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Alternative Treatment Technologies Evaluations - September 2011 to June 2013

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BACKGROUND

The South Florida Water Management District (District) is often approached by individuals and firms with proposals for improving regional water quality on an *ad hoc* basis. The number of such inquiries prompted the District to create a structured process to evaluate these technologies, i.e., the New Alternative Technology Assessment (NATA) Program. The NATA Program provided interested vendors the opportunity to demonstrate the efficacy of potential treatment technologies for reducing phosphorus (P) and/or nitrogen (N) concentrations in waters discharged from the Greater Everglades watershed. Technologies evaluated as part of the NATA Program were selected from respondents to two request-for-proposal (RFP) solicitations issued by the District in October 2010 and November 2011. Potential technologies were vetted through a selection process with a pre-determined set of criteria and evaluated by District scientific staff. The selection criteria were designed to provide a rapid and equitable method for the initial screening of novel nutrient removal technologies that might warrant further investigation by the District for demonstration projects on District and/or cooperative landowner's properties and review of project results. The District generally focuses on water quality in (1) waste streams from confined animal feeding operations; (2) ditch runoff from cattle ranching operations; (3) canal discharges into Lake Okeechobee; (4) Lake Okeechobee discharges and local watershed runoff into the east and west coast estuaries; and (5) water moving south from the Everglades Protection Area into the Water Conservation Areas and other portions of the traditional remnant Everglades. There was no dedicated funding for the NATA Program although the District provided support by contributing considerable staff time, analyzed water quality samples in the District's Chemistry Laboratory free of charge, and assisted in securing sites to conduct field demonstrations. All other direct and indirect costs associated with conducting NATA projects were borne by each vendor. Note that the NATA Program was not intended, nor designed, to provide the data needed for the design of full-scale treatment facilities or to conduct a rigorous cross-comparison of candidate technologies. In addition to the NATA Program, the District evaluated a number of other technologies brought to its attention through avenues other than the NATA RFP process. Both the solicited and unsolicited technologies are collectively referred to as Alternative Treatment Technologies (ATT) in this report. This report summarizes the technology evaluations conducted by the District as part of the NATA Program and tests of unsolicited ATTs between the dates of the first and last NATA project (September 2011 to June 2013, i.e., the "study period").

The District responded to inquiries from 19 different technology vendors during the study period (Appendix 1) and tested nine of these technologies in the laboratory and/or field (Table 1). Six of the nine technologies (Aragonite, ElectroCoagulation™, Phoslock®, STI, ViroPhos™ and WP-1™) were part of the NATA Program. A seventh technology, Ferrate, was evaluated in conjunction with a field demonstration conducted by Highlands County. The eighth technology, AquaLutions™, was tested under a separate contract with the District, as was WP-1™ at one location (Blue Heron Pond). The ninth technology tested was Nclear®. Single field demonstrations were conducted for AquaLutions™, Ferrate, Phoslock® and ViroPhos™. Two separate field demonstrations were conducted for WP-1™. Jar tests were conducted for Aragonite, Nclear®, Phoslock®, STI (two separate jar tests), ViroPhos™ (two separate jar tests) and WP-1™. ElectroCoagulation™ was tested at bench-top scale. It was the District's intention to conduct field demonstrations for all the technologies selected for evaluation. However, the ElectroCoagulation™ apparatus was not suitable for use in the field and we were unable to secure appropriate sites to test Aragonite, Nclear® and STI. All tests were of relatively short duration (days to weeks) and limited scope and as noted above must be regarded as preliminary efforts to characterize the treatment potential of each technology, i.e., can the technology reduce P or N concentrations in District surface waters. In addition, the initial P and N concentrations of waters tested varied considerably among technologies[1], the field demonstrations had no true control to compare against the application treatment(s) and results are from a combination of field and laboratory studies. These factors limited the comparisons we could make among technologies. For example, we cannot legitimately compare the slopes of dose-response curves for different technologies, calculate meaningful removal rate coefficients (*k* values), determine the cost per pound of P or N removed or assess long-term treatment efficacy.

Project reports for each of the nine technologies tested by the District are provided in Appendix 2. These individual reports include the results of all water quality analyses performed by the District's Chemistry Laboratory plus any water quality data provided by outside laboratories[2] and the observations of treatment performance derived from these data. This report employs a simplified approach to cross-compare each technology's treatment performance, based on before- versus after-application changes in constituent levels scored on a nominal scale (Table 1):

- The constituent level increased by more than 5 % = Increase,
- Change in constituent level was less than or equal to 5 % = Little Appreciable Change, or
- The constituent level decreased by more than 5 % = Decrease.

These comparisons were made using only District water quality data generated during each test. The reader is referred to the individual reports in Appendix 2 for the actual measurements of before- and after-application changes. Note that other than the P fractions, the other constituents were not analyzed in every test for a variety of reasons[3].

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[1] For example, initial total phosphorus concentrations ranged from 0.034 mg/L in the WP-1™ - Stormwater Treatment Area (STA)-1W Test Cell field demonstration to 10.232 mg/L in the ViroPhos™ - Turnpike Dairy Pond field demonstration, a three order-of-magnitude difference in concentrations.

[2] Two vendors collected their own water samples that were analyzed by outside laboratories: Ferrate Treatment Technologies LLC during the Ferrate field demonstration and AquaFiber Technologies Corporation during the AquaLutions™ field demonstration. These outside water quality data generally were comparable to the District's data collected in parallel sampling efforts, so much so that these vendors included the District's data in their project reports.

[3] For example, we did not analyze for total iron and aluminum while testing Aragonite and Nclear®, products that contained little iron or aluminum. For technologies tested multiple times, we may not have analyzed for a particular constituent (e.g., sulfate) after the first test characterized how the technology affected that constituent. In jar tests that were sampled multiple times, the total water volume of the jar limited the volume of each sample collected from the jar, which in turn restricted the number of constituents that could be analyzed in each sample.

SUMMARY OF TEST RESULTS

The following comparisons of treatment performance are based on an examination of the results from all field and laboratory tests provided in Table 1:

1. All technologies were able to reduce total P (TP), total dissolved P (TDP) and dissolved organic P (DOP) concentrations to some degree.
2. Most technologies were able to reduce soluble reactive P (SRP) concentrations. Note that SRP was at its method detection level (2 µg/L) at the start of the ViroPhos™ jar test with water from the STA-1W Test Cell and the field demonstration of WP-1™ in the STA-1W Test Cell. The ElectroCoagulation™ test with iron blades appeared to generate a minute amount of SRP, but the concentration increase (2 µg/L) could reflect nothing more than analytical error.
3. Particulate P (PP) concentrations were reduced by Aragonite, ElectroCoagulation™, Ferrate, STI, the ViroPhos™ jar tests and the WP-1™ jar test and STA-1W Test Cell field demonstration while PP increased in the Aragonite and Nclear® jar tests and the field demonstrations for Phoslock® - MacArthur Lake, ViroPhos™ - Turnpike Dairy Pond and WP-1™ - Blue Heron Pond.
4. Total N (TN) and total organic N (TON) concentrations were reduced by all technologies except in the Phoslock® jar test. AquaLutions™ and Nclear® also removed dissolved organic N (DON).
5. Only ElectroCoagulation™ reduced nitrite+nitrate-N (NOX) levels. NOX increased in most of the other tests.
6. Treatment results for ammonia-N (NH4) were mixed. NH4 concentrations were reduced by AquaLutions™, Aragonite, Ferrate, the Phoslock® field demonstration, the STI - Lake Trafford jar test, ViroPhos™ and the WP-1™ - STA-1W Test Cell field demonstration, while NH4 increased in ElectroCoagulation™, Nclear® and both the Phoslock® and STI - C-51 Canal jar tests.
7. Treatment results for total aluminum (TAL) were mixed. Concentrations decreased for ElectroCoagulation™ - iron blades and both the STI and WP-1™ – C-51 Canal jar tests. Concentrations increased for ElectroCoagulation™ - aluminum blades as the blades dissolved and released aluminum ions and for Phoslock™, ViroPhos™ and both WP-1™ field demonstrations, presumably as aluminum dissolved out of these mineral-based products into the water.
8. Treatment results for total iron (TFE) were mixed. Concentrations decreased for ElectroCoagulation™ - aluminum blades, both STI jar tests and both WP-1™ field demonstrations. Concentrations increased (understandably) for both ElectroCoagulation™ - iron blades and Ferrate and for Phoslock®, ViroPhos™ and the WP-1™ jar tests.

9. ElectroCoagulation™, Ferrate, Nclear®, STI and the Phoslock™ - STA-1W Test Cell field demonstrations all reduced sulfate (SO4) concentrations, while concentrations increased in the AquaLutions™, Aragonite, ViroPhos™ and the WP-1™ jar tests.
10. The water pH (PH) decreased during the AquaLutions™ and the Ferrate field demonstrations and increased in Aragonite, ElectroCoagulation™, Nclear® and both the STI and WP-1™ – C-51 Canal jar tests. The spike in PH was dramatic for STI and WP-1™ (3.5 and 2.4 s.u., respectively). There was little appreciable change in PH during the Phoslock® and ViroPhos™ tests.
11. Conductivity (COND) decreased during the ElectroCoagulation™ tests and increased for AquaLutions™, Aragonite, Ferrate, Nclear®, the STI – C-51 Canal jar test and ViroPhos™. There was little appreciable change in COND in the Phoslock® and WP-1™ tests.

CONCLUSION

All the technologies evaluated in this report demonstrated the potential to reduce TP concentrations in surface waters to some degree and many of them reduced TN levels as well. However, these studies were only initial assessments of treatment efficacy and considerable follow-on work would be needed to generate the data needed to conduct a feasibility analysis for a full-scale treatment system using any particular technology. In addition, the scope of the NATA Program was limited to those vendors who approached the District and consequently, the technologies evaluated represent only a small subsample of all available water treatment technologies. Additional RFPs for the NATA Program were not issued due, in large measure, to the unavailability of sites suitable to conduct field demonstrations. Although there are no current plans to conduct additional laboratory or field tests, the District remains interested in potential water treatment technologies**.**

Table 1. Treatment performance summary for alternative treatment technologies evaluated during the study period covered in this report (September 2011 to June 2013). All water quality samples were analyzed by the South Florida Water Management District's Chemistry Laboratory.

Technology	**Study Type**	**Water Source**	**TP**	**TDP**	**SRP**	**DOP**	**PP**	**TN**	**TON**	**DON**	**NOX**	**NH4**	**TAL**	**TFE**	**SO4**	**PH**	**COND**	**Evaluation Samples**‡
AquaLutions™	Field	C-43 Canal	↓	↓	↓	↓	↓	↓	↓	↓	–	↓	na	na	↑	↓	↑	In vs. out @ both sites
Aragonite	Jar test	Taylor Creek	↓	↓	↓	↓	↑	↓	↓	na	↑	↓	na	na	↑	↑	↑	Day 1 highest dose
ElectroCoagulation™	Bench-top	C-51 Canal	↓	↓	↓	↓	↓	↓	↓	na	↓	↑	↑	↓	↓	↑	↓	Al blades highest power
ElectroCoagulation™	Bench-top	C-51 Canal	↓	↓	↑	↓	↓	↓	↓	na	↓	↑	↓	↑	↓	↑	↓	Fe blades highest power
Ferrate	Field	Istokpoga Marsh	↓	↓	↓	↓	↓	↓	↓	na	↑	↓	na	↑	↓	↓	↑	Last day in vs. out
Nclear®	Jar test	MacArthur Lake	↓	↓	↓	↓	↑	↓	↓	↓	↑	↑	na	na	↓	↑	↑	Highest dose
Phoslock®	jar test	C-51 Canal	↓	↓	↓	↓	–	↑	↓	na	↑	↑	↑	↑	–	–	–	Day 1 highest dose
Phoslock®	Field	MacArthur Lake	↓	↓	↓	↓	↑	↓	↓	na	–	↓	na	na	na	–	–	24-hr surface
STI	Jar test	C-51 Canal	↓	↓	↓	↓	↓	↓	↓	na	↑	↑	↓	↓	↓	↑	↑	Day 1 highest dose
STI	Jar test	Lake Trafford	↓	↓	↓	–	↓	–	–	na	∗	↓	–	↓	na	–	–	Day 1 highest dose
ViroPhos™	Jar test	STA-1W Test Cell	↓	↓	∗	↓	↓	na	na	na	na	na	↑	↑	↑	–	↑	24-hr highest dose
ViroPhos™	Jar test	C-51 Canal	↓	↓	↓	↓	↓	↓	↓	na	↑	↓	↑	↑	↑	–	↑	Day 1 highest dose
ViroPhos™	Field	Turnpike Dairy Pond	↓	↓	↓	nc	↑	–	–	na	↑	↓	↑	↑	↑	–	↑	24-hr post application
WP-1™	Field	STA-1W Test Cell	↓	↓	∗	↓	↓	↓	na	na	↑	↓	↑	↓	↓	–	–	Cell 4 batch application
WP-1™	Jar test	C-51 Canal	↓	↓	↓	↓	↓	↓	↓	na	↑	–	↓	↑	↑	↑	–	Day 1 highest dose
WP-1™	Field	Blue Heron Pond	↓	↓	↓	↓	↑	na	na	na	na	na	↑	↓	na	na	na	First application

‡Performance summaries are based on comparison of constituent levels at the start of the test with constituent levels in the samples listed for each technology.

Test Result Key: ↑ = constituent level increased > 5%; ↓ = constituent level decreased > 5%; – = little appreciable change in constituent level (≤ 5% increase or decrease); na = constituent not analyzed; nc = DOP concentration not calculated because the SRP concentration was higher than the TDP concentration; ∗ = initial constituent level at method detection level, could not evaluate technology's performance.

Water Quality Parameter Key: TP = total phosphorus; TDP = total dissolved phosphorus; SRP = soluble reactive phosphorus; DOP = dissolved organic phosphorus; PP = particulate phosphorus; TN = total nitrogen; TON = total organic nitrogen; DON = dissolved organic nitrogen; NOX = nitrite+nitrate-N; NH4 = ammonia-N; TAL = total aluminum; TFE = total iron; SO4 = sulfate; PH = pH; COND = conductivity.

Appendix 1. Vendors who approached the District for consideration of their technology during the study period covered in this report (September 2011 to June 2013).

	Technology	Vendor	Technology Description	Action Taken
1	AquaLutions™	AquaFiber Technologies Corp.	A proprietary system that removes nutrients from surface water. The technology cannot be described due to a confidentiality agreement between the District and AquaFiber Technologies Corp.	Vendor conducted a field demonstration of this technology at two sites on the Caloosahatchee River (C-43 Canal)
2	Aragonite	CaC03 Aragonite Products, Inc. and Ocean Cay, Ltd.	Aragonite is a naturally occurring calcium carbonate mineral that precipitates directly from seawater.	District conducted a jar test with this product.
3	Beemats	Beemats	A hydroponic system that utilizes macrophytes grown in patented floating mats to remove nutrients from water by direct uptake through the plant roots.	One off-site meeting with vendor; technology not selected for testing.
4	ElectroCoagulation (EC/PW™) System	Powell Water Systems, Inc. and Gerber Pumps International, Inc.	A patented technology that operates by generating an electric current across metal electrodes in a reactor vessel thereby generating free electrons and ions released from the electrodes that neutralize the charge of other constituents causing them to coagulate	Vendor conducted a bench-top test of this technology.
5	Ferrate Treatment	Ferrate Treatment Technologies LLC and WesPac Water LLC	Proprietary technology that produces ferrate ($[FeO_4]^{2-}$; Fe^{+6} oxidation state), a strong oxidizing agent, on-site at a commercial scale to treat water.	Vendor conducted a field demonstration of this technology at a single site in Canal B of the Istokpoga Marsh Water Improvement District, Highlands County.
6	Flexi®-Pave	K.B. Industries, Inc. and EnSite, Inc.	Proposed testing the nutrient removal capabilities of a porous paving material.	One meeting at District HQ with vendor; technology not selected for testing.
7	GPS PrO_2 Concentrated Oxygenation System	Greener Planet Solutions North America	Proprietary system that hyper-oxygenates water to increase microbial decomposition of organic compounds and oxidize inorganic contaminants.	One meeting at District HQ with vendor; technology not selected for testing.

Appendix 1. (Continued).

	Technology	Vendor	Technology Description	Action Taken
8	Hydrachar Farming	Windworth Gains, Inc. dba: SIBIRONICS	Proposed testing a water hyacinth-based treatment system to remove nutrients from water then harvest the plants and convert the biomass into a biochar.	Three meetings at District HQ with vendor; technology not selected for testing.
9	LLX Technology	Battelle	Proprietary process based on liquid-liquid extraction (LLX) of pollutants from water with an organic polymer and then stripping the pollutants from the polymer. Originally developed to remove SO4 from acid mine waters; can potentially remove N and P depending on the polymer used.	Two meetings at District HQ with vendor; treatment efficacy of this technology for P and N removal not validated at this time.
10	Nclear 11®	Nclear IP LLC	A mineral-based product that is a proprietary mixture of calcium silicate hydroxides	District conducted a jar test with this product.
11	Phoslock®	Phoslock Water Solutions, Ltd., AMEC and SePRO Corp.	A modified bentonite clay product that is amended with lanthanum, a rare earth element, as the active ingredient.	District conducted a jar test and vendor conducted a field demonstration of the product at MacArthur Lake, Martin County.
12	PoCo Pollution Control	Wise USE International B.V.	Product acts as a biocatalyst to stimulate the growth of microorganisms.	Technology not selected for testing.
13	Salt-Free Water Systems LLC	Vulcan water conditioner	Patented process that prevents lime scale formation in household, agricultural and agricultural equipment.	Technology not selected for testing.
14	SolarBee®	Medora Corp.	A solar-powered mechanical device designed to recirculate water and prevent/reduce stratification in ponds, lakes, and other water bodies.	One meeting at District HQ with vendor; technology was deemed too expensive to deploy.
15	STI (Simtec Triad Ionate)	TKW Consulting Engineers, Inc. and Michael Fitzsimmons	A proprietary mixture of mineral compounds variously described as a calcium oxide-based powder or a calcified granite sodium pyrite-hydrochlorite.	District conducted two jar tests with this product.

Appendix 1. (Continued).

	Technology	Vendor	Technology Description	Action Taken
16	UV Nitrogen Removal	HSA Engineers & Scientists and Conestoga-Rovers & Associates	Proposed testing whether exposure to ultraviolet light could photodegrade recalcitrant organic N compounds to more labile forms as part of a treatment system to reduce dissolved organic N in the Caloosahatchee River.	Not funded for evaluation by Lee County; technology not selected for testing by the District.
17	ViroPhos™	EnviRemed and Virotech Global Solutions, Inc.	A mixture of hematite, hydrated alumina, sodalite, quartz, calcium minerals, magnesium minerals and titanium oxides.	District conducted two jar tests and vendor conducted a field demonstration of this product at the Turnpike Dairy pond, Martin County
18	WE-Biotics™	WE-Biotics	Cultivate and harvest algae on a commercial scale as part of a treatment system to reduce nutrients in surface water.	One meeting at District HQ with vendor; technology not selected for testing.
19	WP-1™	North American Geochemical LLC and US Environmental Resource & Recovery Group LLC	A proprietary mixture of mineral compounds sold for use in phosphate stabilization.	District conducted a jar test and vendor conducted two field demonstrations of this product at the STA-1W Test Cells and Blue Heron Pond, Miami-Dade County

Appendix 2 – Alternative Treatment Technologies Reports and Data Tables

1. **AquaLutions™:** Pilot Study of the AquaLutions™ Treatment Technology at Two Test Sites on the Caloosahatchee River [District report]
2. **AquaLutions™:** Results of AquaKnight™ Mobile Treatment Unit Demonstration at Two Sites on the Caloosahatchee River, Florida [AquaFiber Technologies Corporation report]
3. **Aragonite:** A Jar Test of Aragonite Conducted with Taylor Creek Water [District report]
4. **ElectroCoagulation™** - Electrocoagulation Demonstration Using C-51 Canal Water [District report]
5. **Ferrate:** Ferrate Demonstration at Canal B - Istokpoga Marsh, Water Improvement District, Lake Placid [District report]
6. **Ferrate:** Report on Ferrate Demonstration Submitted to Highlands County [Ferrate Treatment Technologies LLC report]
7. **Nclear®:** A Jar Test of Nclear® Conducted with MacArthur Lake Water [District report]
8. **Phoslock®, STI, ViroPhos™ and WP-1™:** New Alternative Treatment Assessment (NATA) Program - A Jar Test of Phoslock®, STI, ViroPhos™ and WP-1™ Using C-51 Canal Water [District report]
9. **Phoslock®:** A Demonstration Study of Phoslock® Conducted at MacArthur Lake [District report]
10. **STI:** STI Jar Test of Lake Trafford Water [District report]
11. **ViroPhos™:** ViroPhos™ Jar Test of Inflow Water to the STA-1W North Test Cells [District report]
12. **ViroPhos™:** A Demonstration Study of ViroPhos™ Conducted at the Turnpike Dairy [District report]
13. **WP-1™:** Nitrogen and Phosphorus Removal from Natural Waters Using an Activated Mineral Matrix (WP-1™) [US Environmental Resource & Recovery Group LLC report]
14. **WP-1™:** Summary Water Chemistry Data for WP-1™ Treatments of the Blue Heron Pond [District data table]

Pilot Study of the AquaLutions™ Treatment Technology at Two Test Sites on the Caloosahatchee River

Introduction

The South Florida Water Management District (District) funded AquaFiber Technologies Corporation (AquaFiber) of Winter Park, FL to conduct a pilot study to assess the treatment efficacy of their patented technology (AquaLutions™) to remove total phosphorus (TP) and total nitrogen (TN) from surface waters in the Caloosahatchee River. This report presents results of chemical analyses of water samples collected during this study that were analyzed by the District's Chemistry Laboratory. Results and interpretation of water quality analyses performed by Flowers Chemical Laboratories, Inc. for AquaFiber are presented in a separate report that was submitted to the District[1]. The operating principal(s) behind the AquaLutions™ treatment technology cannot be discussed due to a confidentiality agreement between the District and AquaFiber concerning the technology.

Methods

Surface water was treated at two test sites during this study. The first test site was located in the Lake Okeechobee Rim Canal just east of the S-77 structure at the Alvin Ward Boat Ramp in Moore Haven, FL (Fig. 1). The second test site was located along the south side of the C-43 Canal (Caloosahatchee River), east of S-78 and adjacent to the District-owned Boma property near LaBelle, FL (Fig 2). AquaFiber deployed their AquaKnight™, a mobile treatment unit that housed the AquaLutions™ treatment technology (Fig. 3) for a period of five days at each test site: November 26 through 30, 2012 at the first test site and December 3 through 7, 2012 at the second test site. Water was pumped from near-shore locations directly into the AquaKnight™ for treatment over three consecutive days (deployment days 2, 3 and 4) at each test site. Daily pumping rates ranged from approximately 4,700 to 9,900 gal/day during the study. AquaFiber staff adjusted the AquaLutions™ process during this time to optimize nutrient removal efficiency. District staff visited the first test site on November 28, 2012 (the second day of treatment operation) and the second test site on December 6, 2012 (the third day of treatment operation) to collect water quality samples. Pulse releases of water from Lake Okeechobee into the Caloosahatchee River occurred on November 28 and December 6, resulting in flow at both test sites when the District's water quality samples were collected.

Unreplicated inflow (untreated) and outflow (treated) grab samples were collected by AquaFiber staff from within the AquaKnight™ and provided to District staff for field processing and transportation (on ice in coolers) to the District's Chemistry Laboratory for analysis. Unfiltered water samples were analyzed for total phosphorus (TP), total Kjeldahl nitrogen (TKN), chlorophyll A, chlorophyll B, pheophytin A, pH (PH), conductivity (COND), and turbidity (TURB). Field-filtered (0.45 µm pore size) samples were analyzed for total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), ammonia (NH4), nitrate+nitrite-nitrogen (NOX), total dissolved Kjeldahl nitrogen (TDKN) and sulfate (SO4). The following parameters were calculated by dif-

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[1] AquaFiber Technologies Corporation. 2013. Results of AquaKnight™ Mobile Treatment Unit Demonstration at Two Sites on the Caloosahatchee River, Florida. Report submitted January 15, 2013 to the South Florida Water Management District, West Palm Beach, FL under SFWMD Contract #4600002773.

ference: particulate phosphorus (PP = TP-TDP), dissolved organic phosphorus (DOP = TDP-SRP), total nitrogen (TN = TKN+NOX), total organic nitrogen (TON = TKN-NH4) and dissolved organic nitrogen (DON = TDKN-NH4).

Results and Observations

Results of the chemical analyses performed on water samples collected from both test sites and analyzed by the District's Chemistry Laboratory are presented in Table 1. The following observations were made based on comparing untreated inflow against AquaLutions™-treated outflow samples.

1. AquaLutions™ was very effective at removing all forms of P, including TP, where 89% and 96% of inflow TP concentration was removed at test site #1 and #2, respectively. Percent P removal was somewhat higher at test site #2 compared to test site #1 for all forms of P. It is unclear whether this was due to the fact that all inflow P concentrations were higher at the second test site (i.e., there was more P to remove) or that the AquaFiber staff had the treatment process better optimized for P removal at the second location.
2. AquaLutions™ was moderately effective at removing TN, TKN, TDKN, TON and DON, where 36% and 55% of inflow TN concentration was removed at test site #1 and #2, respectively. Percent N removal was somewhat higher at test site #2 compared to test site #1 for all the above-mentioned forms of N. As noted above for P, it is unclear whether this was due to the fact that all these inflow N concentrations were higher at the second test site (i.e., there was more N to remove) or that the AquaFiber staff had the treatment process better optimized for removing these constituents at the second location.
3. AquaLutions™ was not very effective at reducing concentrations of NOX or NH4 at both test sites.
4. Outflow SO4 concentrations more than doubled at both test sites compared to their respective inflow concentrations.
5. AquaLutions™ removed virtually all of the Chlorophyll A and much of the Chlorophyll B and Pheophytin A at both test sites. Correspondingly, TURB was substantially reduced at both test sites.
6. AquaLutions™ caused a slight increase in COND and a slight decrease in pH at both test sites.

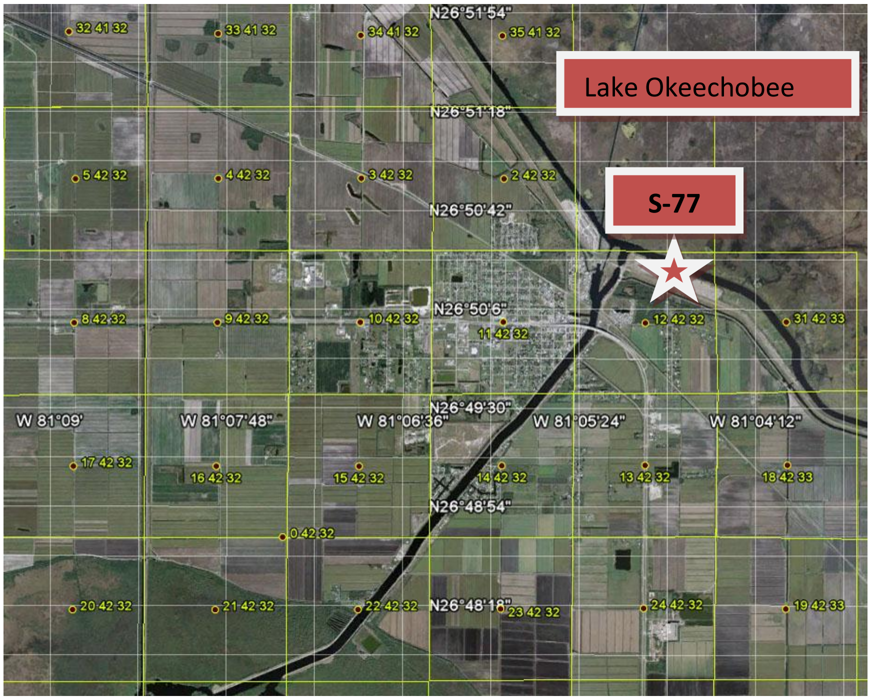

Figure 1. AquaLutions™ test site #1 located in the Lake Okeechobee Rim Canal upstream of S-77 on the Caloosahatchee River.

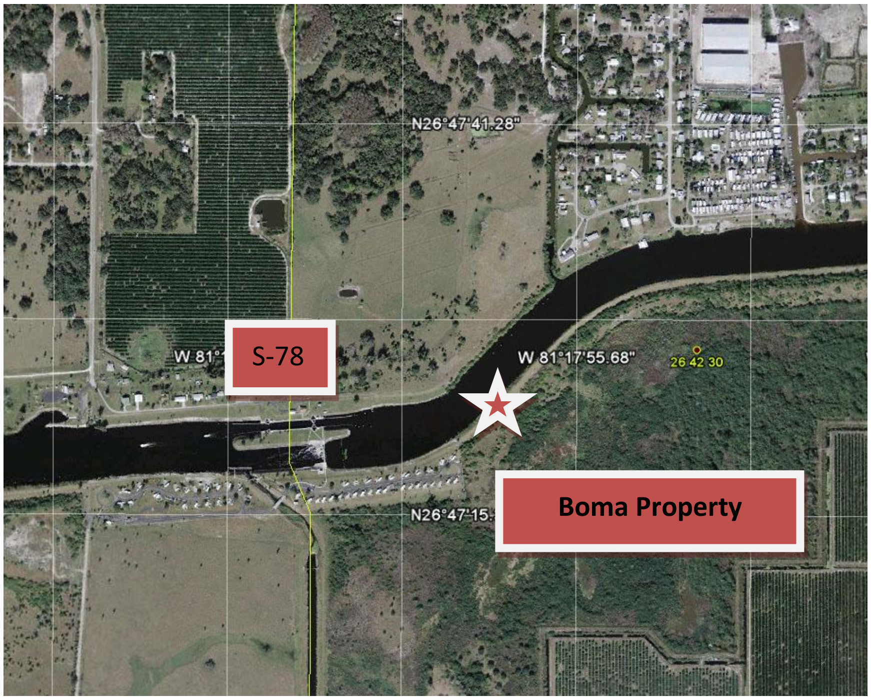

Figure 2. AquaLutions™ test site #2 located on the south side of the C-43 Canal (Caloosahatchee River) east of the S-78 Structure and adjacent to the Boma property near LaBelle, FL.

Figure 3. The AquaKnight™ mobile treatment unit that housed the AquaLutions™ treatment technology demonstrated during this pilot study.

Table 1. Results of chemical analysis of inflow and outflow water quality grab samples collected from two test sites during the AquaLutions™ treatment technology pilot study. All chemical analyses were performed by the District's Chemistry Laboratory.[†]

	TP	TDP	SRP	DOP	PP	TN	TKN	TDKN	TON	DON	NOX	NH4	SO4	Chlorophyll A	Chlorophyll B	Pheophytin A	TURB	COND	PH
TEST SITE #1 – S-77																			
Inflow	0.047	0.019	0.010	0.009	0.028	1.204	1.150	1.130	1.099	1.079	0.054	0.051	30	6.610	0.324	0.885	5.4	455	8.0
Outflow	0.005	0.003	0.002	0.001	0.002	0.765	0.710	0.560	0.667	0.517	0.055	0.043	74	0.134	0.160	0.288	1.4	480	7.4
TEST SITE #2 – S-78																			
Inflow	0.115	0.053	0.041	0.012	0.062	1.791	1.720	1.290	1.572	1.142	0.071	0.148	21	3.410	0.160	1.270	9.8	378	7.9
Outflow	0.005	0.002	0.002	0.000	0.003	0.799	0.730	0.590	0.596	0.456	0.069	0.134	92	0.053	0.089	0.160	1.9	412	6.9
% DIFFERENCE BETWEEN INFLOW AND OUTFLOW AT TEST SITE #1*																			
	-89%	-84%	-80%	-89%	-93%	-36%	-38%	-50%	-39%	-52%	2%	-16%	147%	-98%	-51%	-67%	-74%	5%	-8%
% DIFFERENCE BETWEEN INFLOW AND OUTFLOW AT TEST SITE #2*																			
	-96%	-96%	-95%	-100%	-95%	-55%	-58%	-54%	-62%	-60%	-3%	-9%	331%	-98%	-44%	-87%	-81%	9%	-12%

[†] Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L) => TDP - SRP; PP = particulate phosphorus (mg P/L) => TP - TDP; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TDKN = total dissolved Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (MG N/L) => TKN - NH4; DON = dissolved organic nitrogen (mg N/L) => TDKN - NH4; NOX = nitrate+nitrite-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); SO4 = sulfate (mg/L); Chlorophyll A (mg/L), Chlorophyll B (mg/L), Pheophytin A (mg/L); TURB = turbidity (NTU); COND = conductivity (µS/cm); PH = pH (s.u.)

* % difference = [(outflow-inflow)/inflow]*100

Results of AquaKnight™ Mobile Treatment Unit Demonstration at Two Sites on the Caloosahatchee River, Florida

SFWMD Contract #4600002773

January 15, 2013

AquaFiber Technologies Corporation
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Image AquaFiber: Caloosahatchee River at the S-78 Lock

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& Business Development

Executive Summary

AquaFiber was contracted by the SFWMD to demonstrate the effectiveness of its AquaLutions™ technology at reducing total phosphorus (TP) and total nitrogen (TN), with special interest in reduction of Dissolved Organic Nitrogen (DON) concentrations, from waters of the Caloosahatchee River, Florida. To accomplish this, AquaFiber deployed its AquaKnight™ mobile unit to conduct a short-term demonstration project at two locations along the Caloosahatchee River. AquaFiber was deployed at each field location for 5 days, which provided three consecutive days to fine-tune technology applications and treatment approaches to optimize nutrient removal efficiencies. AquaLutions™ was designed for effective and efficient reduction of TP and TN in high legacy-load lakes with high productivity and water turbidity. While the water quality and intermittent flows on the Caloosahatchee River during field deployment and testing did not represent optimal conditions to showcase the AquaLutions™ technology, AquaFiber was still able to optimize its process to achieve excellent TP, TN and DON reduction results.

During the two field deployments, AquaKnight™ pumped a total of 43,756 gallons of surface water and treated it using AquaLutions™. Influent raw water *vs*. post-treatment water quality results from AquaFiber (with water quality analyses provided by Flowers Chemical Laboratories), in conjunction with independent water testing and analyses by the SFWMD, confirmed a successful dual-nutrient reduction demonstration. AquaFiber did not test for Dissolve Organic Nitrogen (DON), but SFWMD tested this parameter and the results are provided. The Best Results from the combined data sets are provided below (rounded to nearest integer):

AquaFiber/SFWMD Combined Data Summary

Site 1-S77

- Water Treated = 24,938 gallons (Average 8,312.7 gallons per day)
- TSS Reduction = 92%(1)
- TP Reduction = 89%(2)
- TN Reduction = 45%(2)
- DON Reduction = 52%(3)

Site 2-S78

- Water Treated = 18,818 gallons (Average 6,272.7 gallons per day)
- TSS Reduction = 93%(1)
- TP Reduction = 96%(2)
- TN Reduction = 55%(2)
- DON Reduction = 60%(3)

Executive Summary Notes

(1) Daily TSS reduction from composite water samples measured by AquaFiber in field.

(2) Best results of AquaFiber and SFWMD combined TP and TN reduction data. Water chemistry analyzed by Flowers Chemical Laboratories, Altamonte Springs, FL for AquaFiber and SFWMD Laboratory for District data. A summary of Flowers water chemistry data is provided in narrative with Flowers Laboratory reports attached in Appendix 2.

(3) Dissolved Organic Nitrogen (DON) data collected on Treatment Day 2 at both locations provided by SFWMD Laboratory, West Palm Beach, FL. A full summary of SFWMD water chemistry data is provided in Appendix 3.

Introduction

AquaFiber Technologies Corporation (AquaFiber) was approached by the South Florida Water Management District (SFWMD) in 2012 to discuss whether our dual-nutrient remediation technology (AquaLutions™) would provide a nutrient reduction technology option for mitigating high-volume, high-nutrient concentration surface water discharges from Lake Okeechobee into the Caloosahatchee River, Florida. AquaLutions™ was specifically designed as a whole-lake restoration tool for hypereutrophic lakes experiencing algae/cyanobacteria blooms and resulting high loads of total suspended solids (TSS). The technology is flexible, adaptable and able to be adjusted to a wide range of water quality conditions. During AquaKnight™ field deployment and water testing, water quality and flow did not represent optimal conditions to showcase the capacity of the AquaLutions™ technology. Managed water discharges were intermittent during the testing period, nutrient concentrations were low and overall water turbidity was low. Even with these challenges, AquaFiber was still able to optimize its process to achieve excellent TP, TN and DON reduction results.

AquaLutions™ has been proven as a successful and safe dual-nutrient remediation technology at a commercial-scale facility on the shores of Lake Jesup, Florida as part of a technology-demonstration contract with the St. Johns River Water Management District (SJRWMD).

