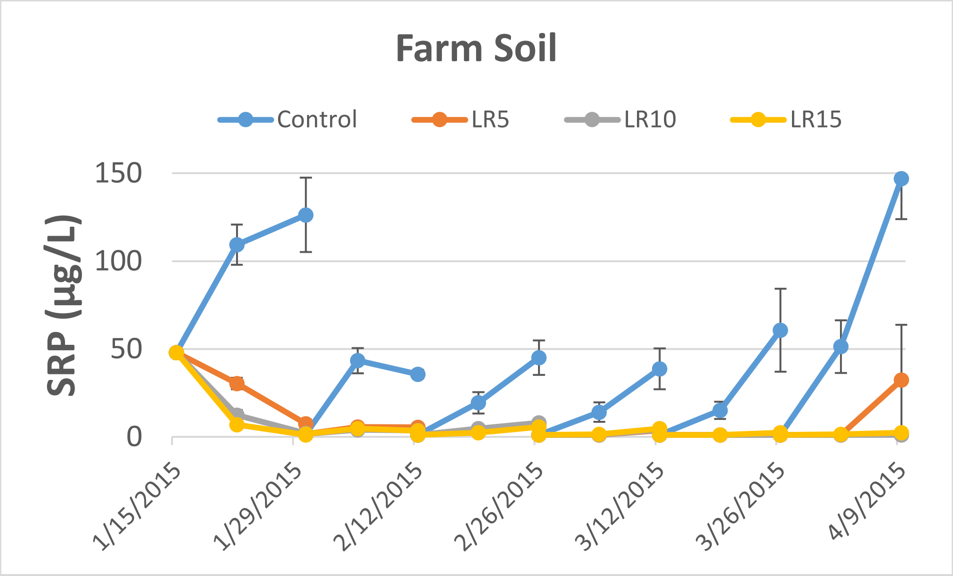


Figure 25. . Soluble reactive phosphorus concentrations in the surface waters overlying Farm Muck soils during 6 consecutive batch cycles of 14 days each. Error bars denote the standard error around triplicate soil cores assigned to each of four limerock cap treatments (0, 5, 10 or 15 cm of limerock added).

4.5.3 Porewater chemistry

The porewater well sampling from within the limerock layer indicated that high SRP concentrations began to accumulate above the Farm muck during the 2nd cycle and remained elevated through the remainder of the study (Figure 26). By contrast, the limerock layer above the STA muck soil showed little evidence of P enrichment. Porewater calcium concentrations were similar between treatments at the end of the first cycle, with 71 ± 3 mg/L and 63 ± 3 mg/L. In subsequent cycles, however, porewater above the farm soil showed increased concentrations of calcium and lower pH levels, as compared to porewater in the LR cap above STA muck soils (Figure 27 and Figure 28). Partial dissolution of the limerock cap by organic acids from the farm muck may have contributed to the changes observed in both parameters.

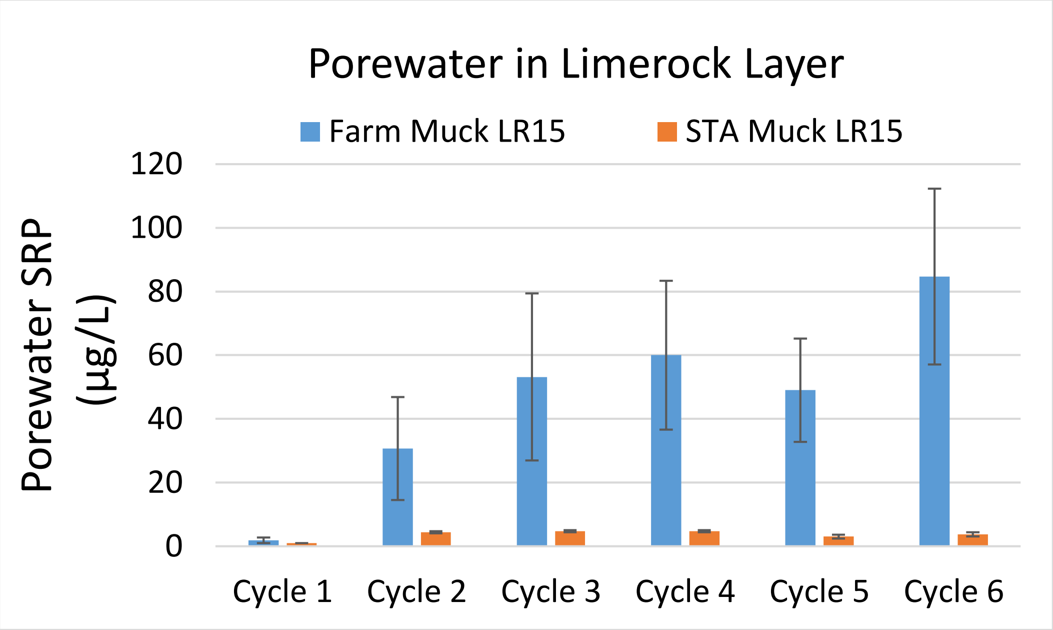


Figure 26. Soluble reactive phosphorus (SRP) concentrations in the porewater of the limerock layer in treatments with 15 cm LR added as a cap above two muck soil types. Error bars denote the standard error around the mean for triplicate cores under each treatment.