The Caloosahatchee River represented a more complicated application for AquaLutions™ than an impaired lake scenario. The 75 mile long Caloosahatchee River is influenced by a watershed basin that encompasses approximately 1,339 square miles. Caloosahatchee River water quality is very dependent on surface water inputs from both the watershed and managed water discharges from Lake Okeechobee. These managed discharges result in periodic high volume and flows. Three locks (S-77, S-78, and S-79) control water volume and flow rate as the water flows from east to west eventually discharging into the Gulf of Mexico at San Carlos Bay. According to the Final TMDL Report for the Caloosahatchee Estuary (FDEP, 2009) nitrogen loading is 52.9% from Lake Okeechobee and 47.1% from the C-43 canal drainage basin. Phosphorus loading is 31.3% from Lake Okeechobee and 68.7% from the C-43 canal drainage basin. These average load contributions are highly variable from year to year. High nutrient loading events are associated with high volume and flow events from managed discharges to the river.

AquaFiber was contracted by the SFWMD to demonstrate the effectiveness of its AquaLutions™ technology at reducing total phosphorus (TP) and total nitrogen (TN), with special interest in reduction of Dissolved Organic Nitrogen (DON) concentrations from waters of the Caloosahatchee River, Florida. To accomplish this, AquaFiber made three pre-contract field trips to evaluate sampling sites, collect grab samples of surface water and conduct bench-scale water testing at AquaFiber's internal lab facility. Pursuant to South Florida Water Management District (SFWMD) Contract No. 4600002773 and subsequent Memorandum of Agreement (MOA) executed on November 21, 2012, AquaFiber Technologies Corporation (AquaFiber) operated its mobile water treatment unit called AquaKnight™ at two sites on the Caloosahatchee River (River) to demonstrate the effectiveness of its proprietary AquaLutions™ dual-nutrient removal process to reduce total phosphorus (TP) and total nitrogen (TN) concentrations from the surface waters of the River. This report documents the methodology and results of those trials.

Methods

Two sites were predetermined by the MOA as water sampling and treatment locations. These are shown in Figure 1.

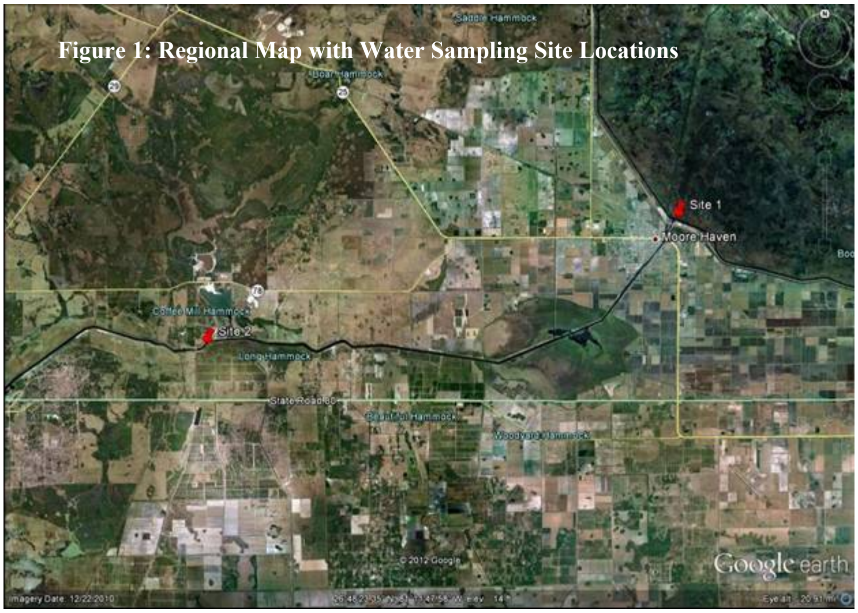


Figure 1: Regional Map with Water Sampling Site Locations

The first site (Site #1-S77) was along the river (also known as C-43 Canal) upstream of the S-77 Control Structure at the Alvin Ward Park in Moore Haven, FL (Figure. 2).

Figure 2:   Site #1-S77 Location Map – Alvin Ward Park, upstream of S-77, Moore Haven, FL


Figure 3: Site #2-S78 Location Map – Ortona South Camp ground, upstream of S-78, near Port Labelle, FL

The second site (Site #2-S78) was along the River, upstream of the S-78 Control Structure, adjacent to the Ortona South Campground, near Port Labelle, FL (Figure 3). AquaKnight™ was deployed at each site for five consecutive days. The first five-day deployment spanned November 26, 2012 through November 30, 2012. The second deployment, spanned December 3, 2012 through December 7, 2012.

The first and last day of each five-day session was dedicated to equipment transport, preparation, system calibration and cleanup. Water was flowed and treated with AquaLutions™ during the three consecutive days for up to eight hours per day (Water Treatment Days 1-3). Table 1 and Table 2 show the operational schedule for each Site.

Table 1: Operational Schedule, Site #1-S77

Date	Activity
11/26/2012	Transport & Setup
11/27/2012	**Water Treatment Day 1**
11/28/2012	**Water Treatment Day 2**
11/29/2012	**Water Treatment Day 3**
11/30/2012	Disassembly & Transport

Table 2: Operational Schedule, Site #2-S78

Date	Activity
12/3/2012	Transport & Setup
12/4/2012	**Water Treatment Day 1**
12/5/2012	**Water Treatment Day 2**
12/6/2012	**Water Treatment Day 3**
12/7/2012	Disassembly & Transport

Figures 4 and 5 show AquaKnight™ deployed at each field location.


Figure 4: Site #1-S77: AquaKnight™ with support equipment.


Figure 5: Site #2-S78: AquaKnight™ with support equipment.

Water was collected from the River and delivered to the AquaKnight™ using a submersible pump . The water intake was regulated at approximately one (1) meter in depth using a float (Figure 6).


Figure 6: Surface Water Float & Intake Apparatus.

Inside the AquaKnight™, water was treated using AquaLutions™ at a targeted rate of approximately 5,000 gallons per day. However, the actual flow rate varied from day-to-day depending on the influent water quality and observed results. During each of the 3-day treatment period, AquaFiber staff made AquaLutions™ process adjustments to optimize nutrient removal efficiency and respond to changing water quality and flow conditions

Individual, 500ml grab samples of the raw influent and treated effluent waters were collected hourly during operation. The individual samples were combined to create a daily composite water sample. Using a Hach DR/980 Portable Colorimeter, AquaFiber field-tested both the grab and composite samples to determine the Total Suspended Solids (TSS) concentrations. Additional field parameters such as: pH, temperature, salinity, conductivity and dissolved oxygen concentrations were also gathered using handheld meters (see AquaFiber Field Data Table - Appendix 1).

At the end of each operational day, AquaFiber collected 50ml samples of the daily influent and effluent composite water in sample bottles prepared by Flowers Chemical Laboratories, Incorporated (Flowers). Flowers is Accredited by the National Environmental Laboratory Accreditation Conference (NELAC), the most comprehensive quality standards in the country. This accreditation authorizes Flowers to submit data to the Florida Department of Environmental Protection under Florida Administrative Code (FAC17-160). Flowers has also been certified by the State of Florida's Department of Environmental Regulation and the Department of Health for more than 20 years.

Composite water samples were refrigerated and delivered to Flowers on the fifth day of each field deployment. Flowers analyzed the composite samples for TP (total phosphorus as P) and TN (NO_3+NO_2+TKN; all as N) concentrations using EPA methods 351.2, 353.2, and 365.2 for surface waters.

In addition to AquaFiber’s water-quality analyses, SFWMD staff visited each location on Treatment Day 2 to conduct a third-party water-quality analysis. SFWMD technicians collected two (2) liters of raw influent and two (2) liters of post-treatment effluent from each Site during operation, and conducted field- and laboratory analyses of water quality similar to those of AquaFiber’s as described above.

Results

Water Flow & Treatment

Figures 7 and 8 present daily water flow and treatment in gallons per day (GPD) for each treatment day at each of the two sites. Water flow rates and total volume of water treated were variable from day-to-day depended on influent water quality and observed results. Flow rates were adjusted as needed to evaluate and optimize treatment efficiency. Based on 4 years of operations on Lake Jesup, AquaFiber has demonstrated that the AquaLutions™ process is not dependent on treatment flow rate for commercial scale operations and optimal efficiency.

Figure 7: Water Flow and Treatment, Site #1-S77

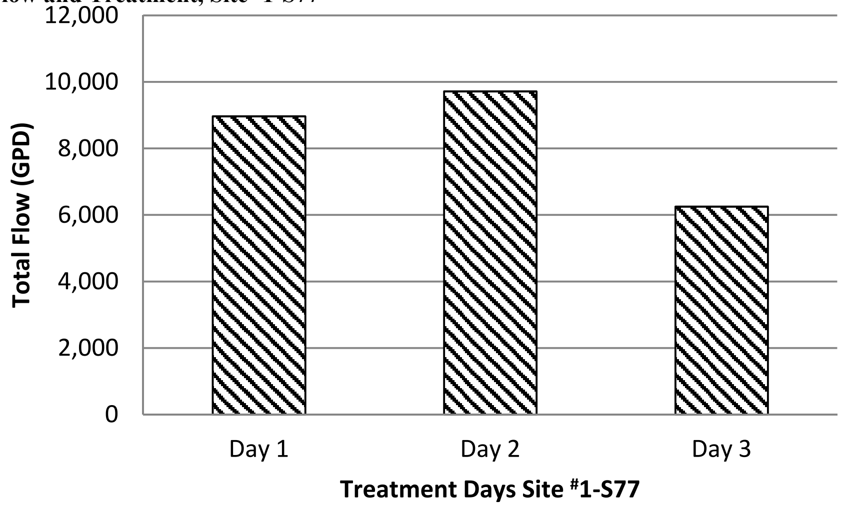
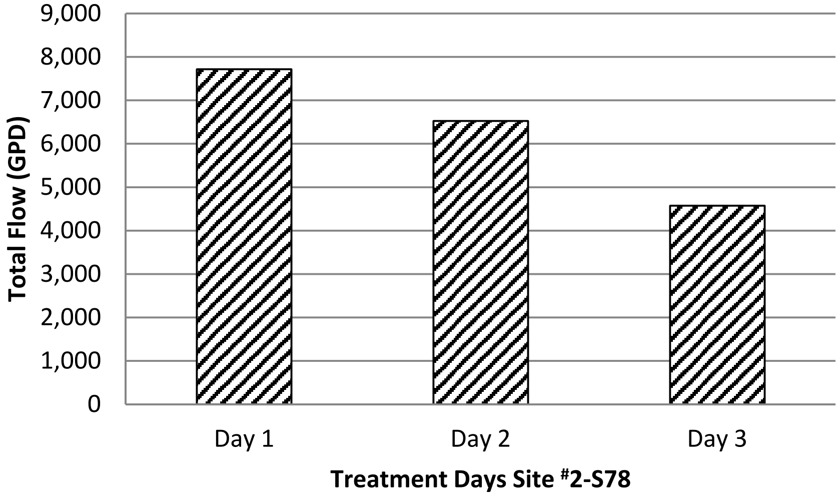


Figure 8: Water Flow and Treatment, Site #2-S78



Total Suspended Solids (TSS) Reduction

TSS removal for Site #1-S77 is detailed in Tables 3-5. TSS removal efficiency is provided for each hourly water sample (grab samples) as well as for the end-of-day composite sample. Influent TSS concentrations for hourly grab samples at Site #1-S77 ranged from 5 mg/L to 14 mg/L during the 3-day treatment period (measured with hand-held meters in field). Daily composite water concentrations for influent water TSS were 8mg/L, 11mg/L and 12 mg/L for treatment days 1, 2 and 3 respectively. Daily TSS removal efficiencies for the composite water sample ranged from 25% to 92%, with best results achieved on Day 3 of the treatment period. AquaFiber TSS data for daily and composite water samples were analyzed in the field using a hand-held meter. TSS data collected by the SFWMD showed similar results from Treatment Day 3 water chemistry analysis (74% TSS reduction at Site #1-S77 and 81% TSS reduction for Site #2-S78). See Appendix 3 for a Table of SFWMD water chemistry data.

Table 3: TSS Data, Treatment Day 1, Site #1-S77

Sample Time (Hours)	Influent TSS (mg/L)	Effluent TSS (mg/L)	TSS Δ (mg/L)	TSS Removal Efficiency (%)
1000	12	7	5	42
1100	8	7	1	13
1200	9	4	5	56
1300	5	4	1	20
1400	9	5	4	44
1500	5	5	0	0
1600	8	6	2	25
1700	10	4	6	60
Composite	**8**	**6**	**2**	**25**

Table 4: TSS Data, Treatment Day 2, Site #1-S77

Sample Time (Hours)	Influent TSS (mg/L)	Effluent TSS (mg/L)	TSS Δ (mg/L)	TSS Removal Efficiency (%)
1000	12	4	8	67
1100	8	4	4	50
1200	12	3	9	75
1300	13	2	11	85
1400	10	5	5	50
1500	11	3	8	73
1600	11	3	8	73
Composite	**11**	**3**	**8**	**73**

Table 5: TSS Data, Treatment Day 3, Site #1-S77

Sample Time (Hours)	Influent TSS (mg/L)	Effluent TSS (mg/L)	TSS Δ (mg/L)	TSS Removal Efficiency (%)
1000	12	0	12	100
1100	10	2	8	80
1200	13	1	12	92
1300	12	2	10	83
1400	14	1	13	93
1500	11	1	10	91
1600	10	2	8	80
Composite	**12**	**1**	**11**	**92**

Best Result

TSS removal for Site $^{\#}$2-S78 is detailed in Tables 6-8. TSS removal efficiency is provided for each hourly water sample (grab samples) as well as for the end-of-day composite sample. Influent TSS at Site $^{\#}$2-S78 ranged from 12 mg/L to 17 mg/L during the 3-day treatment period (measured with hand-held meters in field). Daily composite water concentrations for Influent water TSS were 13mg/L, 12mg/L and 15 mg/L for treatment days 1, 2 and 3 respectively. Daily TSS removal efficiencies for the composite water sample ranged from 15% to 93%, with best results achieved on Day 3 of the treatment period. Water quality data for daily composite water samples were analyzed in the laboratory by Flowers Chemical Laboratories Inc. See Appendix 3 for a Table of SFWMD water chemistry data.

Table 6: TSS Data, Day 1, Site #2-S78

Sample Time (Hours)	Influent TSS (mg/L)	Effluent TSS (mg/L)	TSS Δ (mg/L)	TSS Removal Efficiency (%)
1000	15	10	5	33
1100	15	11	4	27
1200	13	13	0	0
1300	13	11	2	15
1400	17	14	3	18
1500	12	11	1	8
1600	15	14	1	7
Composite	**13**	**11**	**2**	**15**

Table 7: TSS Data, Treatment Day 2, Site #2-S78

Sample Time (Hours)	Influent TSS (mg/L)	Effluent TSS (mg/L)	TSS Δ (mg/L)	TSS Removal Efficiency (%)
1000	14	4	10	71
1100	12	3	9	75
1200	12	3	9	75
1300	13	3	10	77
1400	17	2	15	88
1500	12	2	10	83
1600	12	3	9	75
Composite	**12**	**2**	**10**	**83**

Table 8: TSS Data, Treatment Day 3, Site #2-S78

Sample Time (Hours)	Influent TSS (mg/L)	Effluent TSS (mg/L)	TSS Δ (mg/L)	TSS Removal Efficiency (%)
1000	17	4	13	76
1100	14	2	12	86
1200	13	2	11	85
1300	14	0	14	100
1400	13	1	12	92
Composite	**15**	**1**	**14**	**93**

Best Result

Nutrient Reduction Results

Site #1-S77: Total Phosphorus (TP)

Detailed daily nutrient removal results are summarized for Site #1-S77 in Tables 9-11. For Site #1-S77, TP removal efficiency analyzed from the daily composite water sample ranged from 14.8% to 89.4%, with the best TP reduction efficiency achieved on Treatment Day 2 from the SFWMD analysis (Table 9).

Table 9: Total Phosphorus Data, Site #1-S77

Day	TP Influent (mg/L)	TP Effluent (mg/L)	TP Δ (mg/L)	TP Removal Efficiency (%)
1	0.0520	0.0443	0.0077	14.8(1)
2	0.0384	0.0115	0.0269	70.1(1)
3	0.0419	0.0122	0.0297	70.9(1)
2	0.047	0.005	0.042	**89.4(2)**

Site #1-S77: Total Nitrogen (TN)

For Site #1-S77, TN removal efficiency analyzed from the daily composite water sample ranged from 3.4% to 45.1%, with the best TN reduction efficiency achieved on Treatment Day 3 (Table 10).

Table 10: Total Nitrogen Data, Site 1#1-S77

Day	TKN Influent (mg/L)	$NO_2 + NO_3$ Influent (mg/L)	TN Influent (mg/L)	TKN Effluent (mg/L)	$NO_2 + NO_3$ Effluent (mg/L)	TN Effluent (mg/L)	TN Δ (mg/L)	TN Removal Efficiency (%)
1	1.40	0.0579	1.46	1.35	0.0524	1.41	0.050	3.4(1)
2	1.38	0.0534	1.43	0.856	0.0556	0.911	0.519	36.3(1)
3	1.06	0.0562	1.11	0.551	0.0581	0.609	0.501	**45.1(1)**
2	1.150	0.054	1.204	0.710	0.055	0.765	0.439	36.5(2)

Site #1-S77 Notes

(1) Results of AquaFiber's daily composite water samples analyzed by Flowers Chemical Laboratories (Flower Chemical Laboratory reports are provided in Appendix 2).

(2) Results of Treatment Day 2 composite sample taken by and verified by SFWMD Laboratory. A full summary of SFWMD water chemistry data is provided in Appendix 3. Nutrient reduction data in Appendix 3 are rounded by SFWMD to nearest integer. For reporting purposes in Table above, nutrient-removal percentages shown are calculated to one decimal point.

Site #2-S78: Total Phosphorus (TP)

Detailed daily nutrient removal results are summarized for Site #2-S78 in Tables 11-12. For Site #2-S78, TP removal efficiency analyzed from the daily composite water sample ranged from 14.0% to 96%, with the best TP reduction efficiency achieved on Treatment Day 2 from the SFWMD analysis (Table 11).

Table 11: Total Phosphorus Data, Site #2-S78

Day	TP Influent (mg/L)	TP Effluent (mg/L)	TP Δ (mg/L)	TP Removal Efficiency (%)
1	0.0687	0.0591	0.0096	14.0(1)
2	0.0704	0.0232	0.0472	67.1(1)
3	0.0723	0.0110	0.0613	84.8(1)
2	0.115	0.005	0.010	**95.7(2)**

Site #2-S78: Total Nitrogen (TN)

For Site #2-S78, TN removal efficiency analyzed from the daily composite water sample ranged from 5.2% to 55.4%, with the best TN reduction efficiency achieved on Treatment Day 2 from the SFWMD analysis (Table 12).

Table 12: Total Nitrogen Data, Site #2-S78

Day	TKN Influent (mg/L)	$NO_2 + NO_3$ Influent (mg/L)	TN Influent (mg/L)	TKN Effluent (mg/L)	$NO_2 + NO_3$ Effluent (mg/L)	TN Effluent (mg/L)	Δ TN (mg/L)	TN Removal Efficiency (%)
1	1.66	0.0779	1.74	1.57	0.0770	1.65	0.09	5.2(1)
2	1.60	0.0931	1.69	1.05	0.0884	1.14	0.55	32.5(1)
3	1.59	0.0905	1.68	0.949	0.0693	1.02	0.66	39.3(1)
2	1.720	0.071	1.791	0.730	0.069	0.799	0.992	**55.4(2)**

Site #2-S78 Notes

(1) Results of AquaFiber's daily composite water samples analyzed by Flowers Chemical Laboratories (Flower Chemical Laboratory reports are provided in Appendix 2).

(2) Results of Treatment Day 2 composite sample taken by and verified by SFWMD Laboratory. A full summary of SFWMD water chemistry data is provided in Appendix 3. Nutrient reduction data in Appendix 3 are rounded by SFWMD to nearest integer. For reporting purposes in Table above, nutrient-removal percentages shown are calculated to one decimal point.

AquaLutions™ Dual-Nutrient Removal Performance Summary and Discussion

AquaFiber was contracted by the SFWMD to demonstrate the effectiveness of its AquaLutions™ technology at reducing total phosphorus (TP) and total nitrogen (TN), with special interest in reduction of Dissolved Organic Nitrogen (DON) concentrations from waters of the Caloosahatchee River, Florida. The AquaLutions™ process was designed specifically to restore water bodies impacted by high nutrient concentrations, high turbidity levels, and high nutrient legacy loads. In order to adapt AquaLutions™ to the lower nutrient, low turbidity and high flow characteristics of the Caloosahatchee River, AquaFiber made subtle changes to its process and technology hardware to test nutrient removal efficiencies.

Although the SFWMD-AquaFiber contract focused on TN and TP reduction, with specific interest in DON reduction, the SFWMD conducted a more comprehensive water quality analysis on both influent and effluent water. These data show reductions in almost all nutrient categories. One exception was a significant observed increase in sulfate (SO_4) concentration.

The AquaFiber pilot project demonstrated the effectiveness of AquaLutions™. TSS removal efficiencies reached as high as 93%. Independent water chemistry from Flowers Chemical Laboratories and SFWMD on the composite samples showed TP and TN removal efficiency as high as 96% and 55%, respectively. DON removal rates were 52% at Site $^{\#}$1 and 60% at Site $^{\#}$2.

This short-duration field demonstration showcases the potential efficacy of the AquaLutions™ dual-nutrient removal process. After 4 years of operations at a commercial scale on the shores of Lake Jesup (with up to 6.5 MGD of water flow and treatment), AquaFiber has demonstrated that AquaLutions™ is effective, efficient, scalable to a large range of water volumes and flows, and requires a small land footprint (able to treat 1.0 MGD on 1 acre of land treatment area). AquaLutions™ delivers a unique combination of system-performance characteristics that make it a dual-nutrient remediation technology that is both cost-effective and adaptable to client needs. The design and construction of a regional-scale nutrient remediation facility using AquaLutions™ requires comprehensive study and integration of many factors. Considerations include, but are not limited to, short- and long-term project goals, facility site locations, water quality, hydrology, AquaLutions™ technology configuration and integration, and available funding for both capital construction and operations. In regards to the SO_4 issue, AquaFiber believes that this was a process anomaly that can be addressed and easily resolved in future Caloosahatchee field studies or in the design & engineering of a regional dual-nutrient remediation facility.

Based on 4-years of performance at its Lake Jesup facility, AquaFiber has demonstrated its ability to fine-tune our proprietary technologies and processes in the design and engineering stages of a project to ensure that post-treated effluent water meets targeted TP/TN concentration goals and other environmental safety considerations. AquaLutions™ is scalable to handle very large volumes of water, is adaptable to daily, seasonal and annual changes in water quality parameters, and can be fine-tuned to meet client needs and expectations.

Appendix 1

AquaFiber Field Data

Site #1-S77: Treatment Day 1

AquaFiber Field Data, Site #1-S77, Treatment Day 1 – Influent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	66.7	12	7.13	16.62	1.6	55
2	1100	66.5	8	7.20	9.92	1.6	68
3	1200	66.8	9	7.12	12.70	1.6	73
4	1300	67.5	5	7.27	8.59	1.5	na
5	1400	67.2	9	7.22	7.72	1.6	67
6	1500	68.5	5	7.26	7.84	1.6	97
7	1600	66.6	8	7.24	7.50	1.6	66
8	1700	66.9	10	7.26	5.94	1.6	67
Composite Sample		68.1	8	7.30	7.26	1.6	70

AquaFiber Field Data, Site #1-S77, Treatment Day 1 – Effluent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	67.4	7	7.23	22.39	1.6	47
2	1100	67.6	7	7.26	14.66	1.6	61
3	1200	67.9	4	7.27	13.64	1.6	na
4	1300	68.3	4	7.21	10.48	1.6	na
5	1400	67.9	5	7.33	9.66	1.6	na
6	1500	68.7	5	7.37	8.88	1.6	88
7	1600	68.5	6	7.31	6.39	1.6	61
8	1700	69.8	4	7.3	6.33	1.6	59
Composite Sample		70.1	6	7.39	9.35	1.6	60

Site #1-S77: Treatment Day 2

AquaFiber Field Data, Site #1-S77, Treatment Day 2 – Influent

Sample	Time	Temperature (°F)	TSS (mg/L)	pH	DO (mg/L)	Salinity (mS)	Conductivity (mV)
1	1000	66.9	12	7.36	3.02	1.6	75
2	1100	67.5	8	7.28	7.35	1.6	70
3	1200	67.2	12	7.23	5.51	1.6	66
4	1300	67.9	13	7.26	7.67	1.6	67
5	1400	66.9	10	7.24	5.42	1.6	64
6	1500	66.7	11	7.21	5.57	1.6	59
7	1600	67.1	11	7.27	3.88	1.6	57
Composite Sample		70.9	11	7.34	5.24	1.6	63mV

AquaFiber Field Data, Site #1-S77, Treatment Day 2 – Effluent

Sample	Time	Temperature (°F)	TSS (mg/L)	pH	DO (mg/L)	Salinity (mS)	Conductivity (mV)
1	1000	67.9	4	6.71	7.34	1.6	84
2	1100	68.3	4	6.66	9.57	1.6	92
3	1200	68.3	3	6.62	7.03	1.6	93
4	1300	68.3	2	6.62	8.43	1.6	90
5	1400	68.2	5	6.61	6.36	1.6	87
6	1500	67.9	3	6.54	6.55	1.6	85
7	1600	68.1	3	6.64	4.82	1.6	82
Composite Sample		69	3	6.7	6.95	1.6	90

Site #1-S77: Treatment Day 3

AquaFiber Field Data, Site #1-S77, Treatment Day 3 – Influent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	65.9	12	7.32	2.66	1.6	70
2	1100	65.1	10	7.45	3.45	1.5	50
3	1200	67.4	13	7.29	3.61	1.6	65
4	1300	68	12	7.27	2.04	1.6	74
5	1400	68.9	14	7.28	3.03	1.6	75
6	1500	69.7	11	7.26	2.46	1.6	71
7	1600	69.8	10	7.42	3.03	1.6	87
Composite Sample		71	12	7.42	2.98	1.6	61

AquaFiber Field Data, Site #1-S77, Treatment Day 3 – Effluent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	67.3	0	6.71	4.26	1.6	80
2	1100	67.1	2	6.77	4.62	1.6	77
3	1200	68.4	1	6.72	5.26	1.6	85
4	1300	68.7	2	6.75	4.01	1.6	90
5	1400	69.6	1	6.76	4.46	1.6	89
6	1500	70.2	1	6.72	3.85	1.6	88
7	1600	71.5	2	6.72	4.35	1.6	97
Composite Sample		71.7	1	6.77	4.46	1.6	83

Site #2-S78: Treatment Day 1

AquaFiber Field Data, Site #2-S78, Treatment Day 1 – Influent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	68.3	15	7.53	1.04	1.5	67
2	1100	69.6	15	7.31	4.26	1.5	70
3	1200	70.2	13	7.3	5.45	1.5	98
4	1300	69.4	13	7.38	3.29	1.5	63
5	1400	70.2	17	7.34	5.28	1.5	64
6	1500	70.6	12	7.29	4.7	1.6	73
7	1600	70.9	15	7.38	5.19	1.5	67
Composite Sample		73.9	13	7.54	6.51	1.5	50

AquaFiber Field Data, Site #2-S78, Treatment Day 1 – Effluent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	69.4	10	7.49	3.02	1.5	62
2	1100	70.4	11	7.42	5.77	1.5	66
3	1200	70.6	13	7.39	8.26	1.5	71
4	1300	70.2	11	7.51	5.35	1.5	55
5	1400	70.9	14	7.43	6.99	1.5	57
6	1500	71.7	11	7.45	6.38	1.5	65
7	1600	71.5	14	7.47	6.67	1.5	62
Composite Sample		74.6	11	7.6	6.8	1.5	45

Site $^{\#}$2-S78: Treatment Day 2

AquaFiber Field Data, Site $^{\#}$2-S78, Treatment Day 2 – Influent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	68.8	14	7.41	3.61	1.5	43
2	1100	70.3	12	7.34	6.64	1.5	58
3	1200	71.6	12	7.31	7.95	1.5	80
4	1300	71.7	13	7.34	5.99	1.5	61
5	1400	70.4	17	7.38	5.12	1.5	58
6	1500	70.4	12	7.37	8.69	1.5	54
7	1600	70.7	12	7.32	5.5	1.5	56
Composite Sample		72.9	12	7.51	5.8	1.5	44

AquaFiber Field Data, Site $^{\#}$2-S78, Treatment Day 2 – Effluent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	71.1	4	7.26	8.02	1.6	60
2	1100	71.3	3	7.13	9.25	1.6	67
3	1200	72.4	3	7.1	8.77	1.6	77
4	1300	72	3	7.13	7.5	1.6	63
5	1400	71.8	2	7.09	6.99	1.6	62
6	1500	71.7	2	7.14	8.96	1.6	57
7	1600	71.9	3	7.11	6.65	1.6	58
Composite Sample		73.1	2	7.33	7.01	1.6	50

Site #2-S78: Treatment Day 3

AquaFiber Field Data, Site #2-S78, Treatment Day 3 – Influent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	68.2	17	7.35	7.13	1.5	44
2	1100	67.7	14	7.17	6.87	1.5	48
3	1200	68.5	13	7.17	5.68	1.5	53
4	1300	69.5	14	7.25	4.52	1.5	67
5	1400	69.8	13	7.2	5.56	1.5	55
Composite Sample		70.4	15	7.26	6.15	1.5	57

AquaFiber Field Data, Site #2-S78, Treatment Day 3 – Effluent

Sample	Time	Temperature	TSS	pH	DO	Salinity	Conductivity
		(°F)	(mg/L)		(mg/L)	(mS)	(mV)
1	1000	69.8	4	6.23	8.27	1.5	87
2	1100	69.4	2	6.02	8.56	1.5	96
3	1200	69.9	2	6.12	7.35	1.5	98
4	1300	70.9	0	6.17	6.96	1.5	97
5	1400	70.5	1	6.19	6.14	1.6	94
Composite Sample		70.9	1	6.18	6.5	1.5	95

Appendix 2

AquaFiber/Flowers Chemical Laboratories, Inc.
Laboratory Reports

Provided as PDF copies under separate cover in electronic correspondences
Included in Appendix in Written Report Copy

Appendix 3

South Florida Water Management District Data & Observations

AquaFiber Demonstration – SFWMD Metadata & Worksheet Descriptions

Project Name:	New Alternative Treatment Technologies (NATA) Program
Subproject Name:	AquaFiber Demonstration Study
Study Objectives/Description:	The purpose of this project was to demonstrate the efficacy of the AquaFiber Technologies Corporation's patented process (AquaLutions™) to remove total phosphorus and total nitrogen from surface water.
Project Reports:	
PI / Contractor:	Mike Chimney / AquaFiber Technologies Corporation [AFTC]
Other Project Members & Roles:	Orlando Diaz- water sample collection/field processing
	Odi Villapando- water sample collection/field processing
	Kim O'Dell - water sample collection/field processing
Study Area(s):	The demonstration was conducted at the District's S-77 and S-78 structures on the C-43 canal.
Sampling Locations:	Inflow (before treatment) and outflow (after treatment) samples were collected at the two demonstration sites.
	LIMS codes for AquaFiber treatments:
	AF_IN = raw water inflow to the AquaKnight trailer
	AF_OUT = processed outflow water from the AquaKnight trailer
Methods:	AFTC provided its AquaKnight™ mobile treatment unit for 10 working days. The trailer was deployed for 5 days at each of the two demonstration sites. The District obtained grab water quality samples on the final day of operation at each site. AFTC personnel collected the samples from within the AquaKnight trailer and provided them to the District sampling crew.
Data Collection Start Date:	November 26, 2012
Data Collection End Date:	December 6, 2012

Frequency of Data Collection:	One set of unreplicated inflow and outflow grab samples were collected on a single date at each of the two demonstration sites.
Data Repository:	Database: limsp; Table: SAMPLE_RESULTS_VW; Project: PRODTEST
Variables [units of measure]:	DON = dissolved organic nitrogen (mg N/L) => TDKN - NH4
	DOP = dissolved organic phosphorus (mg P/L) => TDPO4 - OPO4
	LCOND = lab conductivity (µS/cm)
	LPH = lab pH (s.u.)
	NH4 = ammonia nitrogen (mg N/L)
	NOx = nitrate + nitrite nitrogen (mg N/L)
	OPO4 = soluble reactive phosphorus (mg P/L)
	PP = particulate phosphorus (mg P/L) => TPO4 - TDPO4
	SO4 = sulfate (mg/L)
	TDKN = total dissolved Kjeldahl nitrogen (mg N/L)
	TDPO4 = total dissolved phosphorus (mg P/L)
	TKN = total Kjeldahl nitrogen (mg N/L)
	TN = total nitrogen (mg N/L) => TKN + NOx
	TON = total organic nitrogen (mg N/L) => TKN - NH4
	TOTFE - total iron (mg/L)
	TPO4 = total phosphorus (mg P/L)
	TURB = turbidity (NTU)
Data Calculations:	See notes in Variable list for DON, DOP, PP, TN and TON.
Data Compiled By:	Mike Chimney
Data Reviewed By:	Mike Chimney
Workbook Name:	#N/A

SFWMD Summary Water Chemistry Data for the AquaFiber Demonstration Project

Results of chemical analysis of inflow and outflow water quality grab samples collected from two test sites during the AquaLutions™ treatment technology pilot study. All chemical analyses were performed by the District's Chemistry Laboratory.[†]

	TP	TDP	SRP	DOP	PP	TN	TKN	TDKN	TON	DON	NOX	NH4	SO4	Chlorophyll A	Chlorophyll B	Pheophytin A	TURB	COND	PH
TEST SITE #1 – S-77																			
Inflow	0.047	0.019	0.010	0.009	0.028	1.204	1.150	1.130	1.099	1.079	0.054	0.051	30	6.610	0.324	0.885	5.4	455	8.0
Outflow	0.005	0.003	0.002	0.001	0.002	0.765	0.710	0.560	0.667	0.517	0.055	0.043	74	0.134	0.160	0.288	1.4	480	7.4
TEST SITE #2 – S-78																			
Inflow	0.115	0.053	0.041	0.012	0.062	1.791	1.720	1.290	1.572	1.142	0.071	0.148	21	3.410	0.160	1.270	9.8	378	7.9
Outflow	0.005	0.002	0.002	0.000	0.003	0.799	0.730	0.590	0.596	0.456	0.069	0.134	92	0.053	0.089	0.160	1.9	412	6.9

% DIFFERENCE BETWEEN INFLOW AND OUTFLOW AT TEST SITE #1*

-89%	-84%	-80%	-89%	-93%	-36%	-38%	-50%	-39%	-52%	2%	-16%	147%	-98%	-51%	-67%	-74%	5%	-8%

% DIFFERENCE BETWEEN INFLOW AND OUTFLOW AT TEST SITE #2*

-96%	-96%	-95%	-100%	-95%	-55%	-58%	-54%	-62%	-60%	-3%	-9%	331%	-98%	-44%	-87%	-81%	9%	-12%

[†] Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L) => TDPO4 - OPO4; PP = particulate phosphorus (mg P/L) => TPO4 - TDPO4; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TDKN = total dissolved Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (MG N/L) => TKN - NH4; DON = dissolved organic nitrogen (mg N/L) => TDKN - NH4; NOX = nitrate+nitrite-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); SO4 = sulfate (mg/L); Chlorophyll A (mg/L), Chlorophyll B (mg/L), Pheophytin A (mg/L); TURB = turbidity (NTU); COND = conductivity (µS/cm); PH = pH (s.u.)

* % difference = [(outflow-inflow)/inflow]*100

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A Jar Test of Aragonite Conducted with Taylor Creek Water

Introduction

The South Florida Water Management District (District) conducted a jar test with Oolitic Aragonite (hereafter Aragonite)[1] in June 2013 using water collected from the inflow pump station to the Taylor Creek Hybrid Wetland Treatment Technology (HWTT) facility located in Okeechobee County. Aragonite is almost pure calcium carbonate that precipitates when deep, cold ocean water saturated with this mineral interacts with the warm waters of the Gulf Stream on the Great Bahamas Bank. Aragonite is white in color, and as used in this jar test, had the consistency of flour or dry cement (Fig. 1). Aragonite is one of the mineral-based products being evaluated by the Water Quality Treatment Technologies Section. This jar test was conducted to (a) evaluate the effectiveness of Aragonite to reduce phosphorus (P) and nitrogen (N) levels in surface water and (b) assess the product's effect on other water quality parameters when tested over a wide range of dosages using a single source of water. Aragonite acts primarily by sorption of nutrients and other constituents onto the surface of the mineral particles and is effective primarily at sequestering dissolved inorganic chemical species.

Methods

Surface water was collected from the Taylor Creek HWTT on June 25, 2013 by staff from the Water Quality Treatment Technologies Section. Taylor Creek was selected as the water source for this test because it was known from previous sampling to consistently have high levels (> 100 µg/L) of soluble reactive P (SRP). Water was pumped into 5-gal carboys using a small peristaltic pump and immediately transported back to the laboratory. Water was kept at room temperature in the laboratory until the jar test was started the following day. A Phipps and Bird PB-700™ Standard JarTester was used in this evaluation (Fig. 2). Jars were filled with 2 L of Taylor Creek water and dosed with Aragonite at one of the following concentrations: 10, 50, 250, 500 or 1,000 mg/L (Fig. 1). The Aragonite used in this test had been milled to a particle diameter of approximately 3 to 8 µm. A sixth jar was run as a control and was not dosed with Aragonite. The control and Aragonite treatments were unreplicated. All jars were stirred vigorously for 10 minutes at 210 rpm after the Aragonite doses were added and then left undisturbed for the remainder of the test. Water samples were collected on Day 0, i.e., at the start of the jar test before the addition of Aragonite, and at approximately 24 hrs (Day 1) after dosing. Water samples were withdrawn from the jars with a 60-mL plastic syringe. Syringe cartridge filters (0.45 µm) were used for samples that required filtration. Sample preservation followed District protocols. All water samples were analyzed by the District's Chemistry Laboratory for ammonia-nitrogen (NH4), dissolved calcium (CA), conductivity (COND), total Kjeldahl nitrogen (TKN), nitrite+nitrate-nitrogen (NOX), pH (PH), total dissolved phosphorus (TDP), total phosphorus (TP), SRP, sulfate (SO4), and turbidity (TURB). The following chemical parameters were calculated by difference: dissolved organic phosphorus (DOP = TDP – SRP), particulate phosphorus (PP = TP – TDP), total nitrogen (TN = TKN + NOX), and total organic nitrogen (TON = TKN – NH4).

Results and Observations

Results of the chemical analyses performed on water samples collected during the jar test are presented in Table 1 along with the % change in constituent levels between Days 0 and 1 for each Aragonite dose. The changes in constituent level between Days 0 and 1 for all parameters are plotted against each Aragonite dose in Figs. 3 and 4. The relationship between

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[1] Aragonite is a naturally occurring mineral used in a variety of industrial applications, including water treatment. This product is mined by Sandy Cay Development LTD (Nassau, The Bahamas) and marketed by CaCO3 Aragonite Products, Inc. (Timonium, MD). For more information about Aragonite, see http://www.caco3aragonite.com/ or http://sandycaydevelopmentltd.com/About.html

change in constituent level and Aragonite dose was modeled as a linear function for all constituents except PH, which was modeled as a logarithmic function. The following observations were made based on examination of these data summaries and plots:

1. The observed treatment response for most constituents was highly correlated (r ≥ 0.79) with the Aragonite dose, i.e., the more Aragonite that was added to the jar, the greater the change in the constituent level during the jar test (see plots in Figs. 3 and 4).
2. Concentrations of TP, TDP and SRP were reduced in all but the 10-mg/L Aragonite dose for SRP; concentrations of all three constituents were moderately reduced (-22 to -62%) at Aragonite doses ≥ 250 mg/L.
3. There was a modest reduction in DOP concentrations across all Aragonite treatments (-25 to -40% removal). The reduction in DOP concentration was not correlated with Aragonite dose.
4. Reduction in PP concentrations was inversely correlated with Aragonite dose, i.e., the higher the Aragonite dose the smaller the PP reduction. PP concentration actually increased in the 1,000-mg/L dose.
5. Concentrations of TN, TKN and TON were slightly reduced (-2 to -8%) in all Aragonite treatments.
6. Concentrations of NOX increased slightly (3 to 7%) across all Aragonite treatments.
7. Concentrations of NH4 decreased slightly (-4 to -10%) across all Aragonite treatments.
8. Dissolved CA concentrations increased moderately (10 to 36%) in all Aragonite treatments. This would be expected, as Aragonite is largely calcium carbonate.
9. SO4 concentrations increased slightly (1 to 9%) in all Aragonite treatments.
10. TURB increased in all Aragonite treatments except in the 10-mg/L dose where it decreased slightly. TURB increased dramatically (340 to 1,760%) in doses ≥ 250 mg/L.
11. COND increased slightly (4 to 11%) in all Aragonite treatments.
12. PH increased slightly (5 to 8%) in all Aragonite treatments and reached 8.2 s.u. at doses ≥ 250 mg/L.

Future Work

There are no plans to investigate Aragonite further, although this product may be evaluated as part of the District's Everglades Restoration Strategies Science Plan.

Table 1. Results of chemical analysis of water samples collected from control and treatment jars during the Aragonite jar test. All chemical analyses were performed by the District's Chemistry Laboratory.[†]

	TP	TDP	SRP	DOP	PP	TN	TKN	TON	NOX	NH4	CA	SO4	TURB	COND	PH
Day 0															
Control	0.844	0.803	0.746	0.057	0.041	2.554	2.300	1.983	0.254	0.317	24.2	20.1	4.5	390	7.6
Day 1															
Control	0.810	0.792	0.748	0.044	0.018	2.524	2.260	1.951	0.264	0.309	24.9	20.4	2.2	398	7.9
10 mg/L	0.810	0.784	0.750	0.034	0.026	2.492	2.230	1.926	0.262	0.304	26.7	20.7	3.9	404	8.0
50 mg/L	0.793	0.772	0.729	0.043	0.021	2.492	2.230	1.925	0.262	0.305	29.7	20.4	7.5	408	8.1
250 mg/L	0.659	0.625	0.582	0.043	0.034	2.486	2.220	1.915	0.266	0.305	31.8	21.2	19.8	420	8.2
500 mg/L	0.527	0.487	0.450	0.037	0.040	2.436	2.170	1.868	0.266	0.302	32.0	21.1	45.8	426	8.2
1000 mg/L	0.373	0.319	0.283	0.036	0.054	2.391	2.120	1.834	0.271	0.286	32.9	22.0	83.7	434	8.2

% CHANGE BETWEEN DAY 0 CONTROL AND DAY 1 TREATMENTS*

10 mg/L	-4%	-2%	1%	-40%	-37%	-2%	-3%	-3%	3%	-4%	10%	3%	-13%	4%	5%
50 mg/L	-6%	-4%	-2%	-25%	-49%	-2%	-3%	-3%	3%	-4%	23%	1%	67%	5%	6%
250 mg/L	-22%	-22%	-22%	-25%	-17%	-3%	-3%	-3%	5%	-4%	31%	5%	340%	8%	7%
500 mg/L	-38%	-39%	-40%	-35%	-2%	-5%	-6%	-6%	5%	-5%	32%	5%	918%	9%	7%
1000 mg/L	-56%	-60%	-62%	-37%	32%	-6%	-8%	-8%	7%	-10%	36%	9%	1760%	11%	8%

[†] Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L) => TDP - SRP; PP = particulate phosphorus (mg P/L) => TP - TDP; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L) => TKN - NH4; NOX = nitrite+nitrate-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); CA = dissolved calcium (mg/L); SO4 = sulfate (mg/L); TURB = turbidity (NTU); COND = conductivity (µS/cm); PH = pH (s.u.)

* % change = [(Day 1 value-Day 0 Control)/Day 0 Control]*100; negative % change values indicate a concentration reduction, while positive % change values indicate a concentration increase.

Figure 1. Doses of Aragonite added to the treatments during the jar test. Aragonite doses from L-R: 10, 50, 250, 500 and 1000 mg/L, respectively.

Figure 2. Phipps and Bird PB-700™ Standard JarTester apparatus used to conduct the Aragonite jar test. Aragonite concentrations in jars from L-R: 0 (control), 10, 50, 250, 500 and 1000 mg/L, respectively. Photograph was taken on Day 1 approximately 24 hr after the jars had been dosed and the Aragonite was allowed to settle. Note the difference in residual cloudiness in the three jars on the right that had higher initial Aragonite concentrations (250, 500 and 1,000 mg/L) compared to the jars with lower doses on the left (0, 10 and 50 mg/L).

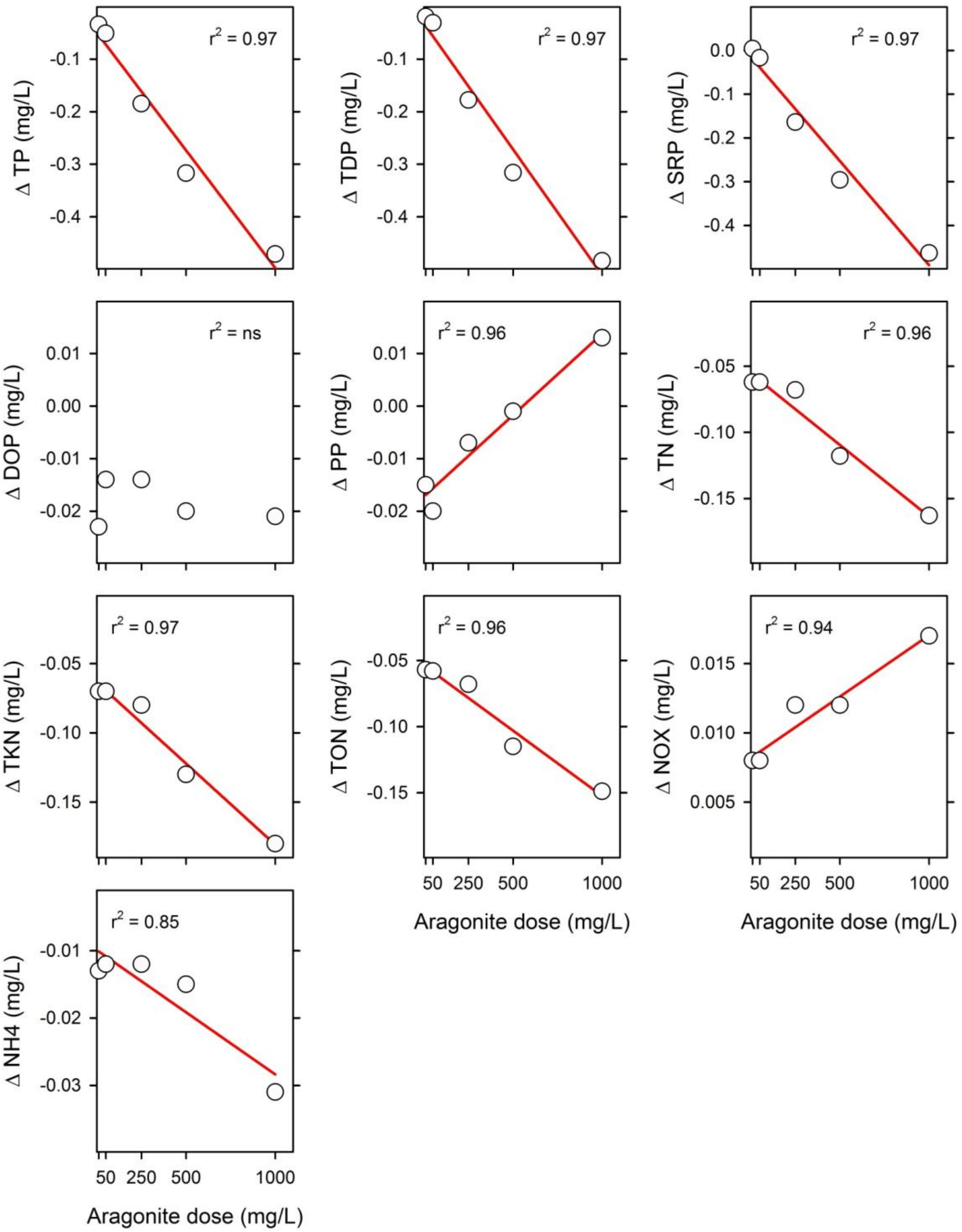

Figure 3. Dose response curves for phosphorus and nitrogen concentrations in treatment jars on Day 1 relative to concentrations in the control on Day 0 for each Aragonite dose (10, 50, 250, 500 and 1,000 mg/L) during the jar test. See Table 1 for the parameter key. Negative change indicates a concentration reduction, while positive change indicates a concentration increase.

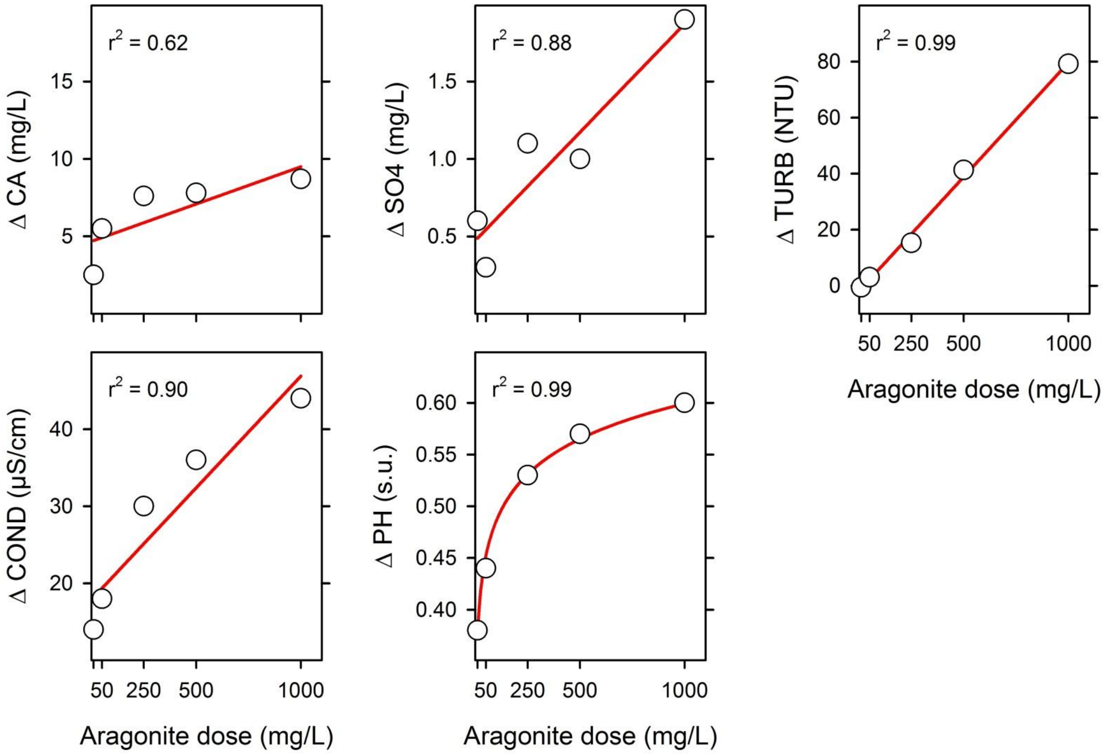

Figure 4. Dose response curves for other water quality parameters in treatment jars on Day 1 relative to levels in the control on Day 0 for each Aragonite dose (10, 50, 250, 500 and 1,000 mg/L) during the jar test. See Table 1 for the parameter key. Negative change indicates a reduction in level, while positive change indicates an increase in level.

Electrocoagulation Demonstration Using C-51 Canal Water

Introduction

The South Florida Water Management District (District) conducted a demonstration of electrocoagulation, one of the water treatment technologies being evaluated by the Water Quality Treatment Technologies Section as part of the District's New Alternative Technology Assessment (NATA) Program. The specific implementation of electrocoagulation technology employed in this test was developed by Powell Water Systems, Inc. (Centennial, CO) and is marketed by GerberPumps International, Inc. (Longwood, FL). This demonstration was conducted to evaluate the ability of electrocoagulation to reduce phosphorus and nitrogen concentrations in surface water and to document the effect that this technology has on other water quality parameters. Electrocoagulation is widely used in the water treatment industry to remove a variety of contaminants. The technology operates by generating an electric current across metal electrodes in a reactor vessel thereby releasing ions from the electrodes into the water that neutralize the charge of other constituents causing them to coagulate[1].

Methods

Water from the C-51 canal was collected in 5-gal carboys from the DB Environmental Laboratory's water pump tap at the S5A Laboratory on August 2, 2012. Water was transported to the laboratory and stored at room temperature until it was used during the electrocoagulation demonstration the following day. Mr. Bert Gerber of GerberPumps International, Inc. conducted the test using the bench-top apparatus illustrated in Fig. 1. A small peristaltic pump was used to lift water from a 5-gal carboy and flow it past charged electrodes (i.e., "blades") positioned within the apparatus. Eight runs were made using aluminum or iron blades at pump settings that resulted in 20 or 32 sec. water retention times and at various power settings (Table 1). The outflow from each run was then filtered through two layers of Whatman™ Grade 1 filter paper (nominal pore size of 11 µm) to remove the floc produced by the electrocoagulation process (Fig. 2). An unreplicated sample of the filtrate from each run was analyzed for conductivity (COND), pH, alkalinity (ALKA), ammonia-nitrogen (NH4), nitrite+nitrate-nitrogen (NOX), total Kjeldahl nitrogen (TKN), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total phosphorus (TP), sulfate, (SO4), total aluminum (Al) and total iron (Fe) by the District's Chemistry Laboratory. A raw (i.e., untreated) water sample of C-51 water was analyzed for the same list of parameters. The following parameters were calculated by difference: dissolved organic phosphorus (DOP = TDP – SRP), particulate phosphorus (PP = TP – TDP), total nitrogen (TN = TKN + NOX) and total organic nitrogen (TON = TKN – NH4). A separate test was conducted on August 21, 2012 to assess how much material was retained by the filter paper alone, i.e., a "filter paper control". Duplicate samples of C-51 water were collected from the S5A Laboratory location and filtered through a double layer of filter paper. The filtrate from these samples was analyzed for TP, TDP and SRP. Duplicate samples of raw (unfiltered) C-51 water were analyzed for the same water quality parameters.

Results and Observations

Results of the chemical analyses performed on water samples collected during the electrocoagulation demonstration and the filter paper control are presented in Tables 2 and 3. The following observations were made based on comparing results from the raw water samples to the electrocoagulation runs or the filter paper control and variation among the electrocoagulation runs:

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[1] The theoretical basis behind electrocoagulation is discussed at http://en.wikipedia.org/wiki/Electrocoagulation.

1. The filter paper alone did not remove any dissolved phosphorus (TDP and SRP) and, at most, only a small amount of TP (Table 3).
2. Electrocoagulation removed most of the color present in the raw water in all runs (Fig. 3).
3. ElectroCoagulation removed a substantial amount of TP and almost all PP in all runs. Runs with Al blades generally removed 50% or more of TDP, SRP and DOP, while runs with Fe blades provided no measureable treatment (treated concentrations > raw water concentration) or were much less effective at removing these constituents (Fig. 4).
4. Electrocoagulation removed a substantial amount of TN, TKN and TON and a smaller amount of NOX, while NH4 levels increased in all runs for both blade types (Fig. 4).
5. Electrocoagulation increased pH slightly and reduced both COND and ALKA in all runs (Fig. 4).
6. Total Al and Fe levels increased markedly in runs that used that type of blade compared to the raw water, i.e., Al levels increased more than ninety-fold in treated vs. raw water, while Fe levels increased by at least seven-fold (Fig. 4).
7. Electrocoagulation reduced SO4 levels in all runs (Fig. 4).
8. Runs with the highest power setting (Runs 4 and 8; Table 1) often exhibited the greatest treatment effect compared to the other runs at lower power (e.g., see plots of NOX, NH4, pH, COND, ALKA, SO4 and Al; Fig. 4).

Future Work

At present, there are no plans within the NATA program to investigate further the treatment capabilities of electrocoagulation. This technology will be compared with all the other products and technologies in the final NATA evaluation and may or may not be applicable as a tool for a scale-up evaluation in the future if warranted.

Table 1. Differences in blade type, water retention time and power setting among runs conducted during the electrocoagulation demonstration.

Run #	Blade type	RT[1]	Volts[2]	Amps[3]	Power[4]
1	Iron	32	50	1.6	80
2	Iron	20	48	1.9	91
3	Iron	32	30	1.0	30
4	Iron	32	97	4.0	388
5	Aluminum	32	52	1.5	78
6	Aluminum	20	55	1.6	88
7	Aluminum	32	36	0.9	32
8	Aluminum	32	99	2.3	228

[1] Water retention time (sec) within the electrocoagulation apparatus.
[2] Electric potential (volts) across the blades.
[3] Electric current (amps) passed across the blades.
[4] Power (watts) applied to the blades; power was calculated as volts x amps.

Table 2. Results from chemical analyses of raw water collected from the C-51 canal and water that had been treated with the electrocoagulation process using aluminum or iron blades at various power levels and water retention times.*

	TP	TDP	SRP	DOP	PP	TN	TKN	TON	NOX	NH4	SO4	TOTAL	TOTFE	ALKA	PH	COND
Raw Water	0.042	0.015	0.005	0.010	0.027	2.156	1.820	1.716	0.336	0.104	47	36	5	180	8.0	798
Run 1	0.018	0.018	0.006	0.012	0.000	1.094	0.790	0.629	0.304	0.161	39	24	44	102	9.2	601
Run 2	0.016	0.016	0.006	0.010	0.000	1.120	0.790	0.642	0.330	0.148	38	27	48	105	8.8	643
Run 3	0.012	0.012	0.005	0.007	0.000	1.207	0.860	0.729	0.347	0.131	37	24	78	142	8.7	713
Run 4	0.017	0.014	0.007	0.007	0.003	0.935	0.710	0.466	0.225	0.244	25	26	40	55	9.6	517
Run 5	0.006	0.005	0.002	0.003	0.001	1.080	0.830	0.629	0.250	0.201	39	3767	9	103	8.7	628
Run 6	0.005	0.005	0.002	0.003	0.000	1.095	0.830	0.644	0.265	0.186	40	3346	5	113	8.6	657
Run 7	0.005	0.006	0.002	0.004	-0.001	1.290	1.000	0.808	0.290	0.192	40	3574	5	123	8.6	669
Run 8	0.004	0.004	0.002	0.002	0.000	1.208	1.050	0.774	0.158	0.276	28	9042	3	81	8.9	540

*TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L); PP = particulate phosphorus (mg P/L); TN = total nitrogen (mg N/L); TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L); NOX = nitrite+nitrate nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); SO4 = sulfate (mg/L); TOTAL = total aluminum (µg/L); TOTFE = total iron (µg/L); ALKA = alkalinity (mg $CaCO_3$/L); PH = pH (standard units); COND = conductivity (µS/cm).

Table 3. Summary statistics (mean values ± 1 standard deviation) for chemical analyses of raw water collected from the C-51 canal and filtrate from the filter paper control.

	TP	TDP	SRP
Raw Water	0.029 (± 0.001)	0.020 (± 0.000)	0.012 (± 0.000)
Filter Paper Control	0.026 (± 0.002)	0.021 (± 0.000)	0.014 (± 0.000)

*TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L).

Figure 1. The bench-top apparatus used for the electrocoagulation demonstration. Note the dark green floc (from iron blades) in processed water collected in the plastic cups (left and center panels) and in the apparatus collection tray (right panel).

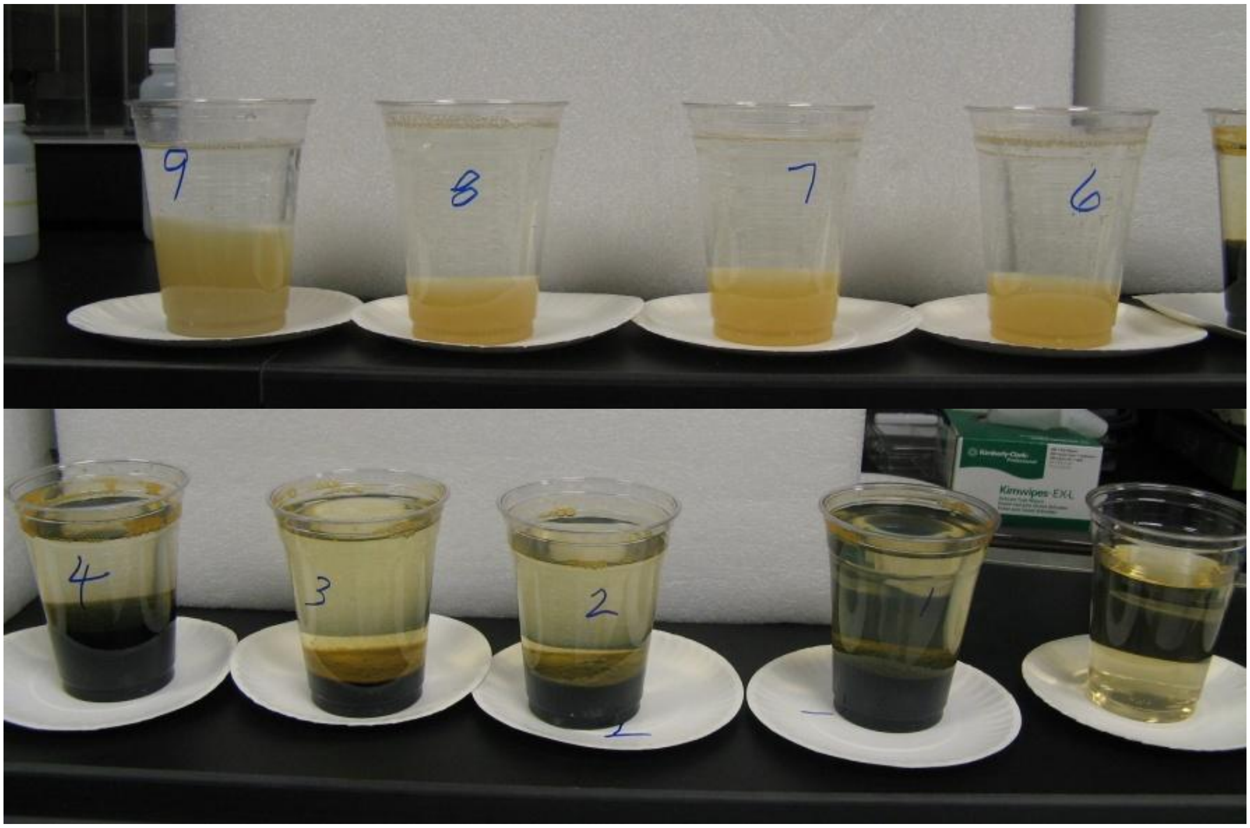


Figure 2. Floc produced during the electrocoagulation demonstration by the aluminum blades (light tan material in the top panel) and the iron blades (dark green material in the bottom panel).

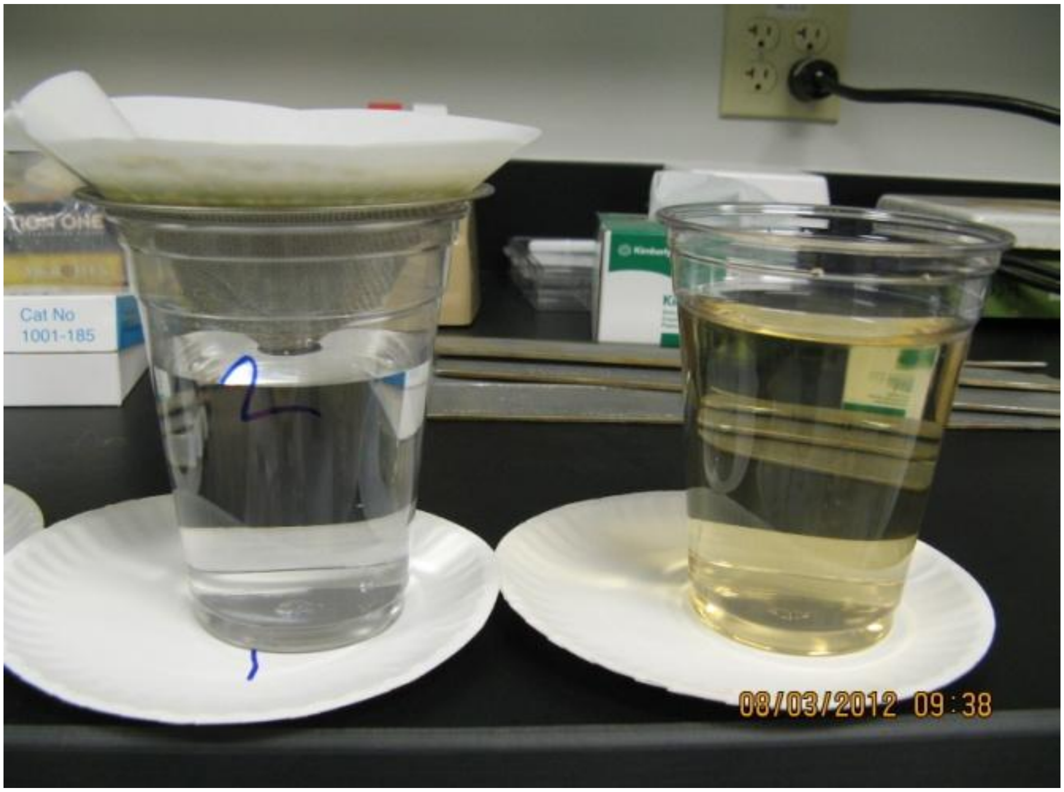


Figure 3. Comparison of color in water that had been processed through the electrocoagulation unit and then filtered through two layers of filter paper (left cup) compared to un-treated water (right cup).

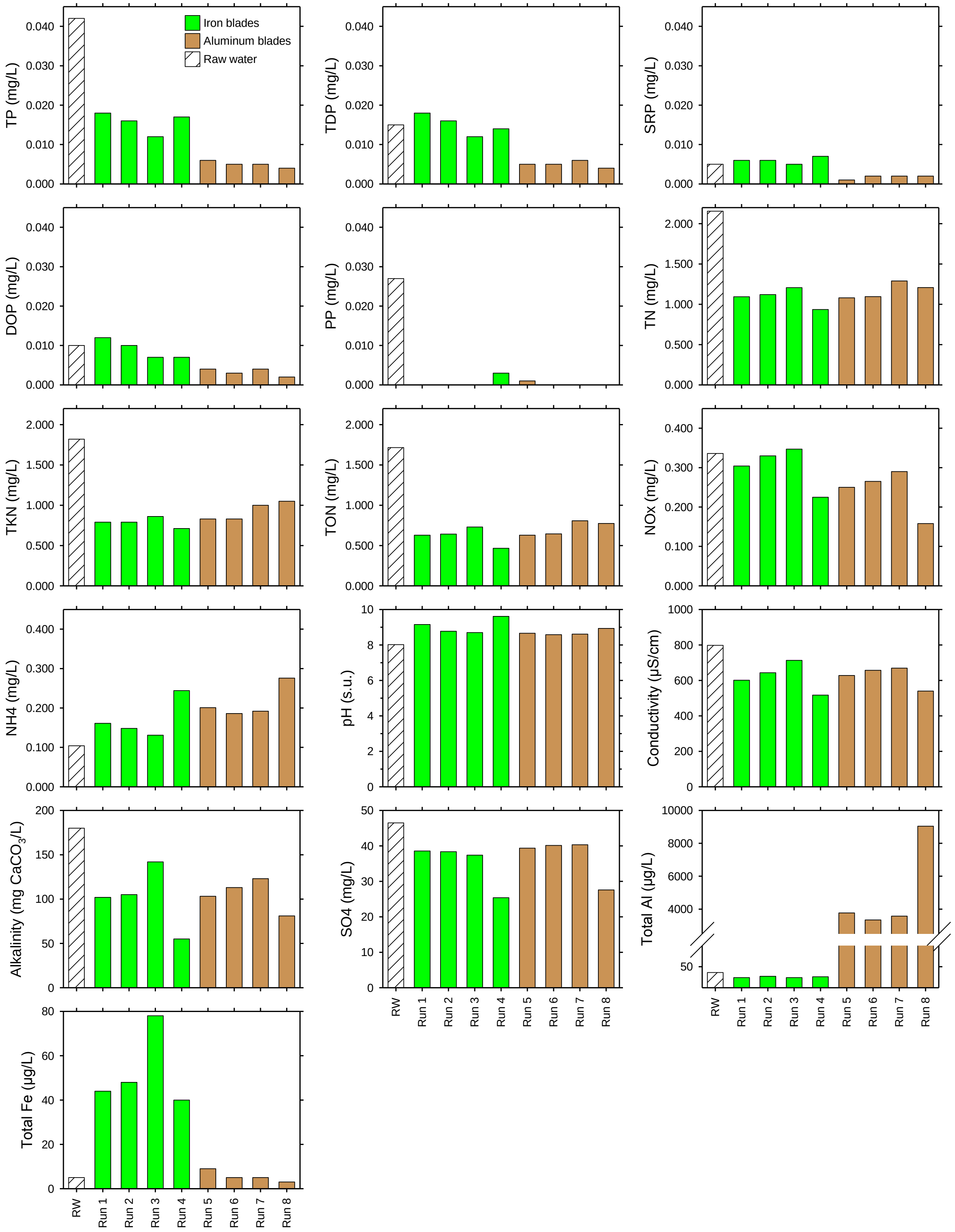


Figure 4. Water quality in raw water from the C-51 canal compared to water treated with the electrocoagulation process using aluminum or iron blades at various power settings and water retention times. See Table 1 for a list of differences in run parameters.

Ferrate Demonstration at Canal B - Istokpoga Marsh, Water Improvement District, Lake Placid

Introduction

The South Florida Water Management District (District) in collaboration with Highlands County Parks and Natural Resources and Ferrate Treatment Technologies (FTT), LLC, conducted a field demonstration of the product "Ferrate" using water from Canal B, Istokpoga Marsh, Water Improvement District (IMWID), Lake Placid, FL (Figure 1). Ferrate (FeO_4^{2-}) is a supercharged iron molecule in which Fe is in the plus 6 oxidation state; better known as Iron (VI), and is one of the products being evaluated by the Water Quality Treatment Technologies Section as part of the District's New Alternative Technology Assessment (NATA) Program. This field demonstration was conducted to evaluate the effectiveness of the Ferrate technology to reduce phosphorus concentrations in surface waters. Ferrate is unstable at neutral pH, which makes it difficult to store and ship to treatment facilities. Because of its instability, ferrate was synthesized at the test site in a patented device called a Ferrator® from caustic, sodium or calcium hypochlorite, and ferric chloride (Figure 2).

Methods

Water from Canal B of the IMWID in Lake Placid FL, was used in this field demonstration that was conducted from September 17 to September 26, 2012. Canal B is one of the main drainage canals from the rich organic caladium fields in the IMWID with high and variable P loadings (Table 1), making it an ideal site to test this new technology. A ferrate dose of 5 mg/L was consistently used during the entire field demonstration. Soon after ferrate addition and reaction, a predetermined amount of ferric chloride was added for initial pH adjustment and coagulation (~ pH 4.5) based on the water quality at this site. Ferric iron reacts and complexes soluble P through coagulation and flocculation as ferric phosphate. The pH of treated water is generally adjusted to a neutral pH by using additional FeO_4 in order to remove excess Fe before the treated water is discharged back to the source water. However, the pH of the treated water from this field trial was not adjusted to neutral values, resulting in high Fe concentrations in treated water samples. Untreated (Inflow) and treated (Outflow) water samples were collected on three different dates (9/18/12, 9/20/12 and 9/25/12), processed in the field (Figure 3) and transported to the District laboratory for analysis. Unfiltered water samples were analyzed for total phosphorus (TPO4), total Kjeldahl nitrogen (TKN), total iron (TOTFE), alkalinity (ALKA), pH (LPH), conductivity (LCOND), and turbidity (TURB). Field-filtered (0.45 µm pore size) samples were analyzed for total dissolved phosphorus (TDPO4), soluble reactive phosphorus (OPO4), ammonia (NH4), nitrate+nitrite-nitrogen (NOX), and sulfate (SO4). The following parameters were calculated by difference: particulate phosphorus (PP = TP-TDP), dissolved organic phosphorus (DOP = TDP-SRP), total nitrogen (TN = TKN+NOX), and total organic nitrogen (TON = TKN-NH4).

Results and Observations

Results of the chemical analyses performed on water samples collected during the 10-days field demonstration are presented in Table 1. The following observations were made based on comparing untreated Inflow and Ferrate-treated Outflow water samples.

1. Initial TPO4 concentrations of inflow waters from this canal were high averaging 1.327 mg/L, with about 95 and 93% present as TDPO4 and OPO4, respectively.
2. Ferrate was very efficient in reducing TDPO4 and OPO4 concentrations, with outflow water samples at method detection levels (0.002 mg/L) on all sampling events. Similarly, ferrate was able to reduce inflow TPO4 concentrations by 97%, which is a reflection of the high soluble P fraction (95%) in the inflow canal waters.
3. Total N and TKN concentrations were also effectively reduced, with outflow samples showing an average of 48 and 56% reduction, respectively. In contrast, NOX outflow concentrations increased by an average of 19%.
4. ALKA levels were reduced (83%) as expected by the Fe levels added to the inflow samples to adjust pH. Water pH was reduced from an average inflow value of 6.5 to an average outflow value of 5.6, representing a 14% reduction. SO4 levels in outflow samples also showed an average reduction of 13%.
5. TURB levels in the outflow samples decreased substantially (70% reduction) as the ferric phosphate flocs dropped from the water column (Figure 3) In contrast outflow COND levels showed a considerably (415%) increased due to the ferrate treatment.
6. Total Fe concentrations in outflow samples showed a significant increase due to the ferrate treatment and the ferric chloride added for pH adjustment and coagulation. However, for a full-scale system, pH of outflow samples are generally adjusted to pH 7, which would allow the excess iron to precipitate before water is discharge from the treatment facility.