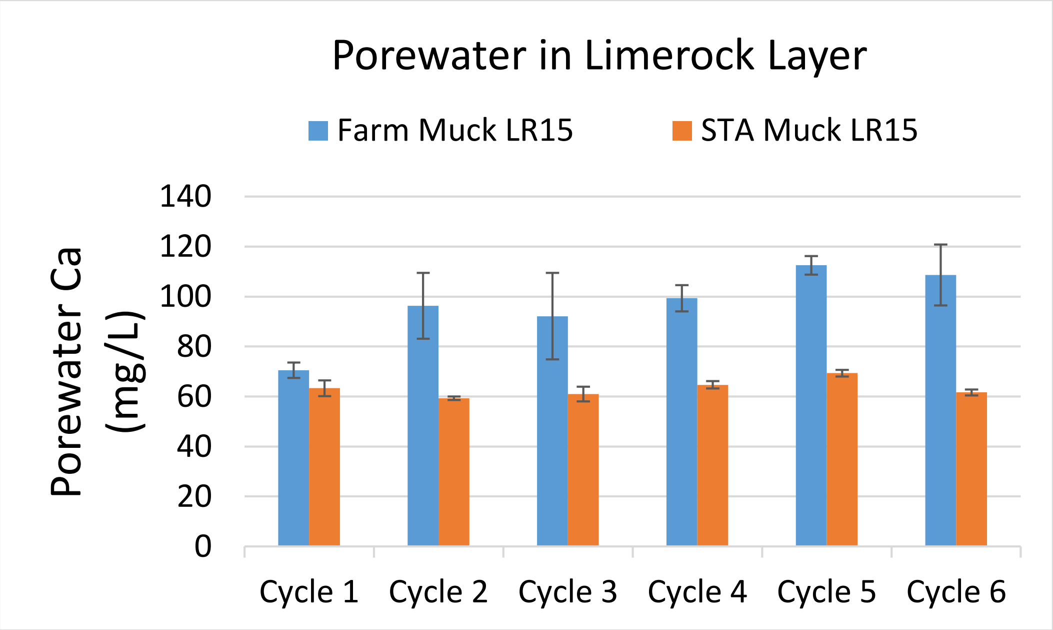


Figure 27. Porewater calcium concentrations in the limerock layer above two muck soil types incubated for six two-week cycles.

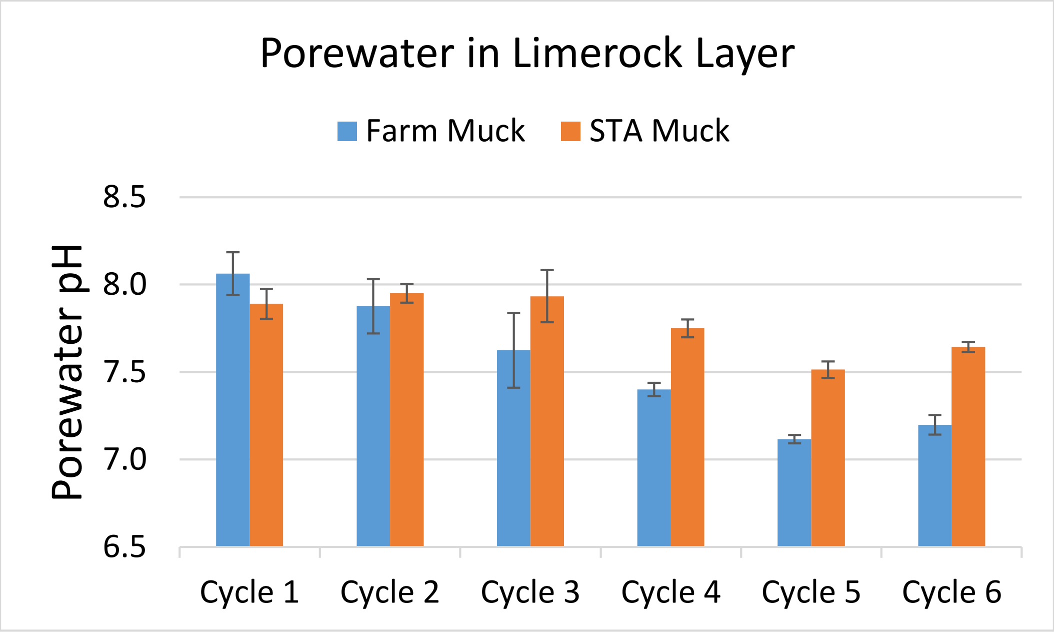


Figure 28. Porewater pH values from limerock over two muck soil types incubated for six two-week cycles.

4.6 Synopsis

The farm muck was P-enriched relative to the STA muck soils or PSTA sediments, and exhibited greater P release. A limerock cap was effective at both reducing P flux from the farm muck, and increasing P uptake by the STA muck, across a range of cap depths (5-15 cm). Porewater SRP and calcium enrichment and lower pH values within the LR layer were observed above farm muck soils.

In order to evaluate the long-term effectiveness of a limerock cap, a follow-up study is planned using larger flow-through mesocosms. This platform will incorporate macrophytes and evaluate the potential adverse effects of macrophyte P uptake from soils (i.e., "mining") on water column P concentration reduction above limerock-capped muck soils.