Future Work

At present, there are no plans within the NATA program to further investigate the effectiveness of this technology. However, FTT is conducting another field demonstration in the Lake Apopka area that will provide additional water quality data to better evaluate this technology.

Table 1. Results from chemical analysis of water samples collected before (inflow) and after (outflow) treatment with ferrate (FeO_4^{2-}).

PARAMETERS† SITE & DATE	TPO4	TDPO4	OPO4	DOP	PP	TN	TKN	TON	NH4	NOX	TOTFE	SO4	ALKA	LPH	LCOND	TURB
Inflow																
09/18/12	1.167	1.099	1.089	0.010	0.068	4.123	3.660	2.338	1.322	0.463	726	42	14.0	6.5	210	12.2
09/20/12	1.490	1.412	1.380	0.032	0.078	4.412	3.980	2.724	1.256	0.432	651	51	10.0	6.4	231	15.2
09/25/12	1.323	1.251	1.229	0.022	0.072	4.293	3.760	2.518	1.242	0.533	622	47	11.0	6.6	219	16.4
Outflow																
09/18/12	0.059	0.002	0.002	0.000	0.057	2.314	1.790	0.548	1.242	0.524	5403	41	2.0	6.1	957	5.4
09/20/12	0.045	0.002	0.002	0.000	0.043	2.265	1.730	0.463	1.267	0.535	4554	38	2.0	4.9	1184	4.7
09/25/12	0.020	0.002	0.002	0.000	0.018	2.097	1.450	0.311	1.139	0.647	1988	41	2.0	5.8	1260	2.4

% DIFFERENCE BETWEEN INFLOW AND OUTFLOW SAMPLES‡																
09/18/12	-95%	-99.8%	-99.8%	-100%	-16%	-44%	-51%	-77%	-6%	13%	644%	-2%	-86%	-6%	356%	-56%
09/20/12	-97%	-99.9%	-100%	-100%	-45%	-49%	-57%	-83%	1%	24%	600%	-25%	-80%	-23%	413%	-69%
09/25/12	-98%	-99.8%	-100%	-100%	-75%	-51%	-61%	-88%	-8%	21%	220%	-12%	-82%	-13%	475%	-85%

†TPO4 = total phosphorus (mg P/L); TDPO4 = total dissolved phosphorus (mg P/L); OPO4 = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L); PP = particulate phosphorus (mg P/L); TN = total nitrogen (mg N/L); TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L); NH4 = ammonia nitrogen (mg N/L); NOx = nitrite+nitrate nitrogen (mg N/L); TOTFE = total iron (µg/L); SO4 = sulfate (mg/L); ALKA = alkalinity (mg $CaCO_3$/L); LPH = pH (standard units); LCOND = conductivity (µS/cm); TURB = turbidity (NTU).

‡% Difference = [(Outflow-Inflow)/Inflow]*100.

Figure 1. Inflow water samples, Canal B, IMWID, Highlands County.

Figure 2. Ferrator® reactor used to synthesize ferrate on site.

Figure 3. Sample preparation in the field.

Figure 4. Floc formation in treated samples.

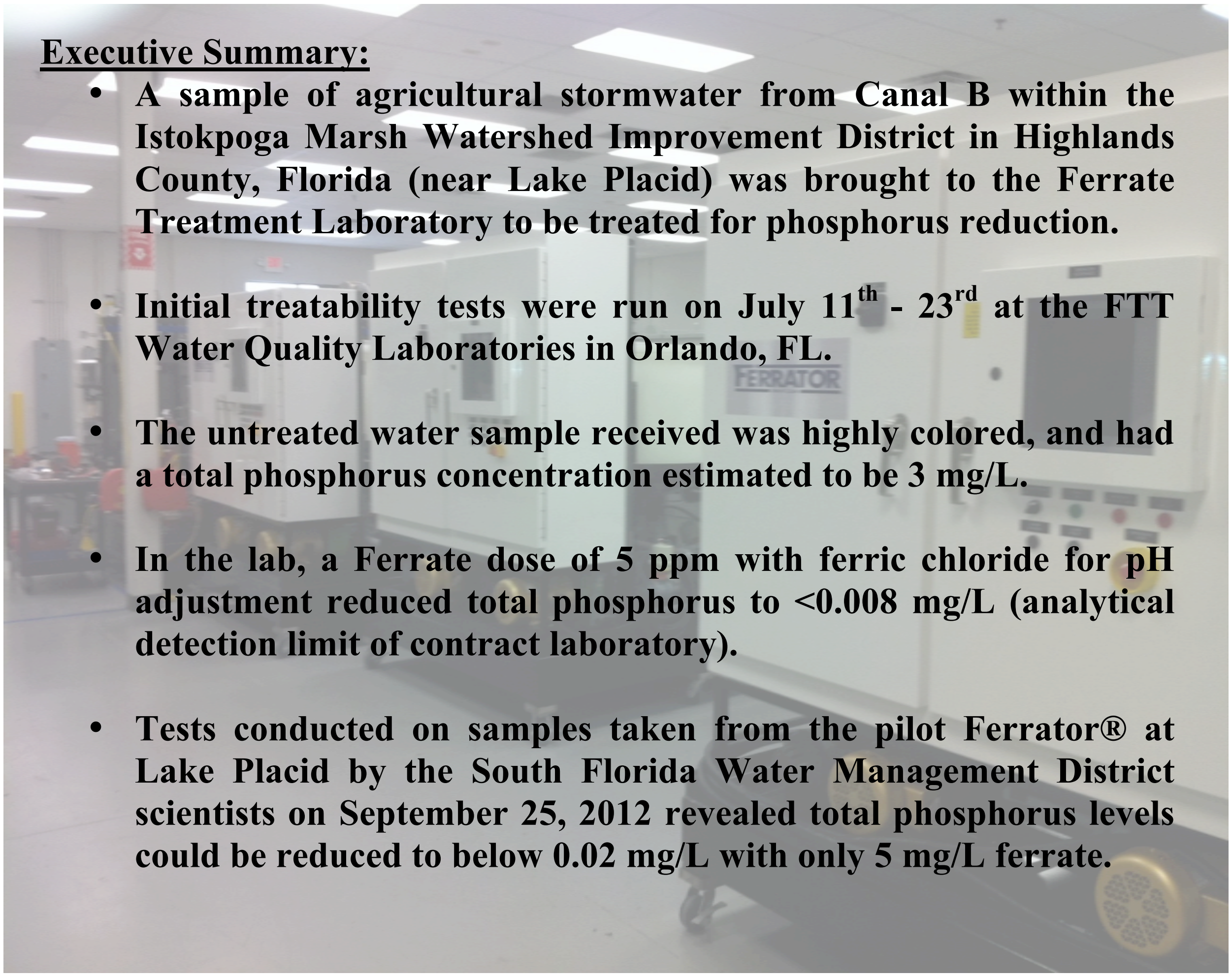
Ferrate Treatment TECHNOLOGIES

300 Sunport Lane Suite 101-A, Orlando, FL 32809 · T: (407) 857-5721 · F: (407) 826-0166 · E: sales@ferrate.biz

Client Name: **Highlands County, Istokpoga Marsh Watershed Improvement District (near Lake Placid, Florida)**

Report Date: **October 17, 2012**

A Ferrate Laboratory Treatability Test incorporates proprietary Ferrate (Iron VI) Treatment System chemistries into a bench test under controlled conditions that are designed to meet treatment objectives specified by the client. The chemical modification or removal of target constituents is achieved by a combination of chemical reactions that can include oxidation, disinfection, complexation, or coagulation followed by the manipulation of one or more operational parameters such as pH adjustment, sedimentation, filtration and mixing.



Executive Summary:

- **A sample of agricultural stormwater from Canal B within the Istokpoga Marsh Watershed Improvement District in Highlands County, Florida (near Lake Placid) was brought to the Ferrate Treatment Laboratory to be treated for phosphorus reduction.**

- **Initial treatability tests were run on July 11th - 23rd at the FTT Water Quality Laboratories in Orlando, FL.**

- **The untreated water sample received was highly colored, and had a total phosphorus concentration estimated to be 3 mg/L.**

- **In the lab, a Ferrate dose of 5 ppm with ferric chloride for pH adjustment reduced total phosphorus to <0.008 mg/L (analytical detection limit of contract laboratory).**

- **Tests conducted on samples taken from the pilot Ferrator® at Lake Placid by the South Florida Water Management District scientists on September 25, 2012 revealed total phosphorus levels could be reduced to below 0.02 mg/L with only 5 mg/L ferrate.**

Introduction

Following successful preliminary testing in the laboratory, a fully supported remote pilot treatment site was built. The Ferrator® was set up to test how effectively a live machine could treat the runoff water. Phosphorus levels must be reduced in runoff water from highly farmed lands in order to prevent the destruction of habitats farther south, such as Lake Okeechobee and The Everglades.

Ferrate(VI) ….. FeO_4^{2-}, is an oxy-anion of iron in the +6 valence state, and is a powerful oxidant, disinfectant and coagulant. It is unstable at neutral pH, and rapidly decomposes to Fe^{3+}, which forms a benign (and useful) coagulating agent. Because of its instability, Ferrate(VI) cannot be easily produced, stored, and shipped to treatment facilities. FTT has made this multi-purpose chemical available for environmental use, by developing an on-site generation system (Ferrator®) which produces an inexpensive, concentrated Ferrate(VI) solution at the point of use.

Objective:

The goal of the lab treatability tests and the pilot system is to reduce the total phosphorus level to 0.12 mg/L or below using minimal amounts of ferrate.

Lab Procedure

Synthesis of Ferrate:

Before each treatment trial, ferrate was synthesized following FTT's proprietary process. Using the concentration of the synthesized ferrate and the doses desired (in ppm) for each trial, the amount of ferrate needed was weighed out, and added.

Treatment protocol:

300 mL samples were collected in beakers for treatability tests. The weighed amounts of ferrate doses were added to the beakers all samples were initially mixed for 30 seconds at 200 rpm. Then the mixing was reduced to 100 rpm for approximately 20 minutes. FeO_4 was observed to have completely reacted after 5 minutes. Ferric chloride (40%) was added to all samples to adjust the pH, except on September 13th when sulfuric acid (93%) was added. No further tests were conducted with sulfuric acid because phosphate removal was unsuccessful. The samples were allowed to coagulate for 12.5 minutes and allowed to settle for 15 minutes. The samples were filtered and analytical tests such as ortho-phosphate, residual iron, and in some cases total organic carbon, were conducted.

Because the pH must be dropped to around 4.5 for optimal phosphate removal, additional FeO_4 was added to the filtrate on September 20th – 24th to bring the pH back to neutral in order to remove excess iron. The samples were filtered again and tested for ortho-phosphate and residual iron again.

The treatment process was carried out in such a way as to simulate the process the water would undergo in the pilot system. The size of the tanks and the flow rates of the pumps determined the mixing, coagulation and settling times in the laboratory. On site treatment was conducted using the Ferrator® pilot system and South Florida Water Management District (SFWMD) scientists took samples from the clarifier tank for further testing on September 18th, 20th and 25th (see results in Appendix).

Analytical

Samples were tested at FTT Water Quality Laboratories for ortho-phosphate following Standard Methods 8048, residual iron following Standard Methods 3113B, and total organic carbon following Standard Methods 5310A. On July 19th and 23rd, the ENCO Laboratory in Orlando, Florida tested some samples for total phosphorus following EPA Method 365.4.

Discussion

The three major variables that are essential to achieve the maximum phosphate removal are: FeO_4 concentration, total iron concentration, and pH. The optimum FeO_4 concentration needed for phosphate removal was 5-6 ppm. As the amount of phosphate in the untreated sample increased, the amount of FeO_4 needed increased as well. This is important to note because the amount of phosphate in Canal B of the Istopokga Marsh Watershed Improvement District is variable throughout the year (SFWMD Jar Test Report, 1-6). The total iron and the pH are also very important because ferric chloride is used to adjust the pH of the treated sample down to around pH of 4.5 for optimal phosphate removal. The amount of total iron added for $\geq$93% phosphate removal (removal needed to meet treatability goal) was between 45-70 mg/L of iron for a dose of 5 ppm and 70-85 mg/L of iron for 6 ppm. The higher the final pH, the more iron needed to be added (see graphs in Appendix). Ferric chloride is used for initial pH adjustment because it is already available as part of the Ferrator® treatment system. Ferric iron captures the released phosphate through coagulation as ferric phosphate. The pH of the treated water can be raised to a neutral pH if needed for discharge using additional FeO_4. This is essential to achieve removal of residual iron, as iron is soluble in water at low pH.

The results received from ENCO laboratories on August 19th – 23rd show that a FeO_4 concentration of 5 ppm, total iron concentration of 48 mg/L, and a pH of 4.86 were the conditions needed to reduce the total phosphorus concentration down to <0.008 mg/L (below the analytical detection limit). Results from the SFWMD of a sample taken from the clarifier tank of the pilot system on September 25th showed that using a FeO_4 concentration of about 5 ppm and bringing the final pH to 5.75 using ferric chloride brought the total phosphorus concentration to 0.02 mg/L and the ortho-phosphate concentration to 0.002 mg/L, well below the goal of treatability tests.

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-- APPENDIX --

Highlands Co, Istokpoga Marsh Watershed Improvement District

In-Lab Treatability Results:

7/19/12 - 7/23/12 300 mL samples

									ENCO Results
Number	**Dose (ppm)**	**Initial pH**	**$FeCl_3$ (µL/L)**	**Total Iron Added (mg/L)**	**Final pH**	**TOC (mg/L)**	**Residual Iron (mg/L)**	**Ortho-Phosphate (mg/L)**	**Total Phosphorus (mg/L)**
1	5	12.01	333.33	49.2	5.0	6.82	0.12	0.02	<0.008*
2	5	12.1	310	45.9	4.3	7.15	0.11	0.03	0.022
3	5	12.16	300	44.5	6.2	---	>3.0**	---	---
4	5	12.2	350	51.5	5.5	9.51	0.44	0.09	---
5	5	12.13	366.67	53.8	3.65	---	0.5	---	---
6	5	12.18	343.33	50.5	4.86	---	---	0.03	0.015
7	5	12.26	363.33	53.4	5.16	---	---	0.21	---
8	3	11.48	233.33	34.2	4.99	19.8	0.35	0.07	0.014

* Readings were under detection limit **Untreated Sample:** **2.4**

** Readings were over detection limit

9/20/12 500 mL samples

Number	**Dose (ppm)**	**weight (gm)**	**Initial pH**	**$FeCl_3$ (µL/L)**	**Final pH- 1**	**Residual Iron (mg/L)**	**Ortho-Phosphate (mg/L)**	**FeO_4^{2-} (ppm)**	**Total Iron Added (mg/L)**	**Final pH- 2**	**Residual Iron (mg/L)**	**Ortho-Phosphate (mg/L)**
1	5	0.172	11.91	380	4.44	0.37	0.17	0.27	55.308	7.55	0.22	0.07
2	5	0.172	11.95	382	4.76	0.55	0.14	0.55	55.7	8.9	0.38	0.15
3	5	0.172	12.02	400	4.7	0.49	0.16	0.66	58.264	9.19	0.35	0.14

9/21/12 500 mL samples

Number	**Dose (ppm)**	**weight (gm)**	**Initial pH**	**$FeCl_3$ (µL/L)**	**Final pH- 1**	**Residual Iron (mg/L)**	**Ortho-Phosphate (mg/L)**	**$NaFeO_4$ (µL/L)**	**Total Iron Added (mg/L)**	**Final pH- 2**	**Residual Iron (mg/L)**	**Ortho-Phosphate (mg/L)**
1	5	0.172	11.7	400	4.4	0.52	0.21	16.67	65.5	7.02	0.06	0.18
2	5	0.172	11.7	386	4.4	0.36	0.24	26.67	68.04	8.44	0.07	0.19
3	5	0.172	11.68	384	4.33	0.32	0.16	36.67	72.26	9.2	0.04	0.16

Untreated Sample: Untreated Sample: 0.54 4.0

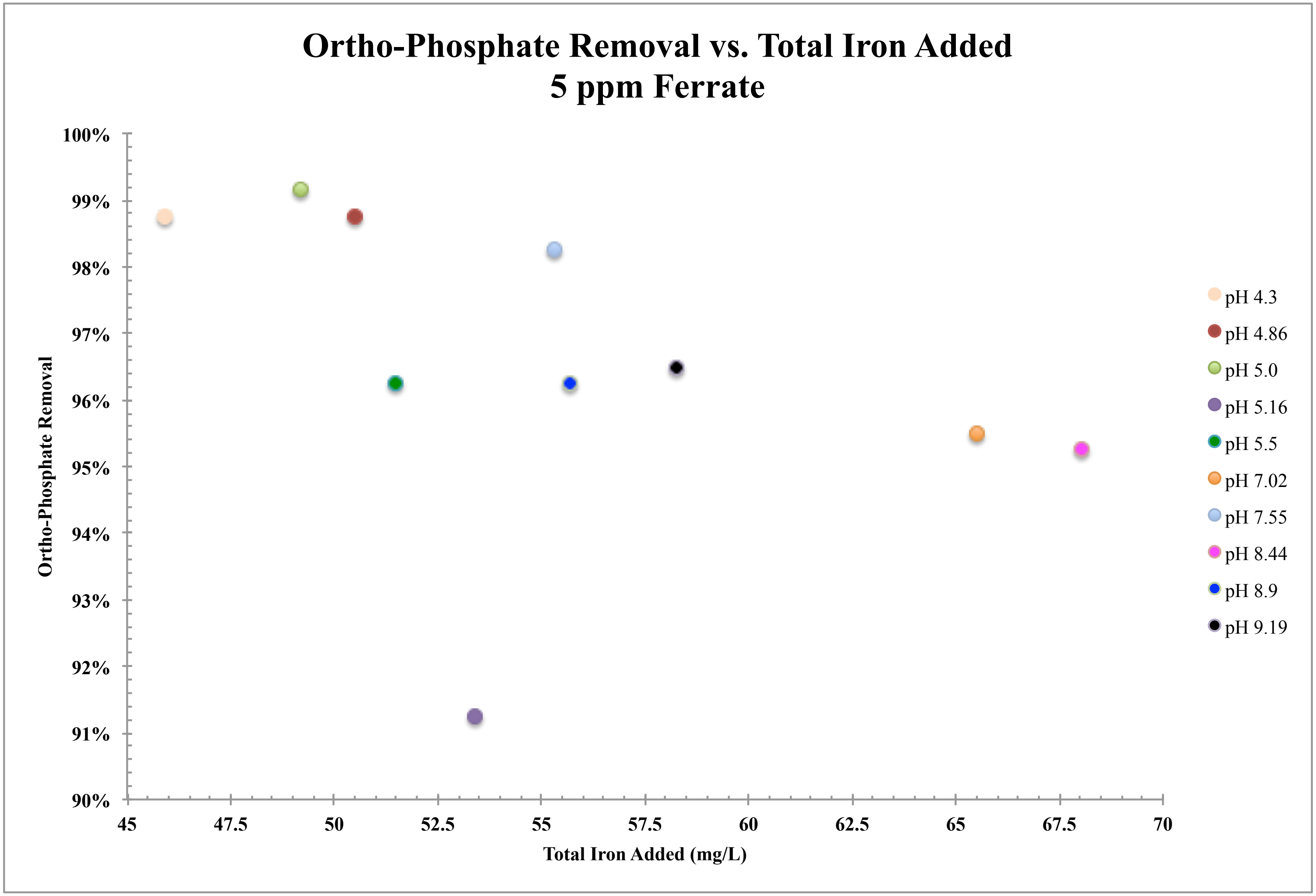
Test 2 1000 mL samples

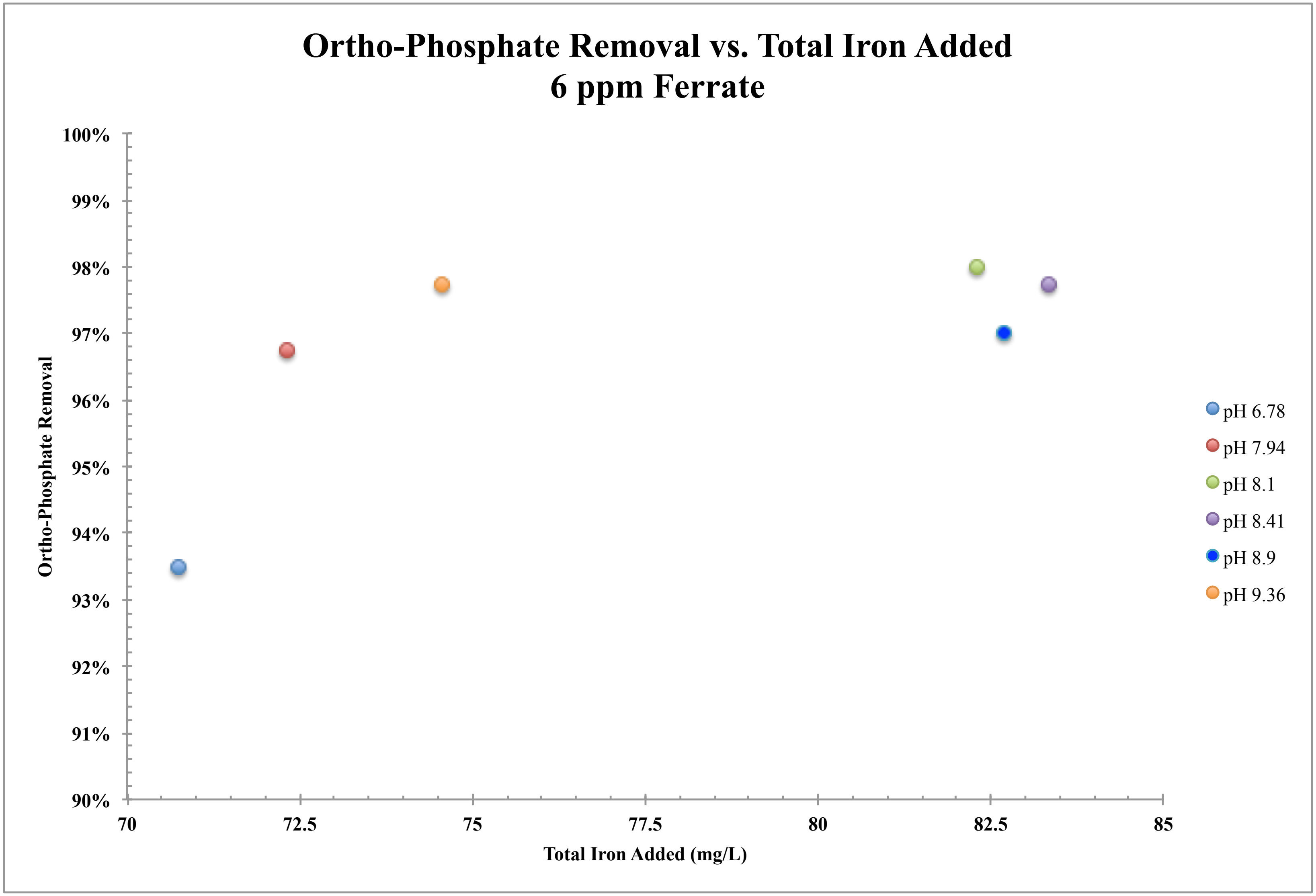
Number	Dose (ppm)	weight (gm)	Initial pH	FeCl$_3$ (µL/L)	Final pH- 1	Residual Iron (mg/L)	Ortho-Phosphate (mg/L)	NaFeO$_4$ (µL/L)	Total Iron Added (mg/L)	Final pH- 2	Residual Iron (mg/L)	Ortho-Phosphate (mg/L)
1	6	0.413	11.84	440	4.59	0.73	0.07	15	70.75	6.78	0.06	0.26
2	6	0.413	11.82	435	4.58	1.08	0.11	20	72.3	7.94	0.10	0.13
3	6	0.413	11.79	435	4.43	0.97	0.08	25	74.55	9.36	0.08	0.09

9/24/12 1000 mL samples

Number	Dose (ppm)	weight (gm)	Initial pH	FeCl$_3$ (µL/L)	Final pH- 1	Residual Iron (mg/L)	Ortho-Phosphate (mg/L)	NaFeO$_4$ (µL/L)	Total Iron Added (mg/L)	Final pH- 2	Residual Iron (mg/L)	Ortho-Phosphate (mg/L)
1	6	0.408	11.93	445	4.71	0.58	0.11	40	82.7	8.9	0.09	0.12
2	6	0.408	11.93	440	4.62	0.16	0.11	43	83.35	8.41	0.07	0.09
3	6	0.408	11.92	455	4.67	0.36	0.10	36	82.3	8.1	0.1	0.08

Note: Additional FeO$_4$ was added on September 20th – 24th after first filtration in order to raise pH to neutral and decrease Residual Iron.


Ortho-Phosphate Removal vs. Total Iron Added
5 ppm Ferrate
Ortho-Phosphate Removal
100%
99%
98%
97%
96%
95%
94%
93%
92%
91%
90%
45
47.5
50
52.5
55
57.5
60
62.5
65
67.5
70
Total Iron Added (mg/L)
pH 4.3
pH 4.86
pH 5.0
pH 5.16
pH 5.5
pH 7.02
pH 7.55
pH 8.44
pH 8.9
pH 9.19


Ortho-Phosphate Removal vs. Total Iron Added
6 ppm Ferrate
Ortho-Phosphate Removal
100%
99%
98%
97%
96%
95%
94%
93%
92%
91%
90%
70
72.5
75
77.5
80
82.5
85
Total Iron Added (mg/L)
pH 6.78
pH 7.94
pH 8.1
pH 8.41
pH 8.9
pH 9.36

Pilot System Test Results (SFWMD):

SITE & DATE	TPO4	TDPO4	OPO4	DOP	PP	TN	TKN	TON	NH4	NOX	TOTFE	SO4	ALKA	LPH	LCOND	TURB
Inflow																
09/18/12	1.167	1.099	1.089	0.010	0.068	4.123	3.660	2.338	1.322	0.463	726	42	14.0	6.5	210	12.2
09/20/12	1.490	1.412	1.380	0.032	0.078	4.412	3.980	2.724	1.256	0.432	651	51	10.0	6.4	231	15.2
09/25/12	1.323	1.251	1.229	0.022	0.072	4.293	3.760	2.518	1.242	0.533	622	47	11.0	6.6	219	16.4
Outflow																
09/18/12	0.059	0.002	0.002	0.000	0.057	2.314	1.790	0.548	1.242	0.524	5403	41	2.0	6.1	957	5.4
09/20/12	0.045	0.002	0.002	0.000	0.043	2.265	1.730	0.463	1.267	0.535	4554	38	2.0	4.9	1184	4.7
09/25/12	0.020	0.002	0.002	0.000	0.018	2.097	1.450	0.311	1.139	0.647	1988	41	2.0	5.8	1260	2.4

% DIFFERENCE BETWEEN INFLOW AND OUTFLOW SAMPLES*																
09/18/12	-95%	-99.8%	-99.8%	-100%	-16%	-44%	-51%	-77%	-6%	13%	644%	-2%	-86%	-6%	356%	-56%
09/20/12	-97%	-99.9%	-100%	-100%	-45%	-49%	-57%	-83%	1%	24%	600%	-25%	-80%	-23%	413%	-69%
09/25/12	-98%	-99.8%	-100%	-100%	-75%	-51%	-61%	-88%	-8%	21%	220%	-12%	-82%	-13%	475%	-85%

* % difference = [(outflow-inflow)/inflow]*100

A Jar Test of Nclear® Conducted with MacArthur Lake Water

Introduction

The South Florida Water Management District (District) conducted a jar test with Nclear®, a water treatment product distributed by Nclear IP LLC, Miramar Beach, FL, in February 2013 using water collected from MacArthur Lake in Martin County. Nclear® is a proprietary mixture of calcium silicate hydroxides that is greenish-gray in color and has the consistency of flour or dry cement (Fig. 1). Nclear® is one of the mineral-based products being evaluated by the Water Quality Treatment Technologies Section. This jar test was conducted to (a) evaluate the effectiveness of Nclear® to reduce phosphorus (P) and nitrogen (N) levels in surface water and (b) assess the product's effect on other water quality parameters when tested over a wide range of dosages using a single source of water. It is assumed that Nclear® acts primarily by sorption of nutrients and other constituents onto the surface of the mineral particles and is effective primarily at sequestering dissolved inorganic chemical species; however, this assumption has not been verified by the vendor to date.

Methods

Surface water was collected from the bank of MacArthur Lake in Martin County on February 12, 2013 by staff from the Water Quality Treatment Technologies Section. MacArthur Lake was selected as the water source for this test because it was known from previous sampling that the lake had high levels (0.2-0.3 mg/L) of soluble reactive P (SRP). Water was pumped into 5-gal carboys using a small peristaltic pump and immediately transported back to the laboratory. Water was kept at room temperature in the laboratory until the jar test was started the following day. A Phipps and Bird PB-700™ Standard JarTester was used in this evaluation (Fig. 2). Jars were filled with 2 L of MacArthur Lake water and then dosed with Nclear® at one of the following concentrations: 10, 50, 250, 500 or 1,000 mg/L (Fig. 1). A sixth jar was run as a control and was not dosed with Nclear®. The control and Nclear® treatments were unreplicated. All jars were stirred vigorously for 10 minutes at 210 rpm after the Nclear® doses were added and then left undisturbed for the remainder of the test. Water samples were collected on Day 0, i.e., at the start of the jar test before the addition of Nclear®, and at approximately 24 hrs (Day 1) after dosing. Water samples were withdrawn from the jars with a 60-mL plastic syringe fitted with a short piece of plastic tubing. Cartridge filters (0.45 µm) were used for samples that required filtration. Sample preservation followed District protocols. All water samples were analyzed by the District's Chemistry Laboratory for ammonia-nitrogen (NH4), dissolved calcium (CA), conductivity (COND), total Kjeldahl nitrogen (TKN), nitrite+nitrate-nitrogen (NOX), pH (PH), total dissolved phosphorus (TDP), total phosphorus (TP), SRP, sulfate (SO4), and turbidity (TURB). The following chemical parameters were calculated by difference: dissolved organic phosphorus (DOP = TDP – SRP), particulate phosphorus (PP = TP – TDP), total nitrogen (TN = TKN + NOX), and total organic nitrogen (TON = TKN – NH4).

Results and Observations

Results of the chemical analyses performed on water samples collected during the Nclear® jar test are summarized in Table 1 and Figs. 3 and 4. The following observations were made based on comparing the Day 0 control to each of the Day 1 Nclear® treatments:

1. The observed treatment response often was proportional to the product dose, i.e., the more Nclear® added to the jar, the greater the change in the constituent level during the jar test (see plots in Figs. 3 and 4).
2. Concentrations of TP, TDP and SRP were reduced in all Nclear® treatments; all three constituents were markedly reduced at Nclear® doses ≥ 250 mg/L. SRP was reduced to its method detection limit (0.002 mg/L) at the highest Nclear® dose (99% removal).

3. There was a modest reduction in DOP concentrations across all Nclear® treatments (maximum 39% removal) compared to reductions observed in TP, TDP and SRP. The reduction in DOP concentrations was not positively correlated with Nclear® dose.
4. PP concentrations increased at Nclear® treatments ≥ 250 mg/L with almost a four-fold increase in PP measured in the highest Nclear® dose.
5. Concentrations of TN, TKN and TON were reduced in all Nclear® treatments with only modest reductions in these constituents (38% to 40%) at the highest Nclear® dose.
6. Concentrations of NOX and NH4 increased across all Nclear® treatments.
7. CA concentrations increased in all Nclear® treatments with a three-fold increase measured in the highest Nclear® dose.
8. SO4 concentrations exhibited a small decrease (< 10%) across all Nclear® treatments.
9. TURB decreased across all Nclear® treatments, although the reduction in TURB was not positively correlated with the Nclear® dose.
10. COND increased in all Nclear® treatments with a three-fold increase measured in the highest Nclear® dose.
11. PH increased in all Nclear® treatments and exceeded 10 s.u. at Nclear® doses ≥ 250 mg/L.

Future Work

There are no immediate plans to investigate Nclear® any further, although this product may be evaluated as part of the District's Everglades Restoration Strategies Science Plan.

Table 1. Results of chemical analysis of water samples collected from control and treatment jars during the Nclear® jar test. All chemical analyses were performed by the District's Chemistry Laboratory.[†]

	TP	TDP	SRP	DOP	PP	TN	TKN	TON	NOX	NH4	CA	SO4	TURB	COND	PH
Day 0															
Control	0.335	0.307	0.271	0.036	0.028	1.388	1.380	1.357	0.008	0.023	42	16.8	5.2	503	8.0
Day 1															
Control	0.338	0.306	0.275	0.031	0.032	1.325	1.310	1.269	0.015	0.041	43	16.0	5.5	514	8.1
10 mg/L	0.313	0.288	0.260	0.028	0.025	1.300	1.290	1.252	0.010	0.038	44	15.9	3.1	527	8.3
50 mg/L	0.295	0.267	0.239	0.028	0.028	1.222	1.210	1.174	0.012	0.036	51	15.9	3.6	551	9.1
250 mg/L	0.134	0.093	0.071	0.022	0.041	1.131	1.120	1.090	0.011	0.030	67	15.8	4.2	638	10.3
500 mg/L	0.189	0.092	0.057	0.035	0.097	1.032	1.020	0.986	0.012	0.034	85	15.8	4.7	939	11.0
1000 mg/L	0.137	0.033	0.002	0.031	0.104	0.865	0.850	0.814	0.015	0.036	129	15.7	3.5	1556	11.4
%DIFFERENCE BETWEEN DAY 0 CONTROL AND DAY 1 TREATMENTS*															
10 mg/L	-7%	-6%	-4%	-22%	-11%	-6%	-7%	-8%	25%	65%	5%	-5%	-40%	5%	3%
50 mg/L	-12%	-13%	-12%	-22%	0%	-12%	-12%	-13%	50%	57%	22%	-5%	-31%	10%	14%
250 mg/L	-60%	-70%	-74%	-39%	46%	-19%	-19%	-20%	38%	30%	58%	-6%	-19%	27%	29%
500 mg/L	-44%	-70%	-79%	-3%	246%	-26%	-26%	-27%	50%	48%	102%	-6%	-10%	87%	37%
1000 mg/L	-59%	-89%	-99%	-14%	271%	-38%	-38%	-40%	88%	57%	205%	-7%	-33%	209%	43%

[†] Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L) => TDP - SRP; PP = particulate phosphorus (mg P/L) => TP - TDP; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (MG N/L) => TKN - NH4; NOX = nitrite+nitrate-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); CA = dissolved calcium (mg/L); SO4 = sulfate (mg/L); TURB = turbidity (NTU); COND = conductivity (µS/cm); PH = pH (s.u.)

* % difference = [(Day 1 value-Day 0 Control)/Day 0 Control]*100

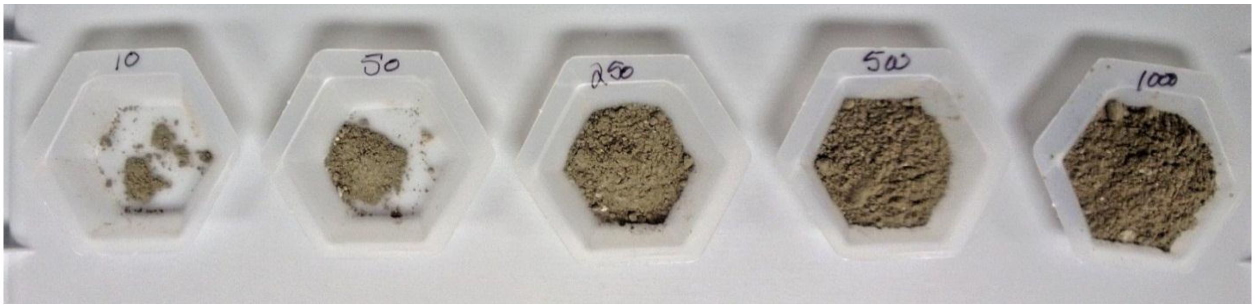


Figure 1. Doses of Nclear® added to the treatment jars during the Nclear® jar test. Nclear® dosages (L-R): 10 mg/L, 50 mg/L, 250 mg/L, 500 mg/L, 1000 mg/L.

Figure 2. Phipps and Bird PB-700™ Standard JarTester apparatus used to conduct the Nclear® jar test.

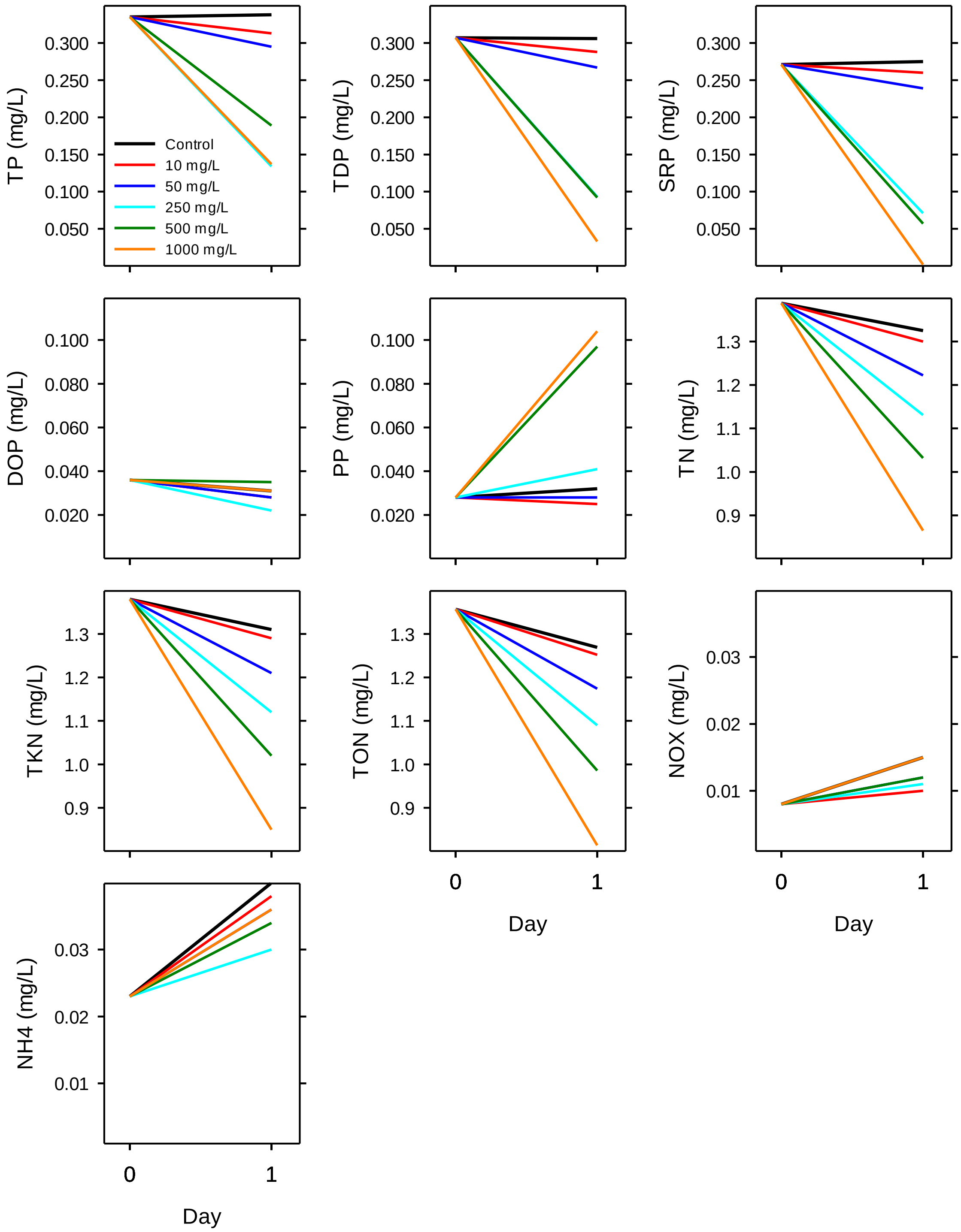


Figure 3. Change in phosphorus and nitrogen concentrations in the control and treatment jars during the Nclear® jar test. Parameter key: TP = total phosphorus (P); TDP = total dissolved P; SRP = soluble reactive P; DOP = dissolved organic P; PP = particulate P; TN = total nitrogen (N); TKN = total Kjeldahl N; TON = total organic N; NOX = nitrite+nitrate-N; NH4 = ammonia-N

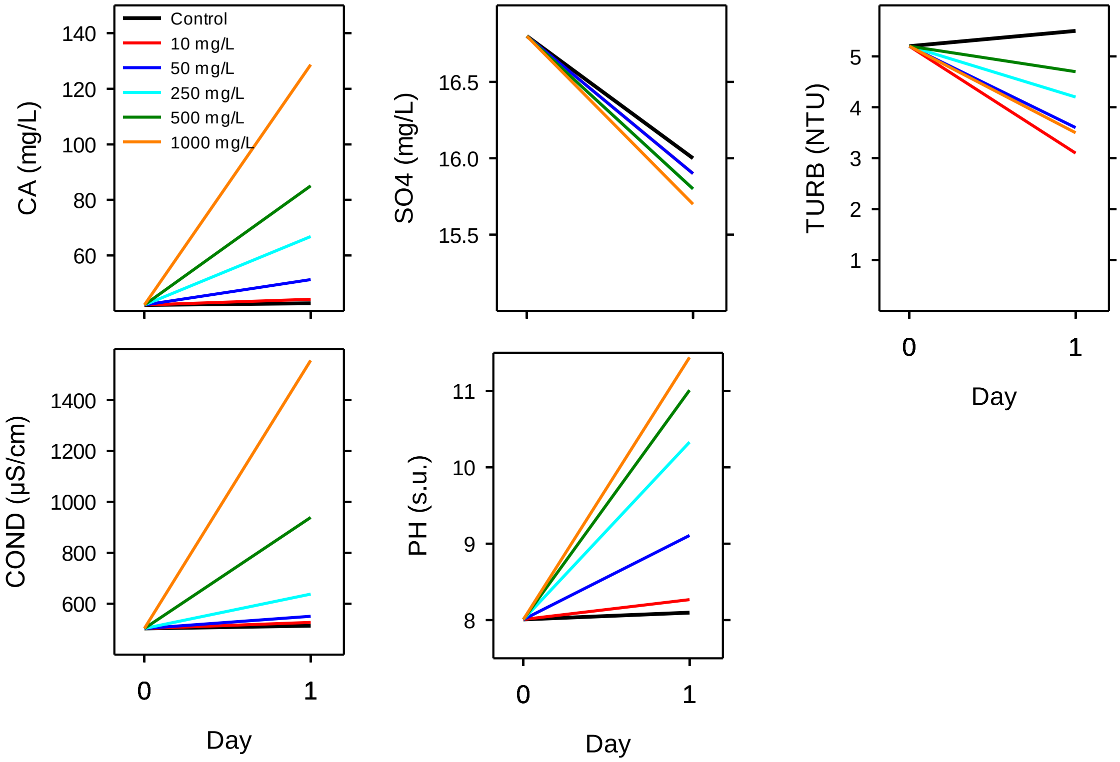


Figure 4. Change in other water quality parameters in the control and treatment jars during the Nclear® jar test. Parameter key: CA = dissolved calcium; SO4 = sulfate; TURB = turbidity; COND = conductivity; PH = pH.

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New Alternative Treatment Assessment (NATA) Program

A Jar Test of Phoslock®, STI, ViroPhos™ and WP-1™ Using C-51 Canal Water

Introduction

The South Florida Water Management District (District) conducted a jar test of four water-treatment products that are being evaluated by the Water Quality Treatment Technologies Section as part of the District's New Alternative Technology Assessment (NATA) Program. The products used in this jar test, the "NATA Product Jar Test", included Phoslock®, STI, ViroPhos™ and WP-1™, all of which are mineral-based compounds. STI, ViroPhos™ and WP-1™ are fine-textured powders with the consistency of flour or dry cement, while the sample of Phoslock® we used had a course granular texture (Fig. 1)[1]. The objective of this jar test was to (a) compare the ability of these products to reduce phosphorus and nitrogen concentrations and (b) assess their effect on other water quality parameters when tested over a range of product doses using a single source of water. Each of these products acts primarily by sorption of nutrients and other constituents onto the surface of the mineral particles and are effective primarily at sequestering dissolved inorganic chemical species according information provided to the District by their manufacturers.

The NATA Program was not designed to cross-compare treatment products; rather, it was intended to be a series of independent product demonstrations. However, difficulty in finding sites with suitably high phosphorus levels to test treatment products prompted the District to conduct this laboratory study. The C-51 canal was selected as a water source because historically it has had moderate to high phosphorus levels during the rainy season (May through November) and is located close to the District's laboratory facilities.

Methods

Water from the C-51 canal was collected from the DB Environmental Laboratory's water pump located at the S5A Laboratory on July 31, 2012, transported to the laboratory in 5-gal carboys and processed immediately for the NATA Product Jar Test. Pre-cleaned 2-L Nalgene sample bottles served as jars (Fig. 2). Each of the four water-treatment products was tested at five different concentrations (10, 50, 250, 500 and 1,000 mg/L) resulting in 20 product treatments. These concentrations spanned the range of product application rates recommended by the manufacturers for their products. Each jar was filled with 2,000 mL of water and dosed with the appropriate amount of product at the start of the test. Two jars were used for each treatment to provide a sufficient volume of water needed for water quality analyses. Because Phoslock® had a course texture, it was ground using a glass mortar and pestle (Fig. 2) prior to adding it to the jars, although the resulting material was not as fine-grained as the other products. Two jars filled only with C-51 canal water were run as a control. The control and product treatments were unreplicated. Each jar was shaken vigorously for two minutes after the addition of the product and then left undisturbed for the duration of the test.

A water sample was collected at the start of the jar test before the addition of the products (Day 0) and at approximately 24, 48 and 144 hrs after dosing (Day 1, 2 and 6, respectively) from each jar. Samples were withdrawn from the jars with a 60-mL plastic syringe fitted with a short piece of plastic tubing and processed immediately after collection following District protocols.

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[1] Phoslock® is manufactured by Phoslock Water Solutions, Ltd., St. Leonards, NSW, Australia and distributed in North America by SePRO, Carmel, IN; STI (Simtec Triad Ionate) is manufactured and distributed by Universal Environmental Solutions, Aguanga, CA; ViroPhos™ is manufactured by Virotech Global Solutions, Inc., Mobile, AL and distributed by EnviRemed, Ocean Isle Beach, NC; WP-1™ is manufactured and distributed by US Environmental Resource & Recovery Group, LLC, Walterboro, SC.

Whatman® Polydisc GW membrane filters (0.45 µm pore size) were used with samples that required filtration. All samples were analyzed for specific conductance (COND), pH (PH), ammonia-nitrogen (NH4), nitrite+nitrate-nitrogen (NOX), total Kjeldahl nitrogen (TKN), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total phosphorus (TP), sulfate, (SO4), total aluminum (TAL), total iron (TFE) and turbidity (TURB) by the District's Chemistry Laboratory. The following chemical parameters were calculated by difference: dissolved organic phosphorus (DOP = TDPO4 – OPO4), particulate phosphorus (PP = TPO4 – TDPO4), total nitrogen (TN = TKN + NOX) and total organic nitrogen (TON = TKN – NH4).

Results and Observations

Results of the chemical analyses performed on water samples collected from the control and each product treatment during the NATA Product Jar Test are presented in Appendix Table 1 and summarized in Figs 3 - 6. The following observations were made based on a qualitative comparison of the control to the product treatments and assessing the variation among product treatments:

1. The purpose of a control is to detect change in a response variable (e.g., constituent concentration) that is not attributable to the factor(s) being manipulated in the experimental treatments (e.g., product dose). Ideally, little to no change in the response variable occurs in the control when compared to the treatments. Conversely, large changes in the control complicate the interpretation of any change observed in the treatments. Relatively little change in TN, TKN and TON concentrations was observed in the control; concentrations of these constituents decreased by less than 10% during the jar test (Figs. 3B and 3D). However, NH4 in the control decreased substantially (> 80%), while there was a small net increase in NOX. Except for DOP, all control P concentrations decreased substantially during the jar test, more than 60% of the TP, TDP, SRP and PP concentrations at the start of the jar test were lost from the control by Day 6. As a result, interpretable data on P loss in the treatments are limited to the first three days of the jar test. We attributed the loss of particulate P in the control to mechanical settling and the loss of dissolved P to some combination of sorption to the jar walls, uptake by microbes in the water column and uptake by biofilm growth on the inside of the jars.
2. The treatment response often was proportional to the product dose, i.e., the larger the product dose added to the jar the greater the observed change in the constituent level during the jar test (see various plots in Figs. 4, 5 and 6). The loss of P from the control (Figs. 3A and 3C) indicates that reduction of TP, TDP, SRP and PP in the treatments was not due entirely to the action of the products; depending on the P species, 16 to 38% of P loss on Days 1 and 2 and 68 to 100% of P loss on Day 6 was attributed to other factors as described in #1 above.
3. TP concentrations on Day 1 and 2 at product doses ≥ 250 mg/L (the high-dose treatments) decreased compared to the control, although ViroPhos™ was much less effective than the other products based on loss of TP from the water (Fig. 4). TP concentrations in the high-dose STI and WP-1™ treatments were similar to the control by Day 6 while TP concentrations in the high-dose Phoslock® and ViroPhos™ treatments actually were higher than the control by the end of the jar test. In contrast, TP concentration reduction in all 10 and 50 mg/L treatments (the low-dose treatments) was no greater than in the control.
4. TDP and SRP concentrations in the high-dose treatments generally decreased compared to the control on Day 1 and 2, although ViroPhos™ was not as effective as the other products at reducing the concentration of either constituent (Fig. 4). SRP and TDP concentrations in the high-dose treatments were little different from SRP and TDP con-

centrations in the control by Day 6. In contrast, TDP and SRP concentration reductions in the low-dose treatments were no greater than in the control for either constituent.

5. DOP concentration exhibited a small reduction in the high-dose treatments relative to the control for Phoslock®, STI and WP-1™ while ViroPhos™ appeared to have little to no treatment effect (Fig. 4). DOP concentration reduction in all low-dose treatments was no greater than in the control.
6. PP concentrations in the high-dose treatments decreased relative to the control for STI and WP-1™, showed little to no change for ViroPhos™ and increased slightly for Phoslock® (Fig. 4). PP concentration reduction in all low-dose treatments was no greater than in the control.
7. TN and TKN concentrations in the high-dose treatments decreased relative to the control for STI and WP-1™, exhibited little or no change for ViroPhos™ and increased for Phoslock® (Fig. 5). TN and TKN concentration reduction in all low-dose treatments was little different from the control.
8. TON concentrations in the high-dose treatments decreased relative to the control for STI and WP-1™ and exhibited little to no change for ViroPhos™ and Phoslock® (Fig. 5). TON concentration reduction in all low-dose treatments was little different from the control.
9. NOX concentrations in the high-dose treatments exhibited little or no change relative to the control for STI, WP-1™ and ViroPhos™ and increased markedly for Phoslock® (Fig. 5). NOX concentrations in all low-dose treatments increased slightly relative to the control.
10. NH4 concentrations in the high-dose treatments increased markedly relative to the control for Phoslock® and by a lesser degree for STI and WP-1™ while there was little difference between treatments and the control for ViroPhos™ (Fig. 5). NOX concentrations in all low-dose treatments were little different from the control.
11. TURB levels in the high-dose treatments were substantially higher relative to the control on Day 1 and, in general, decreased to near control levels by the end of the jar test (Fig. 6). TURB levels in all low-dose treatments were, in general, little different from the control.
12. PH levels increased markedly in most STI and WP-1™ treatments relative to the control but exhibited little change in the Phoslock® and ViroPhos™ treatments (Fig. 6).
13. COND levels were little changed in the Phoslock® and WP-1™ treatments and with one exception (the STI 1000 mg/L dose) increased only slightly in the STI and ViroPhos™ high-dose treatments (Fig. 6).
14. SO4 concentrations in the high-dose treatments increased markedly relative to the control for ViroPhos™ and WP-1™ and were little changed for Phoslock® and STI (Fig. 6). SO4 concentrations in all low-dose treatments were little different from the control. The Material Safety Data Sheet (MSDS) for STI indicates that this product contains sulfur. However, the MSDSs for the other products do not provide any information on sulfur content.
15. TAL and TFE concentrations increased markedly in the high-dose treatments by Day 1 relative to the control for Phoslock®, ViroPhos™ and WP-1™ and then decreased to near control levels by the end of the jar test (Fig. 6). This was similar to the temporal pattern observed for TURB, which suggests that most of the TLA and TFE was associated with mineral particles suspended in the water column. There was a slight increase in TAL concentration and a slight decrease in TFE concentrations in the high-dose STI treatments. TAL and TFE concentrations in all low-dose treatments, in general, were lit-

tle different from the control. The MSDSs (or other data sources) for Phoslock®, ViroPhos™ and STI indicate that these products contain aluminum and iron. However, the MSDS for WP-1™ does not provide any information on aluminum or iron content.

Summary

The data clearly indicate that all four treatment products, to varying degrees, reduced concentrations of TP, TDP and SRP in the high-dose treatments over and above the loss of these constituents that occurred in the control. The high-dose treatments of STI and WP-1™ also reduced DOP, PP TN, TKN and TON concentrations. Treatment efficacy for these latter constituents in the Phoslock® and ViroPhos™ high-dose treatments was mixed; some constituent concentrations decreased (e.g., DOP for Phoslock®), some increased (e.g., TP for both products; PP, TN and TKN for Phoslock®) while others were little changed (e.g., DOP and PP for ViroPhos™; TON for both products) relative to the control by the end of the jar test. None of the high-dose treatments was effective at removing NOX or NH4. The low-dose treatments for all products were almost uniformly ineffective at reducing P and N species concentrations. All high-dose treatments increased TURB at the start of the jar test. Most STI and WP-1™ treatments caused a substantial increase in PH. The ViroPhos™ and WP-1™ high-dose treatments markedly increased SO4 levels. TAL and TFE concentrations increased in the Phoslock®, ViroPhos™ and WP-1™ high-dose treatments at the start of the jar test.

Figure 1. The four water treatment products evaluated in the NATA Product Jar Test (L-R): Phoslock®, STI, ViroPhos™ and WP-1™.

Figure 2. Conducting the NATA Product Jar Test (clockwise from upper left): weighing out a product dose; filling jars with C-51 canal water; arrangement of 2-L Nalgene sample bottles at the start of the test; and grinding Phoslock® with a mortar and pestle.

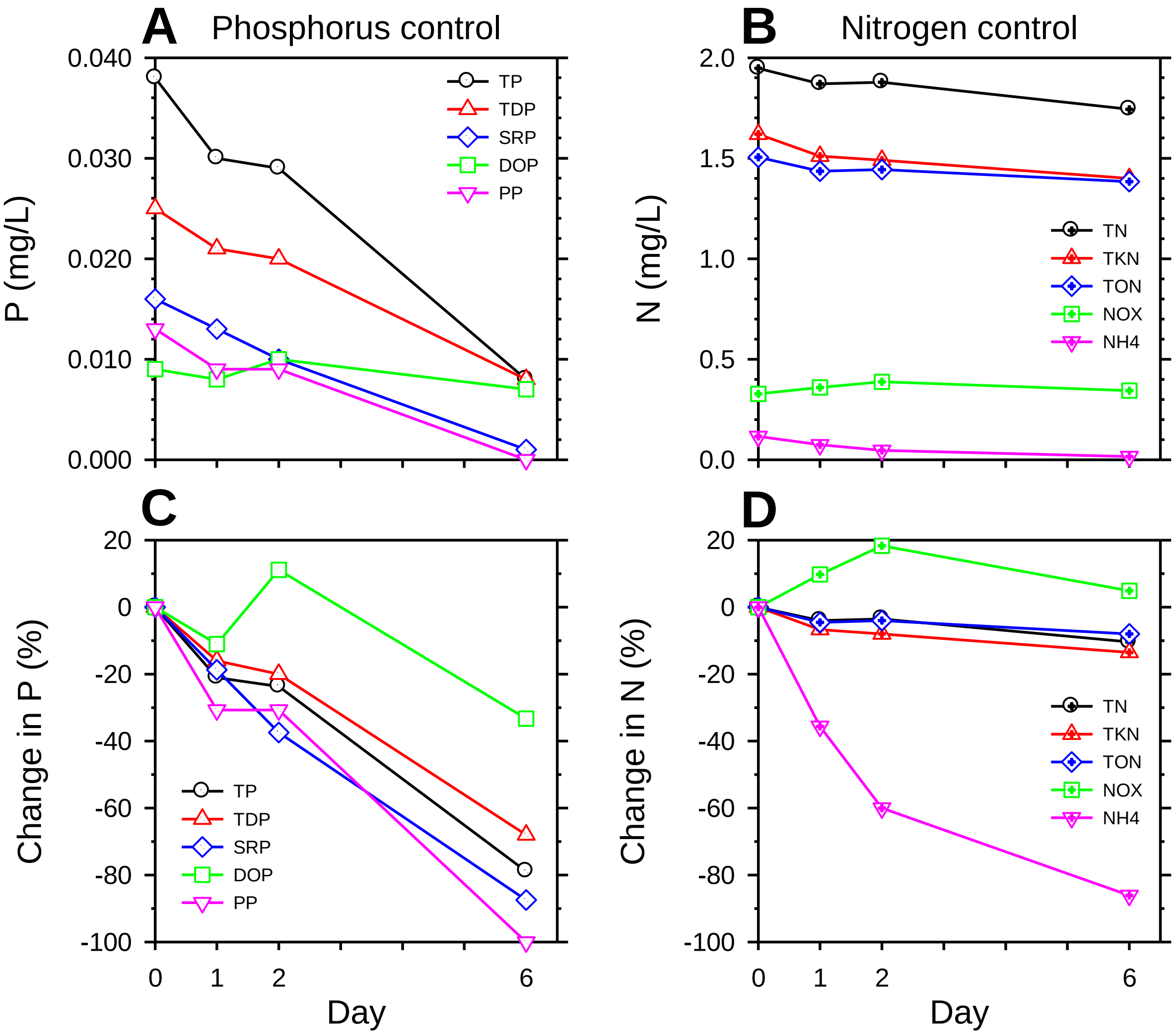

Figure 3. Change in total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), dissolved organic phosphorus (DOP), particulate phosphorus (PP), total nitrogen (TN), total Kjeldahl nitrogen (TKN), total organic nitrogen (TON), nitrite+nitrate-nitrogen (NOX) and ammonia-nitrogen (NH4) concentrations in the control jar during the NATA Product Jar Test. Panels A and B: change in concentration of each P and N constituent; Panels C and D: percent change in concentration of each P and N constituent relative to their concentration on Day 0; positive values indicate an increase in concentration while negative values indicate a decrease in concentration.

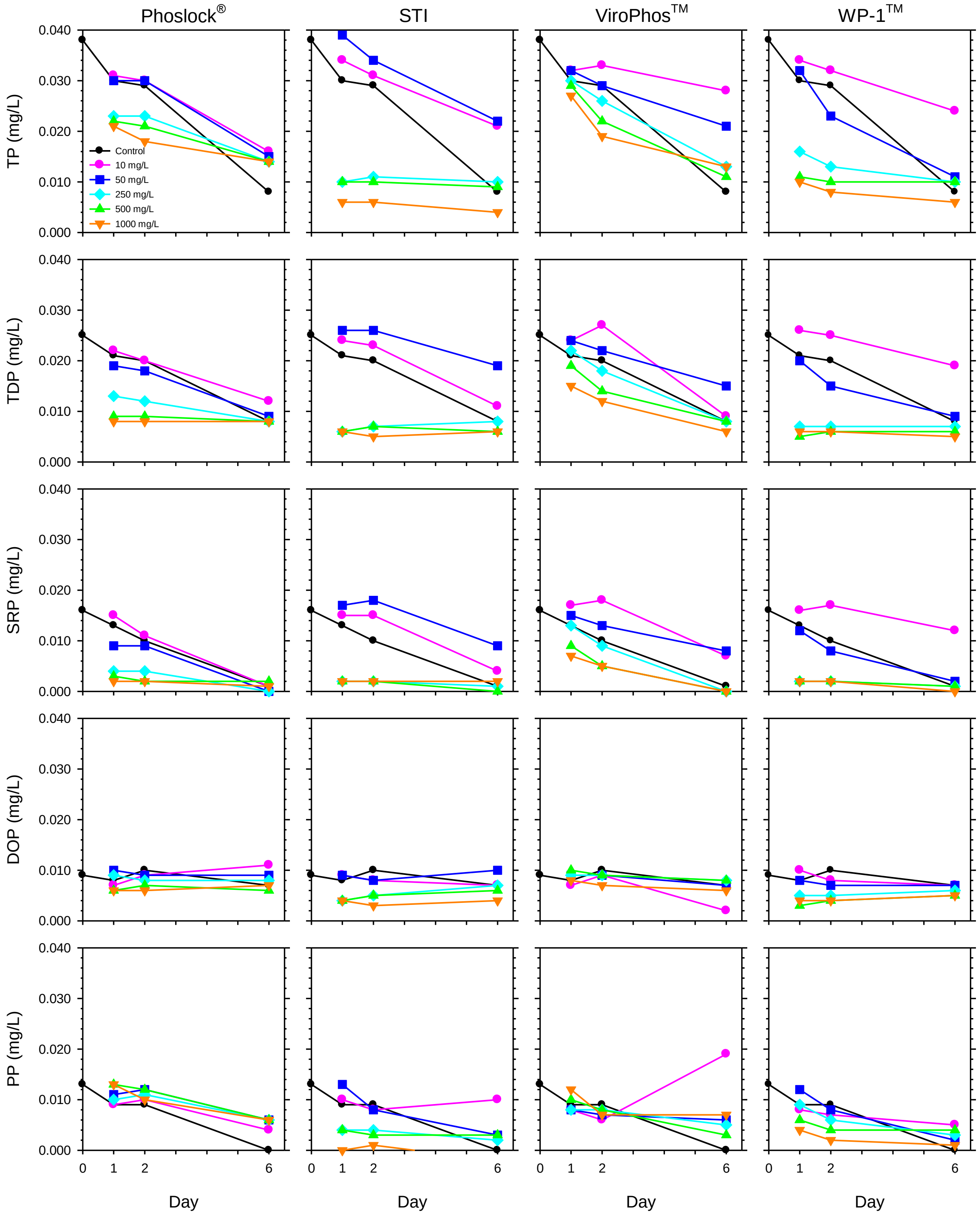

Figure 4. Change in total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), dissolved organic phosphorus (DOP) and particulate phosphorus (PP) concentrations in response to different doses of Phoslock®, STI, ViroPhos™ and WP-1™ during the NATA Product Jar Test.

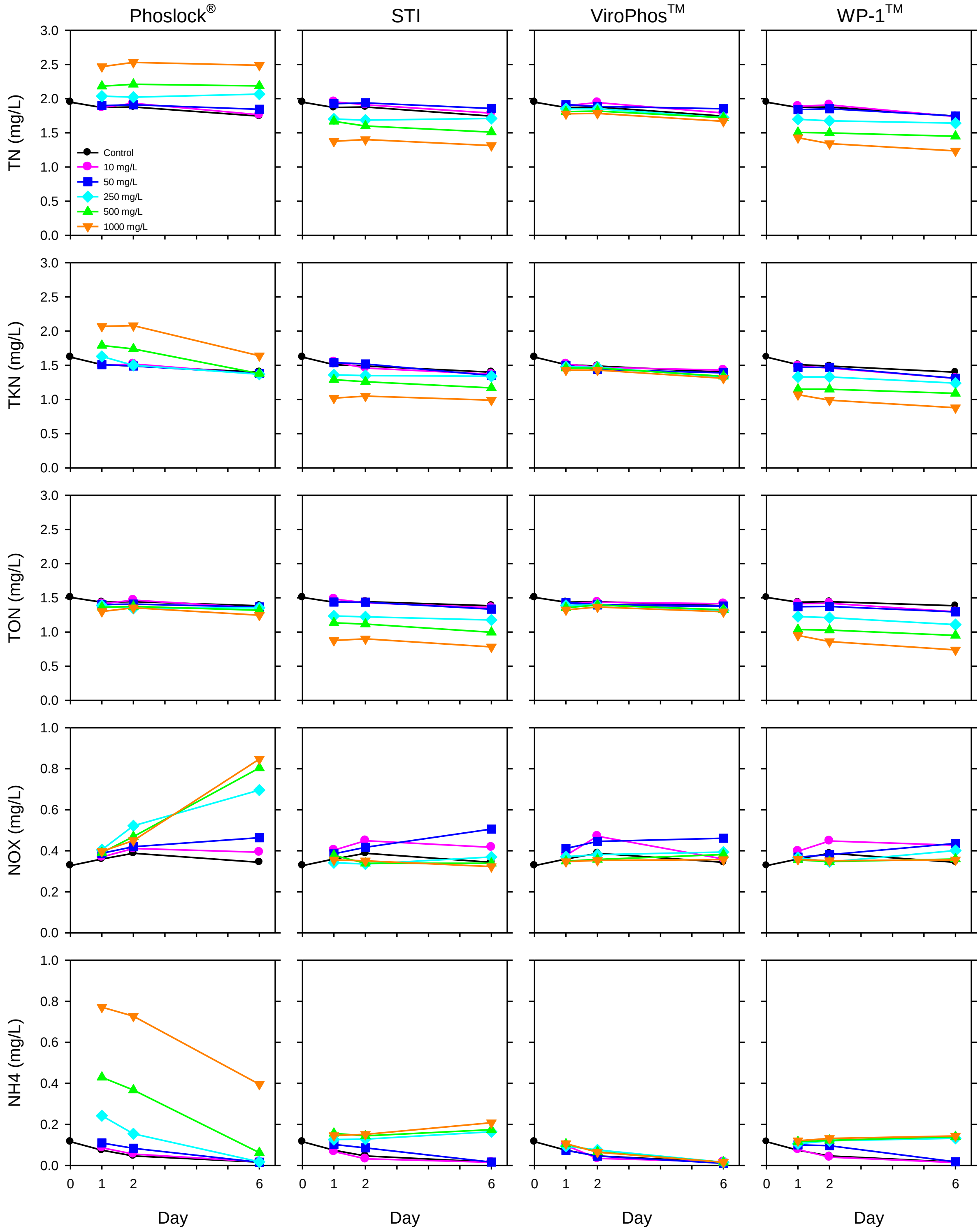

Figure 5. Change in total nitrogen (TN), total Kjeldahl nitrogen (TKN), total organic nitrogen (TON), nitrite+nitrate-nitrogen (NOX) and ammonia-nitrogen (NH4) concentrations in response to different doses of Phoslock®, STI, ViroPhos™ and WP-1™ during the NATA Product Jar Test.

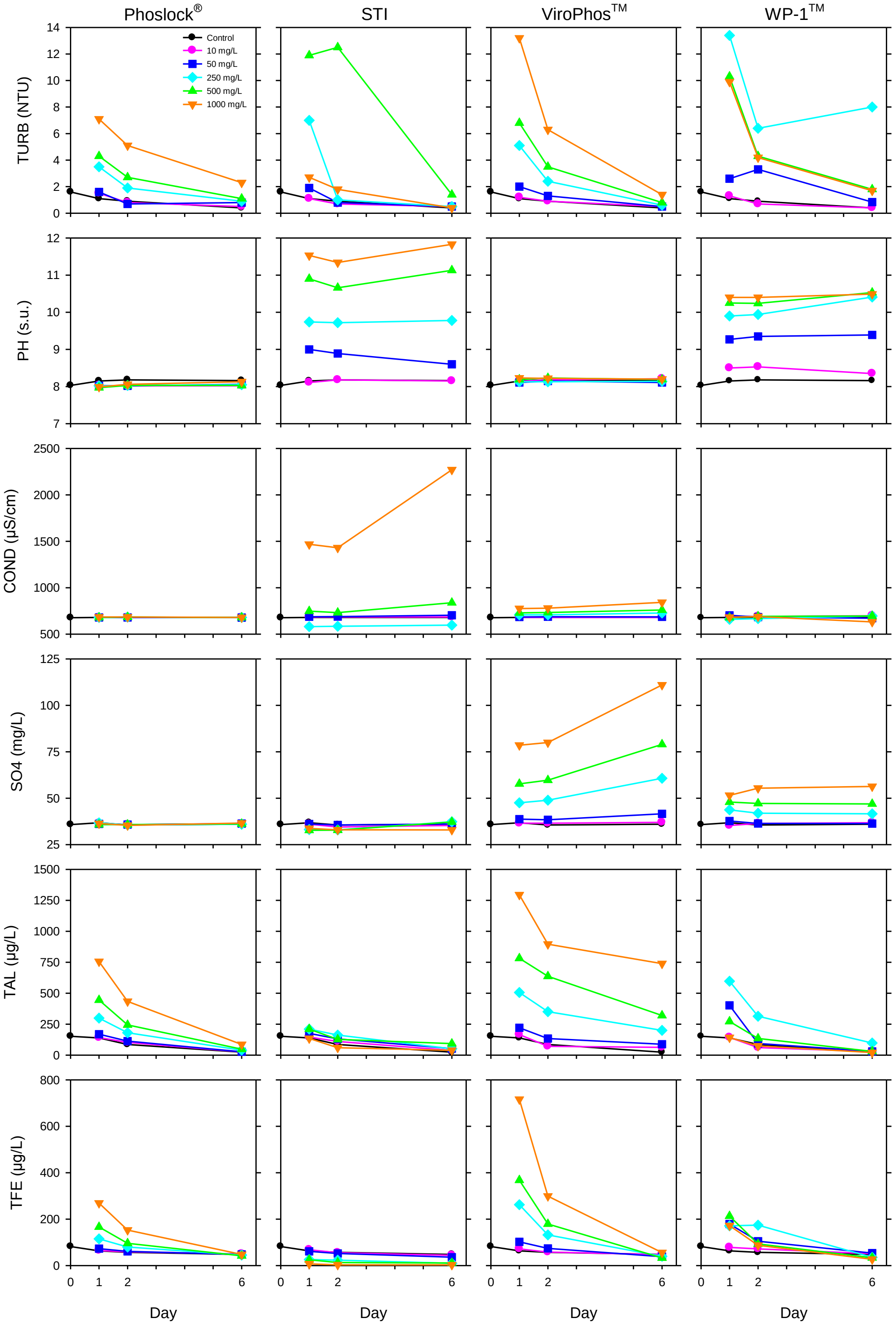

Figure 6. Change in turbidity (TURB), pH (PH), specific conductance (COND), sulfate (SO4) total aluminum (TAL) and total iron (TFE) levels in response to different doses of Phoslock®, STI, ViroPhos™ and WP-1™ during the NATA Product Jar Test.

Appendix 1. Chemical analyses of water samples collected from each product treatment during the NATA Product Jar Test.*

	TPO4	TDPO4	OPO4	PP	DOP	TN	TKN	TON	NOX	NH4	SO4	TOTAL	TOTFE	LPH	LCOND	TURB
CONTROL																
Day 0	0.038	0.025	0.016	0.013	0.009	1.948	1.620	1.505	0.328	0.115	36	152	82	8.0	677	1.6
Day 1	0.030	0.021	0.013	0.009	0.008	1.870	1.510	1.436	0.360	0.074	37	139	63	8.2	679	1.1
Day 2	0.029	0.020	0.010	0.009	0.010	1.878	1.490	1.444	0.388	0.046	36	86	57	8.2	680	0.9
Day 6	0.008	0.008	0.002	0.000	0.006	1.744	1.400	1.384	0.344	0.016	36	24	48	8.2	679	0.4
Phoslock®																
10 mg/L																
Day 1	0.031	0.022	0.015	0.009	0.007	1.870	1.500	1.414	0.370	0.086	36	142	65	8.0	679	1.5
Day 2	0.030	0.020	0.011	0.010	0.009	1.931	1.520	1.465	0.411	0.055	36	103	59	8.0	680	0.8
Day 6	0.016	0.012	0.002	0.004	0.010	1.763	1.370	1.352	0.393	0.018	36	26	50	8.0	679	0.5
50 mg/L																
Day 1	0.030	0.019	0.009	0.011	0.010	1.898	1.510	1.401	0.388	0.109	36	169	73	8.0	679	1.6
Day 2	0.030	0.018	0.009	0.012	0.009	1.910	1.490	1.407	0.420	0.083	36	113	61	8.0	680	0.7
Day 6	0.015	0.009	0.002	0.006	0.007	1.844	1.380	1.365	0.464	0.015	36	27	48	8.1	678	0.8
250 mg/L																
Day 1	0.023	0.013	0.004	0.010	0.009	2.035	1.630	1.388	0.405	0.242	37	299	115	8.0	680	3.5
Day 2	0.023	0.012	0.004	0.011	0.008	2.022	1.500	1.346	0.522	0.154	36	181	80	8.0	683	1.9
Day 6	0.014	0.008	0.002	0.006	0.006	2.066	1.370	1.353	0.696	0.017	36	40	45	8.1	680	0.9
500 mg/L																
Day 1	0.022	0.009	0.003	0.013	0.006	2.181	1.790	1.361	0.391	0.429	36	445	166	8.0	680	4.3
Day 2	0.021	0.009	0.002	0.012	0.007	2.209	1.740	1.373	0.469	0.367	36	244	96	8.0	683	2.7
Day 6	0.014	0.008	0.002	0.006	0.006	2.184	1.380	1.318	0.804	0.062	36	48	42	8.0	680	1.1
1000 mg/L																
Day 1	0.021	0.008	0.002	0.013	0.006	2.467	2.070	1.299	0.397	0.771	36	756	269	8.0	685	7.1
Day 2	0.018	0.008	0.002	0.010	0.006	2.530	2.080	1.353	0.450	0.727	35	434	153	8.1	685	5.1
Day 6	0.014	0.008	0.002	0.006	0.006	2.487	1.640	1.245	0.847	0.395	37	86	48	8.1	680	2.3
STI																
10 mg/L																
Day 1	0.034	0.024	0.015	0.010	0.009	1.953	1.550	1.482	0.403	0.068	36	146	68	8.1	683	1.1
Day 2	0.031	0.023	0.015	0.008	0.008	1.909	1.460	1.428	0.449	0.032	35	110	55	8.2	685	0.7
Day 6	0.021	0.011	0.004	0.010	0.007	1.787	1.370	1.355	0.417	0.015	35	38	44	8.2	685	0.5
50 mg/L																
Day 1	0.039	0.026	0.017	0.013	0.009	1.925	1.540	1.438	0.385	0.102	36	176	61	9.0	687	1.9
Day 2	0.034	0.026	0.018	0.008	0.008	1.937	1.520	1.435	0.417	0.085	36	131	52	8.9	689	0.8
Day 6	0.022	0.019	0.009	0.003	0.010	1.856	1.350	1.334	0.506	0.016	36	53	36	8.6	703	0.5

Appendix 1. (continued).

	TPO4	TDPO4	OPO4	PP	DOP	TN	TKN	TON	NOX	NH4	SO4	TOTAL	TOTFE	LPH	LCOND	TURB
250 mg/L																
Day 1	0.010	0.006	0.002	0.004	0.004	1.702	1.360	1.234	0.342	0.126	33	210	26	9.7	581	7.0
Day 2	0.011	0.007	0.002	0.004	0.005	1.686	1.350	1.222	0.336	0.128	33	162	23	9.7	585	1.0
Day 6	0.010	0.008	0.002	0.002	0.006	1.710	1.340	1.176	0.370	0.164	37	51	10	9.8	597	0.5
500 mg/L																
Day 1	0.010	0.006	0.002	0.004	0.004	1.668	1.290	1.134	0.378	0.156	33	210	25	10.9	748	11.9
Day 2	0.010	0.007	0.002	0.003	0.005	1.599	1.260	1.116	0.339	0.144	33	127	13	10.7	732	12.5
Day 6	0.009	0.006	0.002	0.003	0.004	1.509	1.170	0.996	0.339	0.174	37	93	11	11.1	838	1.4
1000 mg/L																
Day 1	0.006	0.006	0.002	0.000	0.004	1.376	1.020	0.875	0.356	0.145	34	135	7	11.5	1468	2.7
Day 2	0.006	0.005	0.002	0.001	0.003	1.401	1.050	0.899	0.351	0.151	33	60	3	11.3	1430	1.8
Day 6	0.004	0.006	0.002	-0.002	0.004	1.313	0.990	0.782	0.323	0.208	33	39	3	11.8	2270	0.4
ViroPhos™																
10 mg/L																
Day 1	0.032	0.024	0.017	0.008	0.007	1.898	1.520	1.423	0.378	0.097	37	166	72	8.1	680	1.2
Day 2	0.033	0.027	0.018	0.006	0.009	1.941	1.470	1.436	0.471	0.034	37	71	58	8.2	680	0.9
Day 6	0.028	0.009	0.007	0.019	0.002	1.790	1.430	1.413	0.360	0.017	37	63	47	8.2	679	0.5
50 mg/L																
Day 1	0.032	0.024	0.015	0.008	0.009	1.911	1.500	1.427	0.411	0.073	39	221	102	8.1	685	2.0
Day 2	0.029	0.022	0.013	0.007	0.009	1.886	1.440	1.395	0.446	0.045	38	134	74	8.2	687	1.3
Day 6	0.021	0.015	0.008	0.006	0.007	1.851	1.390	1.380	0.461	0.010	42	88	38	8.1	686	0.5
250 mg/L																
Day 1	0.030	0.022	0.013	0.008	0.009	1.851	1.480	1.387	0.371	0.093	48	506	262	8.1	707	5.1
Day 2	0.026	0.018	0.009	0.008	0.009	1.851	1.470	1.395	0.381	0.075	49	351	132	8.1	708	2.4
Day 6	0.013	0.008	0.002	0.005	0.006	1.724	1.330	1.315	0.394	0.015	61	200	40	8.1	728	0.6
500 mg/L																
Day 1	0.029	0.019	0.009	0.010	0.010	1.810	1.460	1.356	0.350	0.104	58	782	368	8.2	729	6.8
Day 2	0.022	0.014	0.005	0.008	0.009	1.818	1.460	1.394	0.358	0.066	60	637	179	8.2	733	3.5
Day 6	0.011	0.008	0.002	0.003	0.006	1.722	1.340	1.325	0.382	0.015	79	320	33	8.2	760	0.8
1000 mg/L																
Day 1	0.027	0.015	0.007	0.012	0.008	1.777	1.430	1.324	0.347	0.106	79	1295	716	8.2	776	13.2
Day 2	0.019	0.012	0.005	0.007	0.007	1.783	1.430	1.366	0.353	0.064	80	896	299	8.2	780	6.3
Day 6	0.013	0.006	0.002	0.007	0.004	1.667	1.310	1.295	0.357	0.015	111	739	56	8.2	842	1.4
WP-1™																
10 mg/L																
Day 1	0.034	0.026	0.016	0.008	0.010	1.888	1.490	1.413	0.398	0.077	35	143	78	8.5	693	1.3

Appendix 1. (continued).

	TPO4	TDPO4	OPO4	PP	DOP	TN	TKN	TON	NOX	NH4	SO4	TOTAL	TOTFE	LPH	LCOND	TURB
Day 2	0.032	0.025	0.017	0.007	0.008	1.908	1.460	1.420	0.448	0.040	36	61	72	8.5	690	0.7
Day 6	0.024	0.019	0.012	0.005	0.007	1.737	1.310	1.296	0.427	0.014	37	29	51	8.4	698	0.4
50 mg/L																
Day 1	0.032	0.020	0.012	0.012	0.008	1.839	1.470	1.370	0.369	0.100	38	402	179	9.3	702	2.6
Day 2	0.023	0.015	0.008	0.008	0.007	1.851	1.470	1.374	0.381	0.096	36	94	105	9.4	684	3.3
Day 6	0.011	0.009	0.002	0.002	0.007	1.746	1.310	1.293	0.436	0.017	36	29	54	9.4	672	0.8
250 mg/L																
Day 1	0.016	0.007	0.002	0.009	0.005	1.697	1.330	1.225	0.367	0.105	44	597	171	9.9	660	13.4
Day 2	0.013	0.007	0.002	0.006	0.005	1.676	1.330	1.210	0.346	0.120	42	314	174	9.9	668	6.4
Day 6	0.010	0.007	0.002	0.003	0.005	1.641	1.240	1.108	0.401	0.132	42	97	36	10.4	696	8.0
500 mg/L																
Day 1	0.011	0.005	0.002	0.006	0.003	1.505	1.150	1.035	0.355	0.115	48	272	213	10.3	678	10.3
Day 2	0.010	0.006	0.002	0.004	0.004	1.497	1.150	1.028	0.347	0.122	47	135	93	10.2	691	4.3
Day 6	0.010	0.006	0.002	0.004	0.004	1.450	1.090	0.950	0.360	0.140	47	30	34	10.5	695	1.8
1000 mg/L																
Day 1	0.010	0.006	0.002	0.004	0.004	1.428	1.070	0.950	0.358	0.120	52	142	172	10.4	682	9.9
Day 2	0.008	0.006	0.002	0.002	0.004	1.342	0.990	0.859	0.352	0.131	55	74	87	10.4	689	4.2
Day 6	0.006	0.005	0.002	0.001	0.003	1.236	0.880	0.737	0.356	0.143	56	20	27	10.5	632	1.7

* TPO4 = total phosphorus (mg P/L); TDPO4 = total dissolved phosphorus (mg P/L); OPO4 = soluble reactive phosphorus (mg P/L); PP = particulate phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L); TN = total nitrogen (mg N/L); TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L); NOX = nitrate + nitrite-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); SO4 = sulfate (mg/L); TOTAL = total aluminum (µg/L); TOTFE = total iron (µg/L); LPH = lab pH (pH units); LCOND = lab conductivity (µS/cm); TURB = turbidity (NTU);

A Demonstration Study of Phoslock® Conducted at MacArthur Lake

Introduction

The South Florida Water Management District (District) conducted a demonstration study of Phoslock®[1], a product designed to remove phosphorus (P) from surface waters, from March 5 through May 7, 2013 at a small lake in Martin County. Phoslock® is a modified bentonite clay product containing lanthanum, a rare-earth element, and is one of the technologies being evaluated by the Water Quality Treatment Technologies Section as part of the District's New Alternative Technology Assessment (NATA) Program. The District previously had assessed the treatment efficacy of Phoslock® in two bench-scale tests (SFWMD 2012a, 2012b). The demonstration study described in this report was conducted to (a) evaluate the effectiveness of Phoslock® to reduce phosphorus (P) and nitrogen (N) concentrations in surface water in the field and (b) assess the product's effect on other select water quality parameters. Phoslock® acts by the sorption of chemical constituents onto the surface of the mineral particles and is effective primarily at sequestering inorganic chemical species.

Study Site and Methods

This demonstration study was conducted at MacArthur Lake, a small (1.46 ha) artificial impoundment located near Hobe Sound in Martin County, FL (Figs. 1 and 2). MacArthur Lake was built in 2005 and receives stormwater runoff primarily from an adjacent residential development and an upstream golf course. The lake normally has an outflow only during large storm events.

Phoslock® was applied to MacArthur Lake by SePRO Corp. (Carmel, IN) and their contractor Clear Waters Inc. (Port Orange, FL) on March 6, 2013. Phoslock® was pumped as a slurry from a VORTEX mixer mounted on small boat onto the lake surface as the boat operator traveled parallel transects to disperse the product over the entire lake (Fig. 3). Two thousand, nine hundred and forty-four kg of Phoslock® were applied during the demonstration study, which corresponded to a surface application rate of 0.211 kg m^{-2}.

Unreplicated grab samples were collected from two depths (the lake surface and approximately 1 m above the lake bottom) at three sampling locations (east, center and west; see Fig. 1) on six dates: pre-application (March 5), 24 hr post-application (March 7) and at 1, 2, 4 and 9 weeks post-application (March 13, March 19, April 4 and May 7, respectively). Surface samples were collected by hand while a small peristaltic pump was used to collect the bottom samples. Water depth was measured at each sampling location on all dates with a Depthmate® SM-5 depth sounder (Speedtech Instruments, Great Falls, VA). Water temperature (TEMP), dissolved oxygen concentration (DO), conductivity (COND) and pH (PH) were measured at the surface and near the bottom at each sampling location on all dates using a YSI 556MPS multiprobe system (YSI Inc., Yellow Springs, OH).

Water quality samples were processed in the field and sample preservation followed District protocols. Cartridge filters (0.45 µm) were used for constituents that required filtration. Water samples were analyzed by the District's Chemistry Laboratory for alkalinity (ALKA), ammonia-nitrogen (NH4), chlorophyll *a* (CHLA), nitrite+nitrate-nitrogen (NOX), total dissolved phosphorus (TDP), total Kjeldahl-nitrogen (TKN), total phosphorus (TP), soluble reactive phosphorus (SRP) and turbidity (TURB). The following chemical parameters were calculated: dissolved organic

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[1] Phoslock® is manufactured by Phoslock Water Solutions, Ltd. (Sydney, Australia) and distributed in North America by SePRO Corp. (Carmel, IN). For more details, see http://www.sepro.com/phoslock/.

phosphorus (DOP = TDP - SRP), particulate phosphorus (PP = TP – TDP), total nitrogen (TN = TKN + NOX) and total organic nitrogen (TON = TKN – NH4).

Results and Observations

Results of all field measurements and chemical analyses performed on water samples collected during the Phoslock® demonstration study are presented in Appendices 1 and 2. These data are summarized as mean values in Table 1 and Fig. 4 where the raw data were first pooled over sampling location by depth and date. The following observations were made based on comparing the pre-application mean data to post-application mean data:

1. MacArthur Lake would be classified as a eutrophic or hypereutrophic system based on the high surface CHLA and TP concentrations observed throughout the study[2]. Eutrophic and hypereutrophic lakes typically are very productive and can support large phytoplankton populations.
2. Surface and bottom TEMP data indicated that MacArthur Lake was thermally stratified throughout the study, i.e., TEMP always was higher at the surface (epilimnion) than at the bottom (hypolimnion) at all stations. Thermal stratification became more intense, i.e., there were larger epilimnion-hypolimnion TEMP differences, after the second sampling date.
3. Surface CHLA concentration increased by almost an order of magnitude between the pre-application and post-application 2-wk sampling dates (27 to 244 mg/L, respectively) indicative of a phytoplankton bloom and then declined in the following weeks, although CHLA levels were still high (> 40 µg/L). Colonies of the cyanobacteria *Microcystis* sp. were abundant at the lake surface on all sampling dates and algal scums were observed on several occasions. In contrast, much less CHLA was found in the bottom samples during the study (8 to 22 µg/L).
4. Changes in surface TURB paralleled the temporal pattern observed in surface CHLA. Bottom TURB was usually less than TURB at the surface. The increase in bottom TURB over the surface value at the end of the study was attributed to some combination of (a) the release of dissolved materials from the sediment into the hypolimnion, (b) the accumulation of phytoplankton detritus settled from the epilimnion or (c) stormwater runoff into the lake[3].
5. Changes in surface DO and PH levels paralleled the temporal pattern observed in surface CHLA concentrations. The rapid increases in surface DO and PH over the first four sampling dates were attributed to high rates of phytoplankton photosynthesis and reached maximum values of 12.0 mg/L and 9.4 s.u., respectively. Conversely, bottom DO decreased rapidly as thermal stratification intensified; bottom DO concentrations were anoxic (< 1 mg/L) by the last two sampling dates.
6. There was relatively little difference between surface and bottom ALKA and COND levels during the first five sampling dates. However, bottom ALKA and COND were both higher than surface values on the last sampling date, which was attributed to the same potential factors listed for TURB.

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[2] Thresholds for eutrophic and hypereutrophic systems are as follows: eutrophic => water column CHLA and TP concentrations that range from 8 to 25 µg/L and 0.03 to 0.10 mg/L, respectively; hypereutrophic => water column CHLA and TP concentrations greater than 25 µg/L and 0.10 mg/L, respectively (Lampert and Sommer, 1997; Wetzel, 2001, Dodds, 2002). The range of mean surface CHLA and TP concentrations in MacArthur Lake exceeded the hypereutrophic thresholds for CHLA and TP on most sampling dates (see Table 1).

[3] The lake level rose by an estimated 0.6 m between the fifth and sixth sampling dates. This change was reflected in the water depth data (see Appendix 2) and attributed to runoff from one or more large rainfall events that entered MacArthur Lake.

7. Concentrations of TP, TDP and SRP decreased by 40, 65 and 70% in surface samples and by 30, 71 and 77% in bottom samples, respectively, between the pre-application and post-application 24-hr sampling dates. These concentration decreases were attributed to the sorption of P onto the Phoslock® particles as they settled through the water column after application. However, reduction of surface P on subsequent sampling dates probably was associated more with nutrient uptake by phytoplankton, although continued sorption of water-column P or inhibition of P flux from the bottom sediments by Phoslock® cannot be ruled out as possible mechanisms. Bottom concentrations of all three constituents on the last sampling date were higher than surface values, which was similar to surface-bottom differences noted for TURB, ALKA and COND.
8. There were small decreases in surface and bottom DOP concentrations immediately after the Phoslock® application (12 and 7%, respectively).
9. Surface and bottom PP concentrations increased substantially immediately after application of Phoslock® (89 and 229%, respectively).
10. Surface and bottom concentrations of TN, TKN and TON decreased by relatively small amounts immediately after the Phoslock® application (7 and 1%, respectively for TN; 8 and 1%, respectively for TKN; and 8 and 0.5%, respectively for TON). Changes in surface concentrations of these constituents on the following sampling dates paralleled the temporal pattern observed in surface CHLA concentration and were attributed to nutrient uptake by phytoplankton. The steady increase in bottom TN concentration during the study was due in large measure to the increase in bottom NH4 concentration (see below).
11. There was a small increase in surface and little change in bottom NOX concentrations immediately after the Phoslock® application. The subsequent decline in surface NOX thereafter to the method detection level (0.005 mg/L) was attributed to nutrient uptake by phytoplankton while the decrease in bottom NOX was attributed to reduction of NOX to NH4 when the hypolimnion became anoxic.
12. There were small relative decreases in surface and bottom NH4 concentrations immediately after the Phoslock® application (6 and 10%). The subsequent decline in surface NH4 thereafter was attributed to nutrient uptake by phytoplankton. Conversely, bottom NH4 concentration increased by an order of magnitude after the hypolimnion turned anoxic.

References

Dodds, W.K. 2002. Freshwater Ecology: Concepts and Environmental Applications. Academic Press, San Diego, CA, .569 pp.

Lampert, W. and U. Sommer. 1997. Limnoecology: The Ecology of Lakes and Streams. Oxford University Press, New York, NY. 382 pp.

South Florida Water Management District (SFWMD). 2012a. A Bench-scale Approach to Evaluate Phosphorus Sequestration by the Amendment Phoslock®. 5 pp.

South Florida Water Management District (SFWMD). 2012b. New Alternative Technology Assessment (NATA) Program: A Jar Test of Phoslock®, STI, ViroPhos™ and WP-1™ Using C-51 Canal Water. 12 pp.

Wetzel, R.G. 2001. Limnology: Lake and River Ecosystems, 3rd Ed. Academic Press, San Diego, CA. 1006 pp.

Table 1. Mean values for field and water quality parameters monitored during the Phoslock® demonstration study conducted at MacArthur Lake and percent change in parameters between pre-application and post-application 24-hr sampling dates†. Means were calculated from data pooled over sampling location by depth and date. Raw data for each parameter are provided in Appendices 1 and 2.

	TP	TDP	SRP	DOP	PP	TN	TKN	TON	NOX	NH4	ALKA	CHLA	TURB	TEMP	DO	PH	COND
Surface																	
Pre-application	0.316	0.265	0.239	0.026	0.051	1.631	1.543	1.428	0.088	0.115	94	27	6.3	17.7	7.0	7.2	0.519
Post-app 24-hr	0.190	0.094	0.071	0.023	0.096	1.515	1.423	1.316	0.092	0.108	94	21	6.9	17.2	8.0	7.5	0.519
Post-app 1-wk	0.145	0.045	0.021	0.023	0.100	1.798	1.793	1.776	0.005	0.017	95	50	11.9	19.1	10.0	8.3	0.526
Post-app 2-wk	0.190	0.022	0.003	0.019	0.168	3.372	3.367	3.359	0.005	0.008	95	244	29.7	20.4	12.9	9.4	0.522
Post-app 4-wk	0.093	0.019	0.003	0.016	0.074	2.368	2.363	2.350	0.005	0.013	94	100	18.2	24.0	9.4	9.4	0.542
Post-app 9-wk	0.125	0.022	0.007	0.016	0.102	2.028	2.023	2.014	0.005	0.009	85	43	18.7	24.1	8.9	8.3	0.471
Bottom																	
Pre-application	0.304	0.263	0.239	0.023	0.041	1.515	1.427	1.315	0.088	0.112	94	18	5.4	16.8	5.7	7.3	0.519
Post-app 24-hr	0.212	0.077	0.056	0.022	0.135	1.498	1.410	1.309	0.088	0.101	94	22	9.9	16.7	6.3	7.5	0.520
Post-app 1-wk	0.116	0.060	0.038	0.021	0.057	1.501	1.417	1.105	0.085	0.311	95	8	3.7	16.9	4.6	7.6	0.521
Post-app 2-wk	0.108	0.056	0.037	0.019	0.052	1.583	1.547	1.113	0.036	0.434	96	8	4.6	17.2	1.4	7.4	0.525
Post-app 4-wk	0.071	0.038	0.020	0.018	0.033	2.218	2.213	1.270	0.005	0.944	97	7	5.2	17.6	0.6	7.2	0.533
Post-app 9-wk	0.164	0.118	0.102	0.016	0.046	4.545	4.540	1.426	0.005	3.114	117	11	25.3	20.8	0.4	7.2	0.510
% change for Pre-app versus Post-app 24-hr where % change = [(Post-app 24-hr - Pre-app)/Pre-app]*100																	
Surface	-40%	-65%	-70%	-12%	89%	-7%	-8%	-8%	5%	-6%	0%	-23%	10%	-3%	14%	4%	<1%
Bottom	-30%	-71%	-77%	-7%	229%	-1%	-1%	-0.5%	-1%	-10%	0%	27%	83%	-1%	10%	3%	<1%

†Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg/L) => TDP – SRP; PP = particulate phosphorus (mg P/L) => TP - TDP; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L) => TKN - NH4; NOX = nitrite+nitrate-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); ALKA = alkalinity (mg $CaCO_3$/L); CHLA = chlorophyll *a* (µg/L); TURB = turbidity (NTU); TEMP = water temperature (°C); DO = dissolved oxygen (mg/L); PH = pH (s.u.); COND = conductivity (mS/cm)

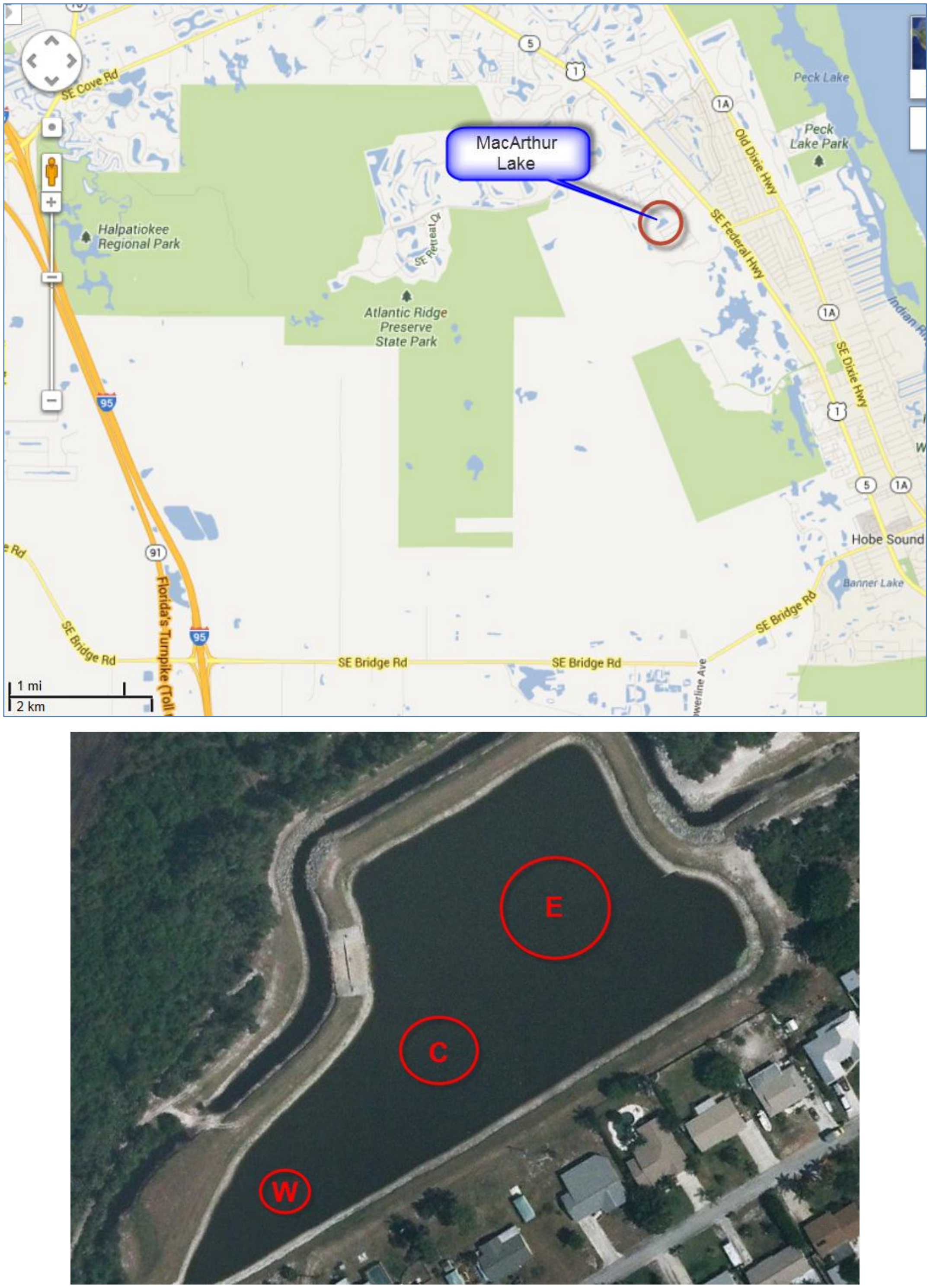

Figure 1. Map showing the location of MacArthur Lake near Hobe Sound in Martin County, FL that was treated in the Phoslock® demonstration study (upper panel) and an aerial photograph of the lake showing the east, center and west sampling locations.

Figure 2. Panoramic photographs of MacArthur Lake taken on February 12 (left panel) and May 8 (right panel), 2013.

Figure 3. Application of Phoslock® to MacArthur Lake on March 6, 2013. Clockwise from upper left: (1) Phoslock® was delivered to the study site in 50-lb bags; (2) Phoslock® was loaded in small batches into a VORTEX mixer mounted on a small boat; (3 to 6) Phoslock® was pumped from the mixer as a slurry through a rear-mounted boom while the boat operator traveled parallel transects to apply Phoslock® over the entire lake, note the Phoslock® plume trailing the boat; (7) close-up of Phoslock® granules.

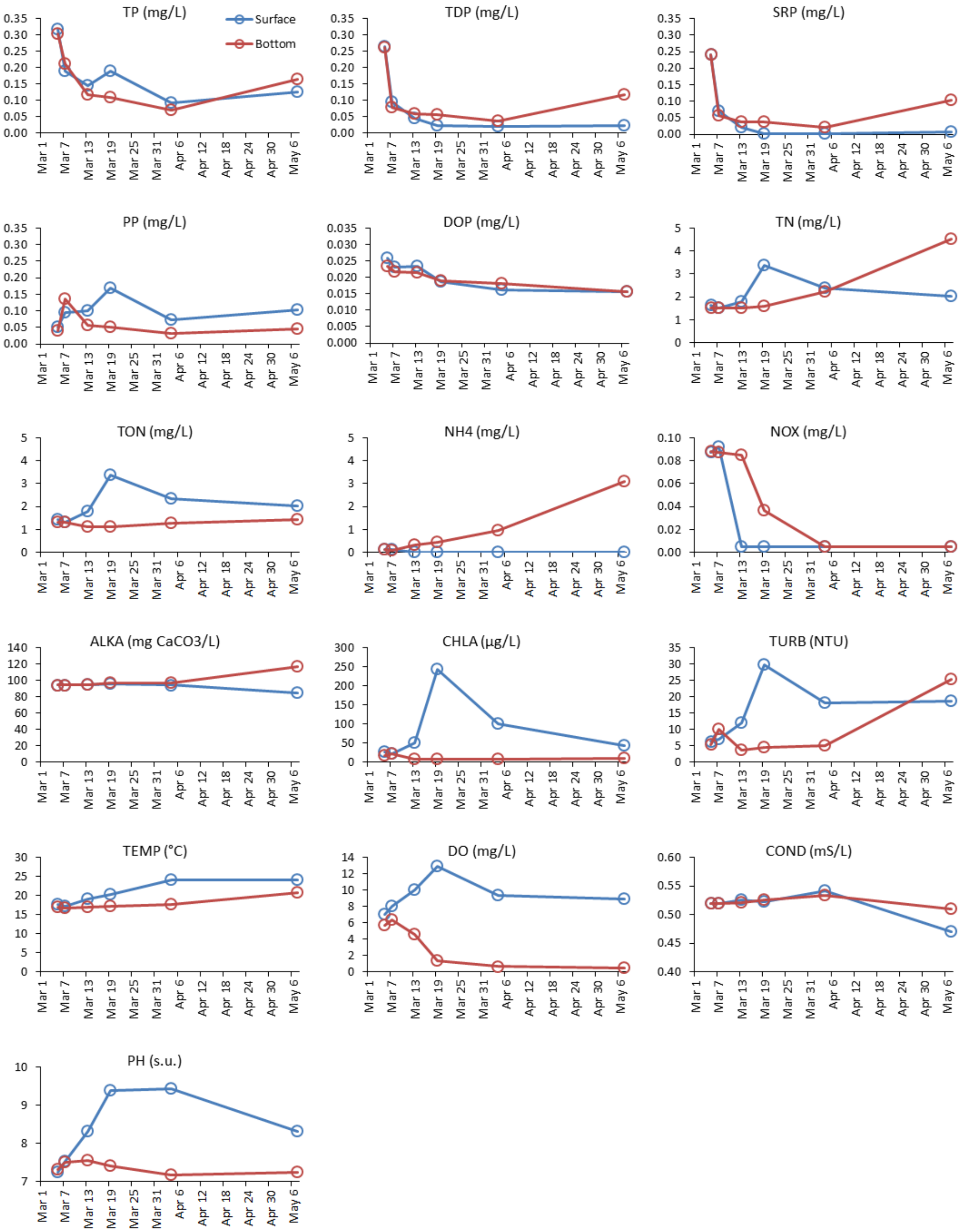

Figure 4. Time series plots of mean values for field and water quality parameters monitored during the Phoslock® demonstration study conducted at MacArthur Lake. Parameter key: TP = total P; TDP = total dissolved P; SRP = soluble reactive P; DOP = dissolved organic P; PP = particulate P; TN = total N; TON = total organic N; NOX = nitrite+nitrate-N; NH4 = ammonia-N; ALKA = alkalinity; CHLA = chlorophyll *a*; TURB = turbidity, TEMP = water temperature (°C); DO = dissolved oxygen; PH = pH; COND = conductivity.

Appendix 1. Results of water quality parameters analyzed in grab samples collected during the Phoslock® demonstration study conducted at MacArthur Lake†.

	TP	TDP	SRP	DOP	PP	TN	TKN	TON	NOX	NH4	ALKA	CHLA	TURB
Pre-application (March 5, 2013)													
East													
Surface	0.323	0.265	0.238	0.058	0.027	1.696	1.610	1.495	0.086	0.115	94	29	6.2
Bottom	0.302	0.263	0.239	0.039	0.024	1.486	1.400	1.281	0.086	0.119	94	16	4.7
Center													
Surface	0.316	0.265	0.240	0.051	0.025	1.608	1.520	1.406	0.088	0.114	94	25	5.5
Bottom	0.305	0.262	0.240	0.043	0.022	1.549	1.460	1.341	0.089	0.119	94	17	5.4
West													
Surface	0.309	0.266	0.240	0.043	0.026	1.589	1.500	1.384	0.089	0.116	94	28	7.2
Bottom	0.304	0.263	0.239	0.041	0.024	1.510	1.420	1.323	0.090	0.097	94	20	6.2
Post-application 24-hr (March 7, 2013)													
East													
Surface	0.192	0.102	0.077	0.090	0.025	1.532	1.440	1.327	0.092	0.113	94	21	7.1
Bottom	0.189	0.099	0.075	0.090	0.024	1.435	1.350	1.242	0.085	0.108	94	18	7.1
Center													
Surface	0.195	0.098	0.075	0.097	0.023	1.492	1.400	1.289	0.092	0.111	94	20	6.5
Bottom	0.185	0.078	0.057	0.107	0.021	1.419	1.330	1.229	0.089	0.101	94	19	9.8
West													
Surface	0.182	0.082	0.061	0.100	0.021	1.522	1.430	1.331	0.092	0.099	94	22	7.1
Bottom	0.263	0.055	0.035	0.208	0.020	1.639	1.550	1.456	0.089	0.094	94	29	12.9
Post-application 1-wk (March 13, 2013)													
East													
Surface	0.144	0.043	0.021	0.101	0.022	1.835	1.830	1.814	0.005	0.016	95	64	14.4
Bottom	0.110	0.061	0.039	0.049	0.022	1.351	1.260	1.016	0.091	0.244	94	6	3.3
Center													
Surface	0.153	0.046	0.021	0.107	0.025	1.895	1.890	1.871	0.005	0.019	95	42	11.2
Bottom	0.110	0.058	0.038	0.052	0.020	1.475	1.390	1.075	0.085	0.315	95	6	3.3
West													
Surface	0.138	0.045	0.022	0.093	0.023	1.665	1.660	1.644	0.005	0.016	95	46	10.1
Bottom	0.129	0.060	0.038	0.069	0.022	1.678	1.600	1.225	0.078	0.375	95	10	4.4
Post-application 2-wk (March 19, 2013)													
East													
Surface	0.175	0.022	0.003	0.153	0.019	3.305	3.300	3.290	0.005	0.010	95	228	29.5
Bottom	0.102	0.055	0.036	0.047	0.019	1.504	1.420	1.072	0.084	0.348	96	7	5.0
Center													
Surface	0.189	0.021	0.003	0.168	0.018	3.395	3.390	3.381	0.005	0.009	95	236	29.1
Bottom	0.113	0.055	0.037	0.058	0.018	1.600	1.580	1.141	0.020	0.439	96	9	4.4
West													
Surface	0.206	0.022	0.003	0.184	0.019	3.415	3.410	3.405	0.005	0.005	96	282	30.5
Bottom	0.108	0.058	0.038	0.050	0.020	1.645	1.640	1.126	0.005	0.514	97	9	4.4

Appendix 1. (Continued).

	TP	TDP	SRP	DOP	PP	TN	TKN	TON	NOX	NH4	ALKA	CHLA	TURB
Post-application 4-wk (April 4, 2013)													
East													
Surface	0.095	0.019	0.003	0.076	0.016	2.515	2.510	2.500	0.005	0.010	94	101	20.5
Bottom	0.091	0.058	0.040	0.033	0.018	2.395	2.390	1.204	0.005	1.186	98	8	4.4
Center													
Surface	0.090	0.020	0.003	0.070	0.017	2.285	2.280	2.268	0.005	0.012	94	100	17.4
Bottom	0.058	0.025	0.008	0.033	0.017	1.925	1.920	1.231	0.005	0.689	96	8	6.3
West													
Surface	0.095	0.019	0.003	0.076	0.016	2.305	2.300	2.282	0.005	0.018	94	100	16.6
Bottom	0.063	0.031	0.012	0.032	0.019	2.335	2.330	1.374	0.005	0.956	97	6	4.8
Post-application 9-wk (May 7, 2013)													
East													
Surface	0.127	0.022	0.007	0.105	0.015	2.075	2.070	2.060	0.005	0.010	85	50	20.1
Bottom	0.200	0.153	0.136	0.047	0.017	5.325	5.320	1.509	0.005	3.811	120	16	28.6
Center													
Surface	0.127	0.020	0.005	0.107	0.015	2.105	2.100	2.091	0.005	0.009	85	40	18.4
Bottom	0.176	0.133	0.118	0.043	0.015	4.995	4.990	1.536	0.005	3.454	120	10	29.1
West													
Surface	0.120	0.025	0.008	0.095	0.017	1.905	1.900	1.892	0.005	0.008	84	40	17.6
Bottom	0.116	0.067	0.052	0.049	0.015	3.315	3.310	1.232	0.005	2.078	111	7	18.1

[†] Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg/L) => TDP – SRP; PP = particulate phosphorus (mg P/L) => TP - TDP; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L) => TKN - NH4; NOX = nitrite+nitrate-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); ALKA = alkalinity (mg $CaCO_3$/L); CHLA = chlorophyll *a* (µg/L); TURB = turbidity (NTU)

Appendix 2. Field parameters measured during the Phoslock® demonstration study conducted at MacArthur Lake[†].

	Location	Depth	TEMP	DO	PH	COND	DEPTH
Pre-application	East	Surface	17.7	7.0	7.4	0.518	5.7
(March 5, 2013)	Center	Surface	17.7	6.7	7.4	0.519	4.4
	West	Surface	17.7	7.4	7.0	0.520	3.7
	East	Bottom	16.8	5.6	7.3	0.519	-
	Center	Bottom	16.8	5.8	7.4	0.519	-
	West	Bottom	16.8	5.7	7.2	0.519	-
Post-app 24-hr	East	Surface	17.3	7.8	7.7	0.520	5.5
(March 7, 2013)	Center	Surface	17.2	7.1	7.5	0.520	4.8
	West	Surface	17.1	9.2	7.4	0.518	3.4
	East	Bottom	16.7	6.2	7.6	0.520	-
	Center	Bottom	16.7	6.2	7.5	0.520	-
	West	Bottom	16.7	6.5	7.4	0.519	-
Post-app 1-wk	East	Surface	19.1	10.0	8.4	0.525	5.4
(March 13, 2013)	Center	Surface	19.1	9.9	8.3	0.525	4.9
	West	Surface	19.0	10.1	8.3	0.527	3.5
	East	Bottom	16.9	5.9	7.6	0.519	-
	Center	Bottom	16.9	4.0	7.5	0.521	-
	West	Bottom	17.0	3.8	7.6	0.523	-
Post-app 2-wk	East	Surface	20.4	12.4	9.3	0.522	5.2
(March 19, 2013)	Center	Surface	20.4	13.0	9.5	0.523	4.4
	West	Surface	20.3	13.3	9.4	0.522	3.5
	East	Bottom	17.2	1.6	7.4	0.523	-
	Center	Bottom	17.2	2.1	7.4	0.527	-
	West	Bottom	17.2	0.6	7.4	0.526	-
Post-app 4-wk	East	Surface	24.1	10.3	9.5	0.541	5.2
(April 4, 2013)	Center	Surface	24.1	9.6	9.5	0.541	3.8
	West	Surface	24.0	8.1	9.4	0.543	3.5
	East	Bottom	17.5	0.6	7.3	0.530	-
	Center	Bottom	17.6	0.7	7.4	0.532	-
	West	Bottom	17.7	0.7	6.8	0.538	-
Post-app 9-wk	East	Surface	24.1	9.8	8.5	0.470	5.9
(May 7, 2013)	Center	Surface	24.0	9.6	8.3	0.471	5.3
	West	Surface	24.1	7.4	8.1	0.471	4.5
	East	Bottom	21.1	0.6	7.4	0.495	-
	Center	Bottom	20.4	0.4	7.3	0.526	-
	West	Bottom	20.8	0.3	7.0	0.510	-

[†] Parameter Key: TEMP = water temperature (°C); DO = dissolved oxygen concentration (mg/L); PH = pH (s.u.); COND = conductivity (mS/cm); DEPTH = water depth (m)

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STI Jar Test of Lake Trafford Water

Introduction

The South Florida Water Management District (District) conducted a jar test of STI (Simtec Triad Ionate manufactured by Universal Environmental Solutions, Aguanga, CA) in June 2012 using water collected from Lake Trafford. STI is a dry white powder with the consistency of flour or dry cement and is one of the products being evaluated by the Water Quality Treatment Technology Section as part of the District's New Alternative Technology Assessment (NATA) Program. This jar test was conducted to evaluate the effectiveness of STI to reduce phosphorus and nitrogen levels in surface water.

Methods

Surface water was collected from the end of the Lake Trafford public pier on June 12, 2012 by staff from the Water Quality Treatment Technology Section. Water was pumped into 5-gal carboys using a small peristaltic pump (Fig. 1) and immediately transported back to the laboratory. Water was kept at room temperature in the laboratory until the jar test was started the following day. Pre-cleaned 2-L Nalgene sample bottles were used as jars (Fig. 2). Jars were filled with 1,800 mL of Lake Trafford water and dosed with STI following the protocol provided to the District by TKW Consulting Engineers, Inc. (see Appendix). The STI treatments with the corresponding mass of product added to the jars were as follows: control (no STI added), 0.5% (5 mg), 1% (11 mg), 2% (21 mg), 3% (32 mg), 4% (43 mg), 5% (53 mg) and 6% (64 mg). The control and STI treatments were unreplicated. The STI percent notation refers to the percentage of one pound of product mixed into one cubic yard of water, e.g., 3% is 0.03 lbs/yd^3, which is equivalent to 17.8 mg/L. The corresponding mass of STI was the amount of product added to each STI treatment prorated for 1,800 mL of water. Each jar was shaken vigorously for two minutes after the addition of the STI dose and then left undisturbed for the duration of the jar test. Water samples were collected on day 0, i.e., water at the start of the jar test before the addition of STI, and approximately 24 and 48 hrs after dosing (day 1 and 2, respectively). Samples were withdrawn from the middle of the jars with a 60-mL plastic syringe fitted with a short piece of plastic tubing and processed following District protocols (Fig. 3). Cartridge filters (0.45 µm) were used for samples that required filtration. Samples were analyzed for chloride (CL), lab conductivity (LCOND), lab pH (LPH), ammonia-nitrogen (NH4), nitrite+nitrate-nitrogen (NOX), total Kjeldahl nitrogen (TKN), soluble reactive phosphorus (OPO4), total dissolved phosphorus (TDPO4), total phosphorus (TPO4), total aluminum (TOTAL), total iron (TOTFE) and turbidity (TURB) by the District's Chemistry Laboratory. The following chemical parameters were calculated: dissolved organic phosphorus (DOP = TDPO4 – OPO4), particulate phosphorus (PP = TOP4 – TDPO4), total nitrogen (TN = TKN + NOX), and total organic nitrogen (TON = TKN – NH4). There was insufficient residual material at the bottom of the jars by the end of the test with which to conduct chemical analysis as recommended in the STI jar test protocol.

Results and Observations

Results of the chemical analyses performed on water samples collected during the STA jar test are summarized in Table 1. The following observations were made based on comparing the control to the STI treatments and the STI treatments over time:

1. Lake Trafford water had considerable phytoplankton as evidenced by the bright green residue observed on all filters during sample processing. The decrease in turbidity in the control from day 0 to 1 was attributed to the settling out of phytoplankton in the jar. We suspect that the control jar was disturbed during sampling on day 2, which remixed some of the settled material back into the water column causing an increase in turbidity

and a number of other parameters. The decrease in turbidity in the STI treatments was attributed to the combined settling out of phytoplankton and the product added to the jars;

2. pH increased with increasing dose of STI;
3. STI did not appear to increase water column conductivity, Cl, Fe or Al levels;
4. STI did not appear to reduce the concentration of any nitrogen form (TN, TKN, TON, NH4 or NOX);
5. OPO4 concentrations were at or near the method detection level (0.002 mg/L) at the start of the jar test and therefore this test cannot be used to assess the effectiveness of STI to remove OPO4. The STI vendor also commented on the very low OPO4 levels in the water used for this jar test;
6. There was no appreciable decrease in TDPO4 or DOP levels in the STI treatments.
7. Ninety-eight percent of the phosphorus mass on day 0 (0.128 mg/L) was either particulate (PP = 0.110 mg/L) or dissolved organic (DOP = 0.015 mg/L) forms;
8. TPO4 levels deceased in all STI treatments, but this can be attributed to the settling out of phytoplankton in the jars (thus removing the phosphorus contained in these cells) rather than any action by STI on the TPO4; note that there was a similar TPO4 decrease across all the STI treatments. In addition, if STI was breaking phosphorus bonds and making it available to biota, we would have expected to see a corresponding increase in TDPO4 and/or OPO4 levels as TPO4 decreased. However, we did not observe any such increase in TDPO4 or OPO4 levels in any of the STI treatments.

Future Work

We have scheduled another jar test of STI using a different source of water (i.e., collected from the C-51 canal at the S5A Pump Station) that should have a higher OPO4 concentration. The STI vendor stated that the sample of product supplied to the District for this jar test was two years old and may have exceeded its shelf life. We requested that the vendor provide us with a fresh sample of STI for the upcoming jar test with C-51 water.

Table 1. Results of chemical analyses of water samples collected from the control and STI treatments during the STI jar test*.

	TPO4	TDPO4	OPO4	PP	DOP	TN	TKN	TON	NOX	NH4	LCOND	LPH	TURB	CL	TOTAL	TOTFE
CONTROL																
Day 0	0.128	0.018	0.003	0.110	0.015	2.855	2.850	2.835	0.005	0.015	427	8.74	12.4	38	131	82
Day 1	0.134	0.019	0.002	0.115	0.017	3.015	3.010	2.998	0.005	0.012	435	8.63	8.4	37	96	41
Day 2	0.141	0.053	0.018	0.088	0.035	2.975	2.970	2.954	0.005	0.016	433	8.60	13.0	37	107	64
0.5% (3 mg/L)																
Day 1	0.106	0.017	0.002	0.089	0.015	3.145	3.140	3.127	0.005	0.013	435	8.79	8.0	37	106	50
Day 2	0.094	0.017	0.002	0.077	0.015	2.885	2.880	2.863	0.005	0.017	434	8.78	6.0	37	99	37
1% (6 mg/L)																
Day 1	0.140	0.016	0.003	0.124	0.013	3.485	3.480	3.466	0.005	0.014	433	8.82	8.1	38	112	55
Day 2	0.088	0.017	0.002	0.071	0.015	2.745	2.740	2.721	0.005	0.019	433	8.75	5.7	37	94	36
2% (12 mg/L)																
Day 1	0.105	0.016	0.002	0.089	0.014	2.905	2.900	2.890	0.005	0.010	435	8.98	8.0	38	110	49
Day 2	0.090	0.017	0.002	0.073	0.015	2.925	2.920	2.903	0.005	0.017	434	8.92	6.0	38	104	37
3% (18 mg/L)																
Day 1	0.104	0.019	0.002	0.085	0.017	3.115	3.110	3.094	0.005	0.016	432	9.12	8.6	38	123	50
Day 2	0.092	0.018	0.002	0.074	0.016	3.025	3.020	3.005	0.005	0.015	434	8.91	5.9	38	101	35
4% (24 mg/L)																
Day 1	0.104	0.016	0.002	0.088	0.014	3.045	3.040	3.035	0.005	0.005	432	9.13	9.4	38	119	47
Day 2	0.083	0.017	0.002	0.066	0.015	2.885	2.880	2.865	0.005	0.015	432	9.02	5.8	39	103	31
5% (30 mg/L)																
Day 1	0.100	0.018	0.002	0.082	0.016	3.245	3.240	3.225	0.005	0.015	421	9.11	10.5	39	116	43
Day 2	0.083	0.018	0.002	0.065	0.016	2.775	2.770	2.755	0.005	0.015	419	9.00	6.6	39	110	30
6% (36 mg/L)																
Day 1	0.101	0.017	0.002	0.084	0.015	2.935	2.930	2.917	0.005	0.013	412	9.11	10.3	38	124	44
Day 2	0.083	0.016	0.002	0.067	0.014	2.725	2.720	2.704	0.005	0.016	412	9.01	6.2	39	109	31

* TPO4 = total phosphorus (mg P/L); TDPO4 = total dissolved phosphorus (mg P/L); OPO4 = soluble reactive phosphorus (mg P/L); PP = particulate phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L); TN = total nitrogen (mg N/L); TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L); NOX = nitrate + nitrite-nitrogen (mg N/L); NH4 = ammonia-nitrogen (mg N/L); LCOND = lab conductivity (µmhos/cm); LPH = lab pH (pH units.); TURB = turbidity (NTU); CL = chloride (mg/L); TOTAL = total aluminum (µg/L); TOTFE = total iron (µg/L).

Figure 1. Water for the STI jar test was collected from the end of the Lake Trafford public pier in 5-gal carboys with a small peristaltic pump on June 12, 2012.

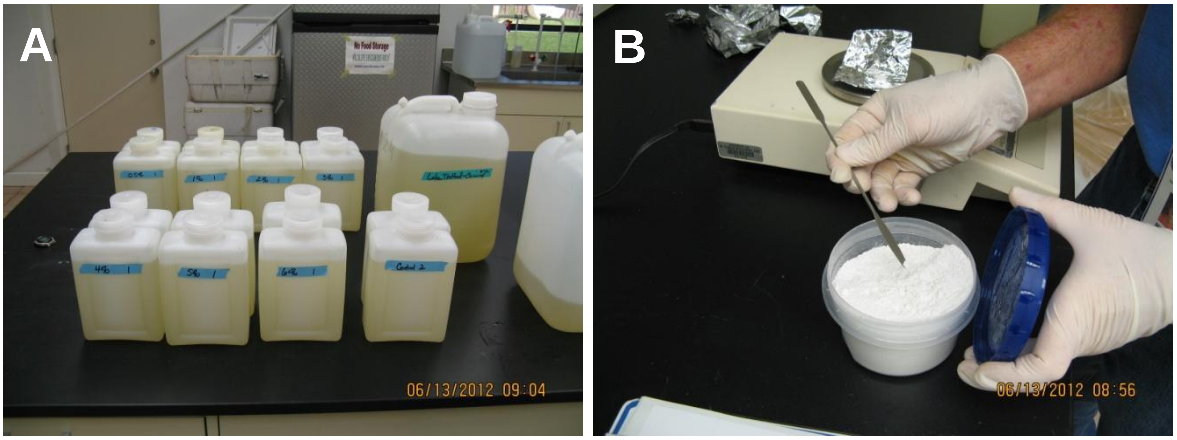

Figure 2. (A) 2-L Nalgene bottles used for the STI jar test of Lake Trafford water; (B) weighing of STI doses at the start of the jar test.

Figure 3. Collecting and processing water samples during the STI jar test of Lake Trafford water, June 13 to 15, 2012.

Appendix – Protocol for Jar Testing ST

PROTOCOL FOR JAR TESTING STI

The goal of this initial jar testing with STI has three components. The first is to ascertain the minimum amount of STI that needs to be added to attain the final water quality desired. The final water quality concentration targets for phosphorous north of the southern boundary of Lake Okeechobee and into the east and west coast estuaries is no more than 40 ppb. Discharges south of the STA's should be in the range of 10 ppb. Our goal for this batch testing is to meet the 40 ppb first and then if we are successful proceed with trying to achieve the lower water quality of 10 ppb.

A secondary component for the jar testing is to determine the levels on Nitrogen removal. We have found that in our previous batch testing that there was significant removal of Nitrogen (50%). For this jar testing, we would like to track the nitrogen removal rates to determine if this is something we might pursue in another future round of jar tests.

The final component of the testing involves examining the residue. STI produces a residue of inert material that is natural. Sampling of this residue should be done to determine the makeup of the residue that is left behind.

Sampling

Sampling should be done on the untreated water for background conditions and then on the treated water and the residue. Since primary concern is the removal of phosphorous, a phosphorous sample should be taken including total phosphorous, total dissolved phosphorous, and soluble phosphorous. Nitrogen removal is also a component so sampling should also include nitrogen.

STI was accepted by FDEP as a safe method of ground water remediation. The FDEP acceptability letter of January 8, 2008 recommends that additional sampling be done for aluminum, chloride, and iron. The sampling plan should include these for both background and treated samples.

Other constituents to sample for would be DO and pH as these are factors in the reaction of the STI.

Sampling should occur on the background sample, and then the treated water and residue in 24 hours and then again in 48 hours.

The analysis of the residue is critical. The sole proprietor of STI, has indicated that the amounts of STI that we are proposing to add will break the bonds of the phosphorous making it available to the natural biota of the water body. However a residue occurs when the amount of STI reaches a saturation point. In previous tests, this residue has not been tested.

Dosage

The dosage of STI to be added to the water to be treated is based on a weight (lbs) of STI per cubic yard of volume of the water body. From previous batch tests we believe this initial starting point should be 3%. In the past, we have found that by adding this amount of STI, the phosphorous levels have been reduced to almost non detectable level. Assuming that a two liter bottle of water is the sample size, then this sample has a volume of 0.00262 cubic yards. 3% of this is 0.0000785 lbs, or 35.6 mg. So in the initial two liter sample bottle, 35.6 mg of STI would be added. There is no need for mixing as the STI will self disperse.

The next round of sampling will depend on the results from the first round of sampling. After analyzing both the results of the two sampling periods, if the phosphorous levels were below the goal of 10 ppb, then the objective of the sampling would be to minimize the amount of STI added and still achieve an adequate removal of phosphorous to meet the final goal. At this juncture the next jar test would be to lower the percentage of STI to 2% and then sampling in the same procedure. These results should then be examined and if the final goal is still being met than the STI rate can be lowered to 1%.

If on the other hand, the removal goal of phosphorous is not being met by using the 3% rate, then using 4% would be the next step.

We have included a chart below that relates the sampling feed rate of STI by weight to the volume of the 2 liter sampling bottle. This chart is based on the STI being added to a 2 liter sample bottle.

% STI	0.5%	1%	2%	3%	4%	5%	6%
mg STI	5.9	11.9	23.7	35.6	47.5	59.3	71.2

Conclusion

The critical elements that need to be determined from this jar test, are the amount of STI required to meet the water quality standards, the nitrogen removal rate, and the analysis of the residue.

If the removal of phosphorous is achieved, further testing could be done at varying percentages of STI to determine the possibilities of Nitrogen removal.

If the residue contains levels of phosphorous, then we can look at processes for harvesting the residue to recycle the phosphorous. The harvesting of the residue is not the purpose of this jar testing. However finding levels of phosphorous in the residue does not mean that the test was a failure. We will simply have to devise ways of harvesting it. The final residue is inert and we may be able to land apply it with no trouble.

We are not completely familiar with lab procedures, so if you see some procedural changes you would make please feel free to do so but please not them so that we are aware of the change.

ViroPhos^{TM} Jar Test of Inflow Water to the STA-1W North Test Cells

Introduction

The South Florida Water Management District (District) conducted a jar test of ViroPhos^{TM} (manufactured by Virotech Global Solutions, Inc., Mobile, AL and distributed by EnviRemed, Ocean Isle Beach, NC) in March 2012 using water collected from the inflow to the STA-1W North Test Cells. ViroPhos^{TM} is a fine-textured red powder formulated from clay minerals (Fig. 1) and is one of the products being evaluated by the Water Quality Treatment Technologies Section as part of the District's New Alternative Technology Assessment (NATA) Program. This jar test was conducted to evaluate the effectiveness of ViroPhos^{TM} to reduce concentrations of phosphorus in surface water. ViroPhos^{TM} acts by sorption of chemical constituents onto the surface of the mineral particles and is effective primarily on sequestering inorganic species.

Methods

Bulk water was collected from the inflow to the STA-1W North Test Cells in 5-gal carboys on March 13, 2012. Water was immediately transported back to the laboratory and stored at room temperature until the jar test was started the following day. The jar test was conducted by District Laboratory personnel (Richard Walker and Meifang Zhou) using a Phipps&Bird^{TM} PB-700^{TM} Standard JarTester (Fig. 2). Jars were filled with 2 L of Test Cell inflow water and dosed with ViroPhos^{TM} at the concentrations recommended by the vendor: 0.5, 1.0 and 2.0 g/L. Each ViroPhos^{TM} treatment was run in duplicate. A control jar (no ViroPhos^{TM} added) was run in a separate vessel. The ViroPhos^{TM} jars were subjected to a 1-minute fast mix @ 200 rpm immediately after the dose was added followed by a 30-minute slow mix @ 30 rpm. Water samples were collected at Hour 0, i.e., the start of the jar test before the addition of ViroPhos^{TM}, and at 3, 6 and 24-hour intervals after the product was added to the jars. Samples were withdrawn from the middle of the jars with a 60-mL plastic syringe and processed following District protocols (Fig. 3). Cartridge filters (0.45 µm) were used for samples that required filtration (Fig. 3). Water samples were analyzed for calcium (CA), chloride (CL), hardness (HARD), lab conductivity (LCOND), lab pH (LPH), magnesium (MG), potassium (K), sodium (NA), sulfate (SO4), soluble reactive phosphorus (OPO4), total dissolved phosphorus (TDPO4), total phosphorus (TPO4), total aluminum (TOTAL), total iron (TOTFE) and turbidity (TURB) by the District's Laboratory. The following chemical parameters were calculated by difference: dissolved organic phosphorus (DOP = TDPO4 – OPO4) and particulate phosphorus (PP = TPO4 – TDPO4).

Results and Observations

Results of the chemical analyses performed on water samples collected during the ViroPhos^{TM} jar test are summarized in Table 1. The following observations were made based on comparing the control to the ViroPhos^{TM} treatments and the ViroPhos^{TM} treatments over time:

1. ViroPhos^{TM} did not appear to alter water-column K or MG concentrations.
2. Water-column levels of CA, CL, HARD, LCOND, NA, SO4, TOTAL and TOTFE all increased to varying degrees with increased dose of ViroPhos^{TM}. Increases in TOTAL and TOTFE in the ViroPhos^{TM} treatments were an order of magnitude greater than concentrations in the control.
3. Turbidity increased substantially in all ViroPhos^{TM} treatments in direct proportion to the amount of product added to the jar but then decreased rapidly to levels that approached turbidity in the control by the end of the jar test.

4. Water-column OPO4 concentrations were at the method detection level (0.002 mg/L) in all jars at the start of the test and therefore these data cannot be used to assess the effectiveness of ViroPhos^{TM} to remove OPO4.
5. There was no appreciable decrease in water-column TDPO4 or DOP levels in the ViroPhos^{TM} treatments over and above concentration changes observed in the control.
6. Water-column TPO4 levels deceased in all ViroPhos^{TM} treatments, but these changes were comparable in magnitude to the TPO4 decrease observed in the control. Loss of water-column TPO4 in all jars was attributed to the settling of particulate material rather than any action by ViroPhos^{TM}.

A ViroPhos^{TM} representative, Mr. James Hudgens of CZR, Inc., attended the jar test start-up and initial water quality sampling. EnviRemed tested the sample of ViroPhos^{TM} used in the jar test and confirmed that it was the correct formulation.

Future Work

We have scheduled another jar test of ViroPhos^{TM} using a different source of water, i.e., water collected from the C-51 canal at the S5A Pump Station, which should have a higher OPO4 concentration.

Table 1. Results of chemical analyses of water samples collected from the control and ViroPhos™ treatments during the jar test*. All values for ViroPhos™ treatments represent means of samples collected from duplicate jars.

	CA	CL	HARD	K	LCOND	LPH	MG	NA	SO4	TOTAL	TOTFE	TURB	TPO4	TDPO4	OPO4	DOP	PP
Control																	
Hour 0	76	137	286	9	976	8.2	23	97	54	221	83	8	0.072	0.013	0.002	0.011	0.059
Hour 3	76	137	285	9	982	8.2	23	95	54	103	63	4	0.058	0.010	0.002	0.008	0.048
Hour 6	76	137	288	9	980	8.3	24	97	54	96	38	4	0.055	0.011	0.002	0.009	0.044
Hour 24	77	140	288	9	978	8.3	24	96	55	54	23	2	0.041	0.011	0.002	0.009	0.030
0.5 g/L																	
Hour 3	84	139	304	9	1039	8.3	23	103	82	1339	1242	27	0.062	0.011	0.002	0.009	0.051
Hour 6	84	139	305	9	1040	8.3	23	103	84	869	877	20	0.054	0.011	0.002	0.009	0.043
Hour 24	86	143	310	9	1051	8.5	23	105	92	447	158	4	0.040	0.011	0.002	0.009	0.030
1.0 g/L																	
Hour 3	92	140	326	9	1085	8.3	23	108	107	1881	2810	39	0.063	0.011	0.002	0.009	0.052
Hour 6	94	141	331	9	1090	8.4	23	111	110	886	699	33	0.055	0.010	0.002	0.008	0.045
Hour 24	96	145	335	8	1103	8.5	23	112	123	732	155	5	0.039	0.010	0.002	0.008	0.029
2.0 g/L																	
Hour 3	105	143	356	8	1167	8.5	23	118	155	2986	2579	80	0.067	0.010	0.002	0.008	0.057
Hour 6	106	146	357	8	1174	8.5	23	120	163	1860	1567	43	0.056	0.010	0.002	0.008	0.046
Hour 24	106	147	358	8	1201	8.5	23	124	183	804	251	9	0.039	0.011	0.002	0.009	0.029

* CA = calcium (mg/L); CL = chloride (mg/L); HARD = hardness as mg $CaCO_3$/L; K = potassium (mg/L); LCOND = lab conductivity (µmhos/cm); LPH = lab pH (pH units.); MG = magnesium (mg/L); NA = sodium (mg/L); SO4 = sulfate (mg/L); TOTAL = total aluminum (µg/L); TOTFE = total iron (µg/L); TURB = turbidity (NTU); TPO4 = total phosphorus (mg P/L); TDPO4 = total dissolved phosphorus (mg P/L); OPO4 = soluble reactive phosphorus (mg P/L); DOP = dissolved organic phosphorus (mg P/L); PP = particulate phosphorus (mg P/L).

Figure 1. Collecting a sample of ViroPhos^{TM} for use in the jar test.

Figure 2. (A) Weighing of ViroPhos^{TM} doses at the start of the jar test; (B) Laboratory mixer used to conduct the jar test with duplicate jars for the (L-R) 0.5, 1.0 and 2.0 ViroPhos^{TM} treatments.

Figure 3. (A) Processing water samples collected during the ViroPhos^{TM} jar test; (B) Comparison of ViroPhos^{TM} retained on 0.45 µm filters for the (L-R) 0.5, 1.0 and 2.0 g/L treatments run during the jar test.

A Demonstration Study of ViroPhos™ Conducted at the Turnpike Dairy

Introduction

The South Florida Water Management District (District) conducted a demonstration study of ViroPhos™, a product designed to remove phosphorus (P) from surface and waste waters[1], from March 25 to April 30, 2013 at a small pond located on the Turnpike Dairy near Indiantown, FL (i.e., the test pond labeled in Fig. 1). ViroPhos™ is a mixture of mineral compounds (primarily hematite (Fe_2O_3), hydrated alumina ($Al(OH)_3$), sodalite ($Na_4(Al_6Si_6O_{24})Cl_2$), quartz (SiO_2) and lesser amounts of other constituents) that has a reddish-brown color and the consistency of a dry powder. ViroPhos™ is one of the mineral-based products being evaluated by the Water Quality Treatment Technologies Section as part of the District's New Alternative Technology Assessment (NATA) Program. The District previously assessed the treatment efficacy of ViroPhos™ in two jar tests conducted in the laboratory (SFWMD 2012a, 2012b). The demonstration study described in this report was conducted to (a) evaluate the effectiveness of ViroPhos™ to reduce phosphorus (P) and nitrogen (N) concentrations in surface water in the field and (b) assess the product's effect on other select water quality parameters. ViroPhos™ acts by the sorption of chemical constituents onto the surface of the mineral particles and is effective primarily at sequestering inorganic chemical species.

Study Site and Methods

The pond used for this demonstration study was a small (0.53 ha) flat-bottomed rectangular impoundment (Figs. 1 and 2) that historically received wash water from a milking barn. Although the test pond was fenced off from adjacent cow pastures, we observed that the property owner frequently allowed livestock to graze within the fenced area. Due to low water levels in the test pond during this study, there was no surface connection between the test pond and the upstream impoundment so the only source of inflow to the test pond would have been from direct rainfall, surface runoff or groundwater infiltration. Average water depth in the test pond was 56 cm at the start of the study and decreased to 38 cm by the last sampling event.

The ViroPhos™ application was performed by EnviRemed, LLC. ViroPhos™ was pumped from a water tanker truck and sprayed as a slurry onto the surface of the test pond (Fig. 3). The vendor estimated that 1.5 metric tons of ViroPhos™ were used during the demonstration study, which corresponded to an application rate of 0.28 kg m^{-2}. It was anticipated that the product could be applied to the test pond in a single day. However, a number of unforeseen equipment problems caused delays; as a consequence, ViroPhos™ application started on March 26 and was not completed until March 28.

Unreplicated surface grab samples were collected on March 25 (Pre-Application), March 29 (Post-Application) and April 30 (1-Month) 2013 at three sites spaced equidistant down the long axis of the test pond.[2] We avoided collecting samples in areas of the test pond that were covered by duckweed (*Lemna* sp.). Water quality samples were processed in the field and sample preservation followed District protocols. Cartridge filters (0.45 µm) were used for constituents that required filtration. Conductivity (COND) and pH (PH) were measured in the field each during sampling event using a YSI 556MPS multiprobe system. Water samples were analyzed by the District's Chemistry Laboratory for total dissolved aluminum (AL), ammonia-nitrogen (NH4), dissolved calcium (CA), total dissolved iron (FE), nitrite+nitrate-nitrogen (NOX), soluble reactive

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[1] ViroPhos™ is manufactured by Virotech Global Solutions, Inc. (Coomera Waters, Queensland, Australia) and distributed by EnviRemed, LLC (Ocean Isle Beach, NC).

[2] Split samples were collected by District staff at all three sampling locations on March 25 at the vendor's request and submitted to an outside laboratory for analysis (Everglades Laboratories, West Palm Beach, FL). This report presents results only of analyses performed by the District's Chemistry Laboratory.

phosphorus (SRP), sulfate (SO4), total dissolved phosphorus (TDP), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and turbidity (TURB). The following chemical parameters were calculated by difference: particulate phosphorus (PP = TP – TDP), total nitrogen (TN = TKN + NOX) and total organic nitrogen (TON = TKN – NH4).

Results and Observations

Results of field measurements and chemical analyses performed on water samples collected during the ViroPhos™ demonstration study are summarized in Table 1 and Fig. 3. The following observations were made based on comparing the Pre-Application data to the Post-application and 1-Month data:

1. The Turnpike Dairy test pond would be classified as a hypereutrophic system based on the high TP concentrations measured throughout this study[3]. Hypereutrophic systems typically are very productive and can support high plant biomass. The rapid increase in duckweed coverage (see Fig. 2) and the amount of phytoplankton retained by the cartridge filters during field processing of water samples were seen as evidence for high productivity and plant biomass in the test pond.
2. Concentrations of TP, TDP and SRP decreased by more than 2 mg/L between the Pre-Application and Post-Application sampling events although this represented only a 22 to 27% change. These concentration reductions were attributed largely to sorption of P onto the ViroPhos™ particles as they settled through the water column after application. However, concentration reductions between the Post-Application and 1-Month sampling events probably reflect P removal associated more with biological activity (i.e., the growth of duckweed [see Fig. 2] and phytoplankton[4] populations) rather than sorption by ViroPhos™.
3. PP concentrations increased on both sampling dates after ViroPhos™ application.
4. TN and TKN concentrations decreased slightly (-5%) and TON concentrations increased slightly (2%) immediately after ViroPhos™ application. During the same period, NH4 levels exhibited a modest decrease (-28%), while NOX experienced more than a three-fold increase. Subsequent changes in these constituents between the Post-Application and 1-Month sampling events were attributed to biological activity rather than any action by ViroPhos™.
5. Concentrations of CA, SO4, AL and FE all increased immediately after application of ViroPhos™ and was attributed to the leaching of these constituents from the ViroPhos™ particles to the water column. The changes in AL and FE concentrations were substantial, corresponding to more than two- and three-fold increases, respectively. Subsequently, concentrations of SO4, AL and FE on the 1-Month sampling event decreased to levels that were near Pre-Application levels.
6. TURB increased throughout the study. The TURB increase immediately after application was attributed largely to the ViroPhos™ particles that remained suspended in the

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[3] The generally accepted criterion for hypereutrophic lakes and ponds is water column TP concentrations greater than 0.1 mg/L (Lampert and Sommer, 1997; Wetzel, 2001). The range of TP levels observed in the test pond during this study (3.546 to 10.232 mg/L, Table 1) was 35 to 100 times above this threshold.

[4] Filtering water samples was difficult throughout the study due to the filters quickly becoming clogged with phytoplankton. Based on the number of filters required to process water samples, algae were more abundant during the 1-Month sampling event than on the previous sampling dates, i.e., more filters were needed to process the 1-Month water samples.

water column, while the increase by the 1-Month sampling event probably reflected an increase in phytoplankton abundance[5].

7. PH increased slightly (0.23 s.u.) immediately after the application of ViroPhos™. The subsequent PH increase by the 1-Month sampling event was attributed to biological activity (i.e., high photosynthetic activity by phytoplankton) and not any action by ViroPhos™.
8. COND increased slightly (0.080 µS/cm) immediately after the application of ViroPhos™, but returned to Pre-Application levels by the 1-Month sampling event.

References

Lampert, W. and U. Sommer. 1997. Limnoecology: The Ecology of Lakes and Streams. Oxford University Press, New York, NY. 382 pp.

South Florida Water Management District (SFWMD). 2012a. ViroPhos™ Jar Test of Inflow Water to the STA-1W Test Cells. 5 pp.

South Florida Water Management District (SFWMD). 2012b. New Alternative Technology Assessment (NATA) Program: A Jar Test of Phoslock®, STI, ViroPhos™ and WP-1™ Using C-51 Canal Water. 12 pp.

Wetzel, R.G. 2001. Limnology: Lake and River Ecosystems, 3rd Ed. Academic Press, San Diego, CA. 1006 pp.

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[5] Note that the increase in TURB for the 1-Month sampling event coincided with our observation of increased difficulty in filtering samples on this date, which was attributed to an increase in phytoplankton abundance.

Table 1. Results of water quality parameters analyzed during the ViroPhos™ demonstration study conducted at the Turnpike Dairy test pond.[†]

	TP	TDP	SRP	PP	TN	TKN	TON	NH4	NOX	CA	SO4	AL	FE	TURB	PH	COND
Pre-Application (March 25, 2013)																
Rep 1	10.255	9.664	9.923	0.591	10.035	10.030	7.455	2.575	0.005	65	110	25	5	16	7.52	0.934
Rep 2	10.202	9.660	9.945	0.542	10.885	10.880	8.353	2.527	0.005	65	111	25	4	17	7.66	0.936
Rep 3	10.240	9.770	9.826	0.470	10.595	10.590	8.061	2.529	0.005	66	112	23	5	15	7.66	0.933
Post-Application (March 29, 2013)																
Rep 1	8.112	7.372	7.469	0.740	9.653	9.640	7.625	2.015	0.013	73	148	79	23	24	7.76	1.020
Rep 2	8.078	7.089	7.199	0.989	10.167	10.140	8.350	1.790	0.027	74	149	97	22	26	7.90	1.013
Rep 3	7.903	6.993	7.032	0.910	10.066	10.040	8.328	1.712	0.026	73	149	106	23	27	7.89	1.009
1-Month (April 30, 2013)																
Rep 1	3.549	2.016	1.846	1.533	11.555	11.550	11.469	0.081	0.005	53	121	43	10	37	8.78	0.931
Rep 2	3.485	1.971	1.848	3.485	11.716	11.720	11.651	0.069	0.005	53	121	34	9	40	8.81	0.934
Rep 3	3.605	1.902	1.663	1.703	11.405	11.400	11.327	0.073	0.005	53	121	35	8	40	8.79	0.934
Mean Values																
Pre-Application	10.232	9.698	9.898	0.534	10.505	10.500	7.956	2.544	0.005	65	111	24	5	16	7.62	0.934
Post-Application	8.031	7.151	7.233	0.880	9.962	9.940	8.101	1.839	0.022	73	149	94	23	26	7.85	1.014
1-Month	3.546	1.963	1.786	1.583	11.559	11.557	11.482	0.074	0.005	53	121	37	9	39	8.79	0.933
% CHANGE IN CONSTITUENTS																
Pre-App vs. Post-App[*]	-22%	-26%	-27%	65%	-5%	-5%	2%	-28%	340%	13%	34%	286%	386%	65%	3%	9%
Pre-App vs. 1-Month[**]	-65%	-80%	-82%	196%	10%	10%	44%	-97%	-0%	-18%	9%	53%	95%	149%	15%	-0.1%

[†] Parameter Key: TP = total phosphorus (mg P/L); TDP = total dissolved phosphorus (mg P/L); SRP = soluble reactive phosphorus (mg P/L); PP = particulate phosphorus (mg P/L) => TP - TDP; TN = total nitrogen (mg N/L) => TKN + NOX; TKN = total Kjeldahl nitrogen (mg N/L); TON = total organic nitrogen (mg N/L) => TKN - NH4; NH4 = ammonia-nitrogen (mg N/L); NOX = nitrite+nitrate-nitrogen (mg N/L); CA = dissolved calcium (mg/L); SO4 = sulfate (mg/L); AL = total dissolved aluminum (µg/L); FE = total dissolved iron (µg/L); TURB = turbidity (NTU); PH = pH (s.u.); COND = conductivity (µS/cm)

[*] % change = [(Post-App - Pre-App)/Pre-App]*100
[**] % change = [(1-Month - Pre-App)/Pre-App]*100

Figure 1. Map showing the location of the Turnpike Dairy near Indiantown in Martin County, FL (top panel) and an aerial photograph of the test pond that was used for the Viro-Phos™ demonstration study (bottom panel).

Figure 2. Panoramic photographs of the Turnpike Dairy test pond taken on March 26, 2013 during the ViroPhos™ application (left panel) and on April 30, 2013 during the 1-Month water quality sampling event (right panel). Note the increase in duckweed coverage between the two dates.

Figure 3. Application of ViroPhos™ at the Turnpike Dairy test pond on March 26-28, 2013. Clockwise from upper left: (1) ViroPhos™ was delivered to the site in supersacs that each held one metric ton of product; (2 & 3) ViroPhos™ was released from a chute at the bottom of the supersac, transferred to 5-gal buckets and loaded into a water tanker truck; (4) the tanker truck was filled with water pumped from the test pond; and (5 & 6) ViroPhos™ was pumped from the tanker truck and sprayed as a slurry onto the surface of the test pond.

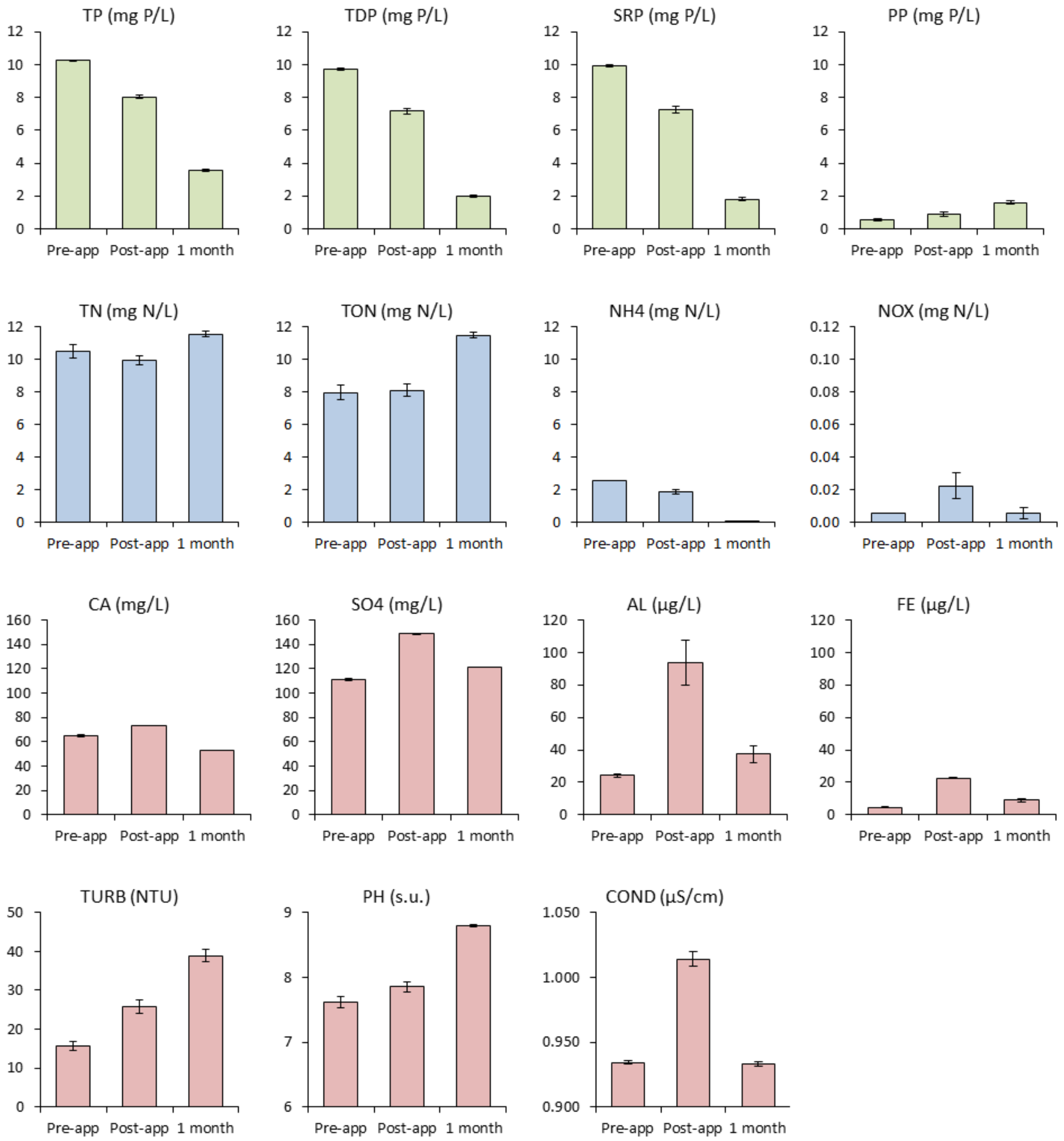

Figure 4. Mean values for water quality parameters monitored during the Pre-Application, Post-Application and 1-Month sampling events for the ViroPhos™ demonstration study conducted at the Turnpike Dairy test pond. Spreader bars represent ±1 sample standard deviation. Parameter key: TP = total P; TDP = total dissolved P; SRP = soluble reactive P; PP = particulate P; TN = total N; TON = total organic N; NH4 = ammonia-N; NOX = nitrite+nitrate-N; CA = dissolved calcium; SO4 = sulfate; AL = total dissolved aluminum; FE = total dissolved iron, TURB = turbidity; PH = pH; COND = conductivity.

Nitrogen and Phosphorus Removal from Natural Waters Using an Activated Mineral Matrix (WP-1^{TM}).

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Abstract

Nitrogen (N) and phosphorus (P) removal by WP-1 ^{TM}, a novel activated mineral adsorbent, was investigated in the natural water of the South Florida Water Management District (SFWMD), FL, USA. The results of the 43 day batch field trial indicate that WP-1^{TM} (dosage rate = 0.021 mg/L) reduced both TN and TP from initial concentrations of 2.347 mg/L TN and 0.034 mg/L TP by 21.4% and 54.9%, respectively. Final equilibrium TN and TP concentrations were 1.845 mg/L TN and 0.016 mg/L TP. Bulk constant flow WP-1^{TM} testing was less conclusive, indicating only small initial and continuous reductions of soluble P species concentrations over the 28 day experimental period (e.g. TDPO4 - 14.3% Day 4, 6.5% Av.). The results of both experiments are generally compromised by the absence of replication and full treatment controls making elucidation of direct WP-1^{TM} responses complicated in the presence of potential confounding artefacts (e.g. submerged macrophyte nutrient sequestration). Water quality assessment after both batch and bulk treatments with WP-1^{TM} indicates that none of the trace elements tested are released in significant quantities from the adsorbent. Moreover**,** WP-1^{TM} was shown to simultaneously reduce the concentrations of several trace elements/ions including iron (51.7%) and sulfate (21.4%) during batch experiments. Generally, **t**hese findings suggest that WP-1^{TM} could, under certain conditions, be used as an efficient adsorbent for treating N and P contaminated waters and warrants further study.

Extra Keywords: Nitrogen, phosphate, adsorption, WP-1^{TM}, eutrophication, SFWMD.

Introduction

The widespread dispersal of nitrogen (N) and phosphorus (P) in sewage, industrial wastes and runoff from urban and agricultural lands has been documented as a major factor in the eutrophication of many aquatic ecosystems (Webster, 2001; Liu *et al*., 2009). The removal of P from waste and natural waters can be achieved either through physical treatment (e.g., detention/retention basins), biological treatment (e.g., Enhanced Biological Phosphate Removal [EBPR]; Mullan *et al*., 2002; treatment wetlands) or chemical precipitation (e.g., aluminium sulfate; Kopatek *et al*., 2006; Liu *et al*., 2009). However, these approaches are generally expensive, require strict control of the operating conditions, potentially introducing new contaminants into the water such as chloride or sulfate ions, and may require disposal of considerable volumes of nutrient-rich sludge (Subramanian and Arnot, 2001; Altundogan and Tumen, 2003). Consequently, alternative techniques for the removal of N and P are the subject of continual investigation, of which *in situ* adsorbents are widely acknowledged as a potential management option (Akhurst *et al*., 2004; 2006).

WP-1^{TM} is the fine-grained residue produced following the activation (trade secret) of a mixture of insoluble minerals. To date, applications of WP-1^{TM} technology have primarily been based on its capacity to neutralize acid, adsorb trace metal cations (e.g., Cu, Cr and Zn), reduce hydrogen sulfide (H_2S) odor emissions and bind high concentrations of soluble nutrients (N and P) from industrial/municipal water treatment facilities and Concentrated Animal Feeding Operations (CAFO's). However, WP-1^{TM} may also provide an innovative adsorbent for both N and P from low-concentration natural waters.

In this investigation, WP-1^{TM} was tested as a novel adsorbent for N and P removal from natural water. The findings potentially provide valuable information for the future management and remediation of N and P- enriched water where it poses a potential environmental risk such as the sensitive areas managed by the South Florida Water Management District (SFWMD), FL, USA (e.g., Lake Okeechobee and the Everglades Protection Area [EPA]). Generally, the SFWMD is focused on (*i*) waste streams from CAFO's; (*ii*) ditch runoff from cattle ranching operations; (*iii*) Lake Okeechobee discharges and local watershed runoff into the east and west estuaries; and (*iv*) water moving south of the Stormwater Treatment Areas (STA's) into the Water Conservation Areas and other portions of the remaining Everglades ecosystem. Given this background, this study has the following objectives: (*i*) to investigate the N and P adsorption capacity of WP-1^{TM}

under both batch and constant flow (bulk) treatment conditions and (*ii*) to evaluate whether unwanted contaminants are released from WP-1^{TM} during the adsorption process.

Materials and Method

Regional Setting

South Florida has a sub-tropical climate. Lake Okeechobee (27^{o}N, 81^{o}W) is the largest lake in the south-eastern United States and is the central component of the hydrology and environment of South Florida (Fig. 1). The Lake has a surface area of 1,730 km^{2}, is shallow (mean depth 2.7 m), turbid and eutrophic and supplies water for nearby towns, agriculture, downstream ecosystems and provides flood control for nearby areas (James *et al*., 1995; Zhang *et al*., 2007).

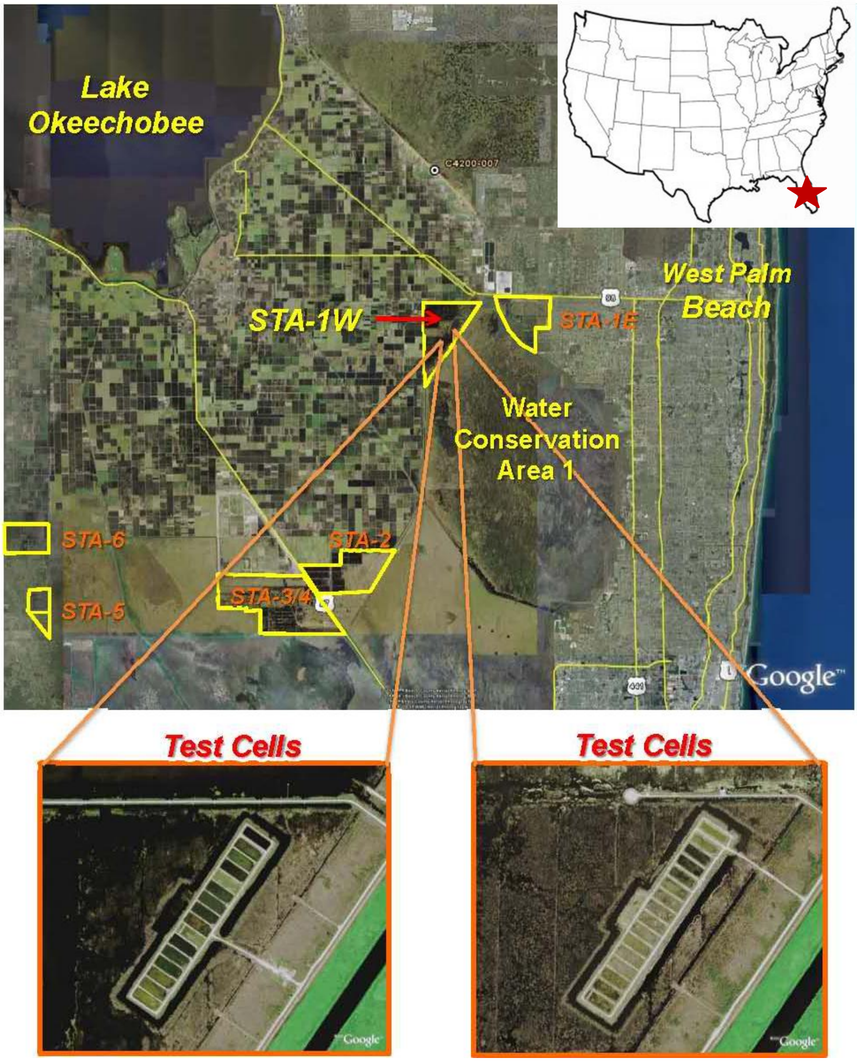

Fig. 1. Regional location map and hydrologic features of the south Florida catchment.

Lake Okeechobee receives water from a 14,000 km^2 water shed that includes the Upper Kissimmee Chain of Lakes, the Kissimmee River, Lake Istokpoga, Fisheating Creek and other sub-basins. Lake waters flow south, east and west to the EPA, the St. Lucie River (C-44 canal) and the Caloosahatchee River (C-43 canal), respectively (Zhang *et al*., 2007). The Lake and region, in general, has significant ecological and economic value providing habitat for migratory waterfowl, wading birds, federally endangered species, including the Everglade Snail Kite (*Rostrhamus sociabilis*), and supports a multimillion-dollar recreational and commercial fishery (Furse and Fox, 1994; Zhang *et al*., 2007). The region faces several major environmental challenges, including: (*i*) excessive nutrient, particularly TP, loadings, (*ii*) disruptions to the regional hydrology, and (*iii*) rapid spread of exotic and nuisance plants (Zhang *et al*., 2007). Excessive loads of nutrients to the Lake and catchment originate from agricultural and urban activities that dominate land use in the catchment (Zhang *et al*., 2007).

Stormwater Treatment Area (STA) test cells

Experiments undertaken as part of this study were conducted in a STA test cell facility (STA-1W North test cells; Cells #2 and #4) managed by the SFWMD (Fig 1). The test cells are small (0.2 ha in size), shallow (< 1.8 m deep), wetlands arranged into banks of 15 cells each; one group is located at the northern end of STA-1W and the other at the southern end. The test cells are fully lined to isolate them hydrologically from adjacent test cells and the surrounding STA and to allow for independent control of water inflow and depth.

The test cell facility is supplied with water pumped from the surrounding STA into a water storage area, which is maintained at a stage up to 2 - 3 m above water levels in the test cells. Water from the storage area gravity flows into a 76.2 cm diameter feeder pipe and is delivered in parallel fashion to the test cells through 20.3 cm diameter lateral pipes, each fitted with a 4-inch gate valve. The end of the feeder pipe has an open valve, which constantly drains the pipe, and keeps the water delivery system well-flushed even when all the test cells are operating at low flow rates or are shut-off altogether. Outflow from each test cell is controlled by an adjustable 90° v-notch weir. Raising or lowering the weir controls the depth within that cell. Based on historical water quality monitoring data, inflow TP concentrations at the north test cells range between 60 and 150 μg P/L and represent "high" TP conditions.

Preparation of WP-1^{TM}

The WP-1^{TM} used in this study was manufactured and supplied by North American Geochemical, LLC, Walterboro, SC, USA. WP-1^{TM} is principally composed of mineralised aluminium, calcium, iron and magnesium oxides/hydroxides, however, details of the specific mineralogy and activation process are a trade secret. WP-1^{TM} has a specific gravity between 3.1 - 3.8, an alkaline pH (9.5 - 10.5), a specific surface area of 19 – 21 m^2/g and a fine particle size distribution (90% < 75µm in diameter) depending on the specific WP-1^{TM} blend and activation process.

Batch application experiment

A batch application experiment was undertaken between September 19 and October 31, 2011. At the start of the experiment, fresh water from the water storage area (Fig. 2) was flushed through Cell #4 for seven days. Water quality parameters were monitored on Days 1, 3 and 5 to document baseline conditions. On Day 7, cell inflow and outflow were stopped and the closed system was allowed to settle for 24 hr prior to WP-1^{TM} application. On Day 8, approximately 50 gallons of water was pumped using a small gasoline-powered transfer pump from Cell #4 into a 300 gallon plastic bulk container, which was positioned at the edge of the test cell. WP-1^{TM} (15 lbs) was then added to the container and the water-WP-1^{TM} mixture recirculated within the container for 15 minutes using the same transfer pump. The WP-1^{TM} slurry was then sprayed over the surface of the entire cell. WP-1^{TM} was applied repeatedly to the cell using the same procedure on Days 9, 10, 11, 14, 15, 16, 17 and 18. A total of 135 lbs of WP-1^{TM} was applied to Cell #4 over the course of this experiment, which amounted to a cumulative dose of 0.019 mg WP-1^{TM}/L. Note that this experiment did not employ a treatment control, i.e., we did not monitor an adjacent test cell that was not dosed with WP-1^{TM}.

Water quality parameters (dissolved oxygen [DO], temperature, pH and conductivity) were measured in the field with a multi-probe meter. In addition, unreplicated grab samples were collected by hand and returned to the laboratory for analysis of soluble reactive P, total dissolved P, TP, nitrite+nitrate-N, total Kjeldahl N, alkalinity, total aluminium, dissolved calcium, total calcium, color, total iron, hardness, potassium, magnesium, sodium, sulphate and total suspended solids. Field measurements and grab samples were collected at the cell inflow and outflow during the baseline period (Day 1, 3, and 5). From Day 8 through 22, field measurements and grab samples were collected from the water surface at four stations within the cell at least 24 hr after each application of WP-1^{TM}; these stations were located along a transect oriented down the center of the cell. Field measurements and grab samples were collected on a weekly basis for three weeks (Days 29, 36 and 43) after the final application of WP-1^{TM}.

Bulk application experiment

A single bulk application experiment was undertaken in test Cell #2 between October 3rd and 31st 2011. Prior to WP-1^{TM} application freshwater was flushed through the cell for 3 consecutive days at a flow rate of 204 gal/min. On October 6th, 2011 water flow was stopped and 300 lbs of WP-1^{TM} was applied to Cell #2 using the identical techniques as described previously for the batch experiment. Twenty four hours after WP-1^{TM} application, water flow was re-established in the cell at the previously used 204 gal/min flow rate. The resultant hydraulic retention time in the cell was approximately 68.6 hrs. The treatment hypothesis was that WP-1^{TM}, settled at the sediment-water interface, may continue to remove additional P from the system as water flows over the top of it.

The same suite of water quality parameters were monitored during the bulk application experiment as described above for batch application experiment. Baseline data for the bulk experiment were collected at the inflow and outflow of Cell #2 on Days 1, 2 and 3. Following application of WP-1^{TM} on Day 4, field measurements and unreplicated grab samples were collected at the cell inflow and outflow on Day 5, 8, 9, 10, 11, 12, 15 and 22. A final sampling was conducted at four stations located along a transect oriented down the center of Cell #2 on Day 29.

Results and Discussion

Batch Experiment

N and P adsorption

Results are shown in Table 1 where it can be seen that application of WP-1^{TM} resulted in reductions of all N and P species investigated with the exception of NO_x and Ortho-P (OPO_4). WP-1^{TM} has been shown during previous testing to preferentially remove OPO_4 over other P species (D. Akhurst unpub. data). However, as there was almost no OPO_4 to start with, this expectation cannot be tested with these data. As anticipated, the highest removal efficiencies were obtained for soluble species of phosphate ($TDPO_4$ – 72.3%; DOP – 79.7%).

Table 1. Various N and P species concentrations before and after WP-1^{TM} application in STA-1W test cell #4 and comparison with the Class III Florida Administrative Code surface water quality criteria (FAC 62-304; FDEP 2010). (mg/L unless otherwise noted).

Parameter	Method reference	Before WP-1^{TM}	After WP-1^{TM}	% Reduction	FAC 62-304
TKN	EPA 351.2	2.347	1.845	21.4	
NO_x	EPA 300.0	0.006	0.01	0	≤ 10
TP	EPA 365.4	0.034	0.016	54.9	≤ 0.01
$TDPO_4$		0.022	0.006	72.3	
OPO_4		0.002	0.002	0	-
DOP		0.02	0.004	79.7	-
PP		0.013	0.01	25	-

Total N and TP concentrations decreased with time corresponding to additional applications of WP-1^{TM} (Figs. 3, 4). Notably, TN and TP concentrations continued to decrease consistently after completion of WP-1^{TM} applications on Day 18 (Figs. 2, 3). It is not possible to conclusively state whether additional TN and TP removal that occurred between Day 19 – 43 (post treatment) occurred as a consequence of further uptake by unreacted WP-1^{TM} at the sediment-water interface or from the establishment of the submerged macrophyte *Chara* spp. that visually appeared to increased in biomass during the experiment (M. Chimney pers. obser.). The absence of a control cell for comparison in combination with the presence of *Chara* spp. somewhat muddies the interpretation of the data for the entire experiment. It is known that *Chara* spp. removes nutrients directly from the water column. What we do not know is how much P and N *Chara* spp. removed relative to what was removed by WP-1^{TM}.

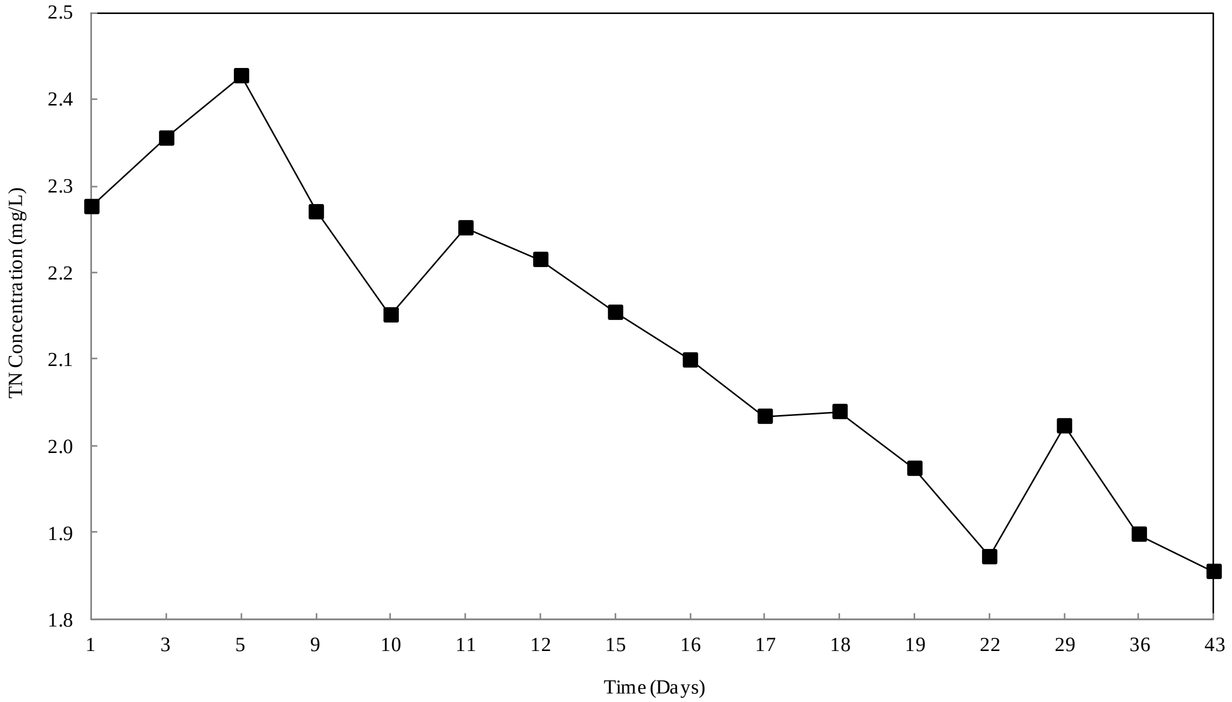

Fig. 2. Removal of TN in SFWMD STA test cell #4 by WP-1TM technology. Treatment Notes: test cell volume ~ 3,179,925 L (840,139 gallons); Day 1, 3, 5 are background control values. Dosage = 6.804 kg (15 lbs) of WP-1TM reagent was applied on Day 8, 9, 10, 11, 14, 15, 16, 17 and 18; 6.804 kg WP-1TM = 0.00214 g/L;

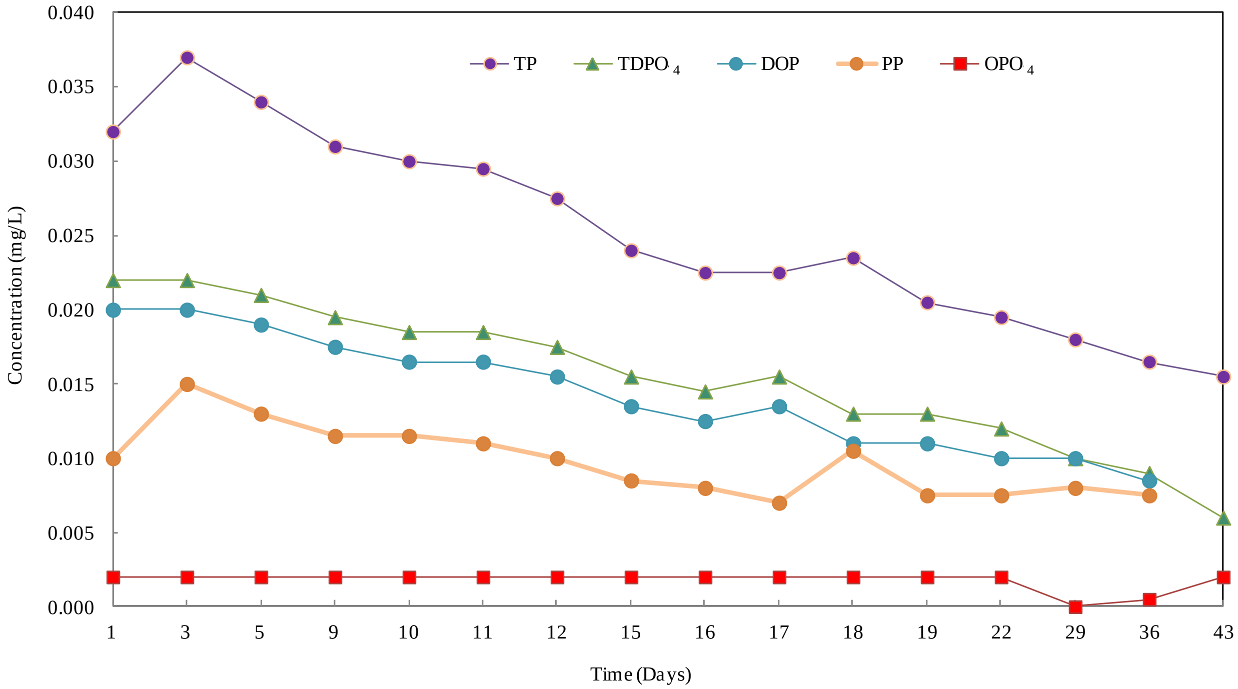

Fig. 3. Removal of various P species in SFWMD STA Test Cell #4 by WP-1TM adsorbent technology. Treatment Notes: STA Volume = 3,179,925 L (840,139 gallons); Day 1, 3, 5 are background control values. Dosage = 6.804 kg (15 lbs) of WP-1TM reagent was applied on Day 8, 9, 10, 11, 14, 15, 16, 17 and 18; 6.804 kg WP-1TM = 0.00214 g/L.

The release of contaminants from WP-1^{TM} and physico-chemical changes during adsorption

The possible release of contaminants and changes in water column physico-chemical parameters by WP-1^{TM} was investigated. This is because WP-1^{TM} has a complex matrix, and some ions may be released to the water during adsorption. The results from the test cell batch additions are given in Table 2 and Figure 4, as are the Florida Administrative Code Surface Water Quality Criteria (FAC 62-304). These results indicate that negligible quantities of the contaminants investigated were released and that basic physico-chemical water parameters were not dramatically altered during WP-1^{TM} adsorption reactions. Furthermore, WP-1^{TM} simultaneously reduced color (44%), hardness (26%) and the concentrations of Ca (39%), Fe (57%), K (20%), Na (14%), SO_4 (21%; Table 2; Fig. 4).

Table 2. Results of water quality analysis before and after using WP-1^{TM} and comparison with the Florida Administrative Code Class III surface water quality criteria (FAC 62-304). (mg/L unless otherwise noted).

Parameter	Method reference	Before WP-1^{TM}	After WP-1^{TM}	% Reduction	FAC 62-304
Alkalinity		262	191	27.2	$\geq$ 20
Aluminum	EPA 6010C	19	26	0	$\leq$ 1.5
Calcium (dissolved)		92	54	41.2	-
Calcium (total)		94	57	39.6	-
Color (PCU)		130	72	44.8	-
Conductivity (mS)		0.97	0.85	12.4	$\leq$ 1.28
Dissolved oxygen		4.7	4.2	10.6	$\geq$ 5
Hardness		335	247	26.5	-
Iron	EPA 6010C	50	21	57.7	$\leq$ 1.0
Magnesium		26	27	0	-
pH		7.99	8.33	0	6.0 – 8.5
Potassium		10	8	20	-
Sodium		82	70	14.2	-
Sulfate	EPA 9056A	70	55	21.4	-
TSS		3	3	0	-

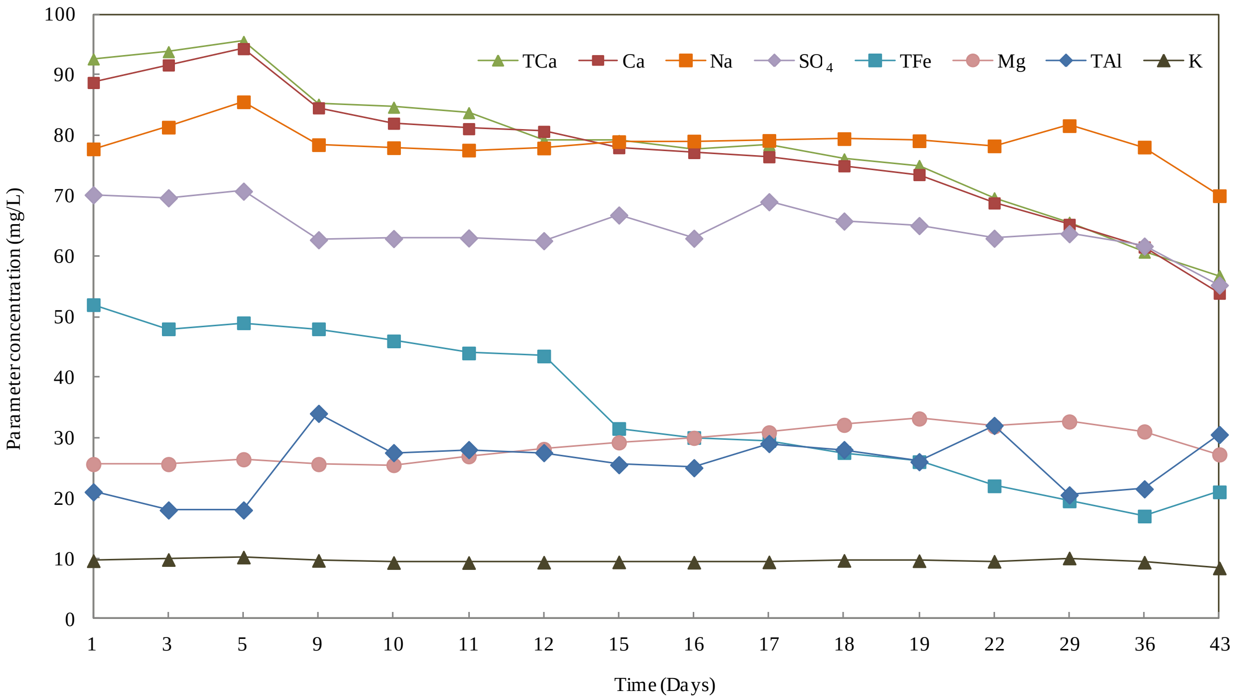

Fig. 4. Concentrations of analytes of interest in SFWMD STA Test Cell #4 before, during and after application of WP-1^{TM} technology. Treatment Notes: STA Volume = 3,179,925 L (840,139 gallons); Day 1, 3, 5 are background control values. Dosage = 6.804 kg (15 lbs) of WP-1^{TM} reagent was applied on Day 8, 9, 10, 11, 14, 15, 16, 17 and 18; 6.804 kg WP-1^{TM} = 0.00214 g/L; Sampling occurred at least 24 hrs after each WP-1^{TM} application.

Effect on pH

Results indicate that removal of N and P by WP-1^{TM} from STA Cell #4 increased pH from 7.94 ± 0.03 (background) to 8.52 ± 0.02 (Day 19; Fig. 5) before gradually decreasing over the 43 day experimental period to pH 8.33 ± 0.01 (Fig. 5). This is typical of WP-1^{TM} where alkaline carbonate and hydroxyl minerals in the media matrix raise pH to higher values. Nevertheless, mean test cell pH values by the final WP-1^{TM} application (Day 19) were marginally above the FAC surface water quality criteria of 6.5 – 8.5 (Fig. 5). Consequently, field applications necessitating higher WP-1^{TM} dosage rates (e.g., > 20 mg/L) in waters with either high initial pH's and low alkalinity will require *in situ* monitoring and manipulation of pH values. In this study, commercial grade muriatic acid (HCL; 11.3 L) was added to the reaction tank prior to WP-1^{TM} application on Day 8 only. No further pH buffering was conducted after this initial treatment. Increases in pH may be effectively negated by buffering WP-1^{TM} with additional HCL prior to application or using split applications, days apart, to enable the system to re-equilibrate before re-application. Modified pH values are an intrinsic feature of most "chemical" treatments.

For example, applications of alum and hydrated lime typically require pH adjustment either pre or post treatment with caustic and acidic substances, respectively (e.g., limestone rock or hydrochloric acid, respectively).

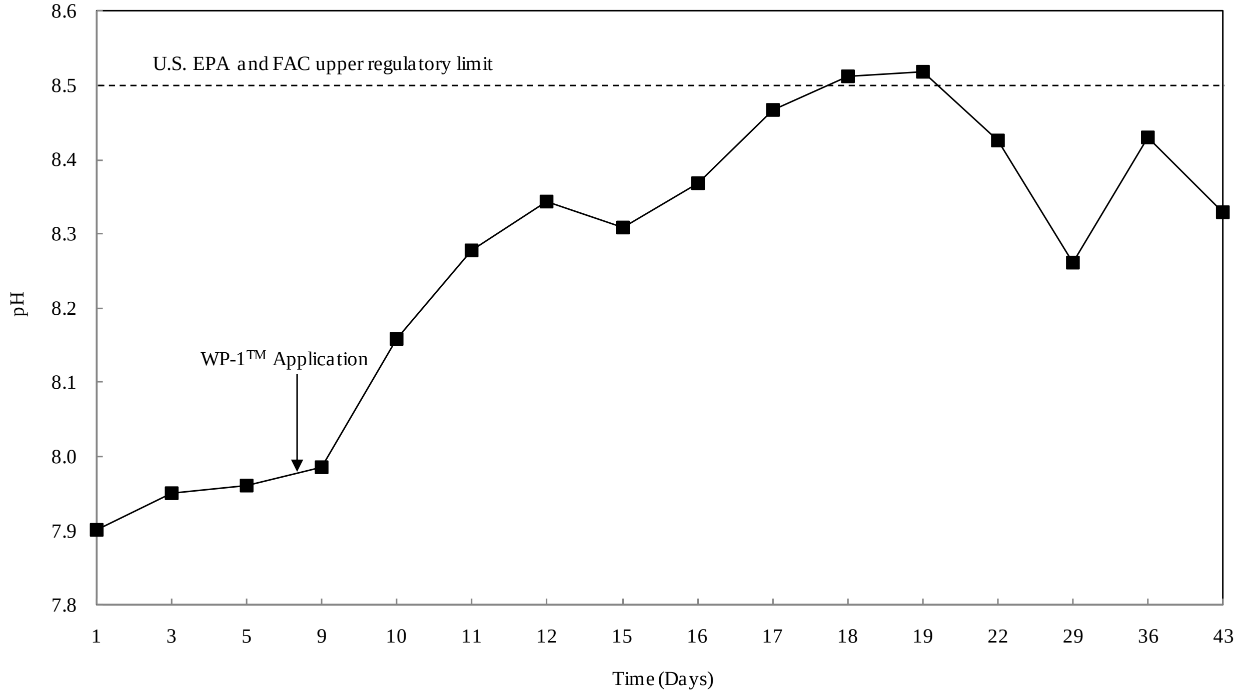

Fig. 5 The effect of WP-1^{TM} applications (Day 8 – 19) on pH in SFWMD STA-1W, Test Cell #4.

Bulk Experiment

N and P adsorption

Results are shown in Table 3 and Figure 6 where it can be seen that bulk application of WP-1^{TM} resulted in immediate reductions in soluble P species TDPO$_4$ (14.3%) and DOP (16.7%). On average, small continuous reductions of the various N and P species investigated were also observed throughout the 28 day experimental period. Again, as anticipated the largest reductions were observed for TDPO$_4$ (Av. 6.5% daily reduction) and DOP (Av. 8.6% daily reduction), compared to untreated baseline data (Table 3; Fig. 6). Again the results of this experiment are not unequivocal owing to the absence of replication and a full control. The calculated hydraulic retention time (HRT) of 68.6 hr was also clearly to short. The system had completely re-equilibrated itself within 2 days (48 hr) after WP-1^{TM} application. The presence of a longer retention time may have permitted additional N and P removal from the water column above those obtained using the 68.6 hr HRT. Additionally, it is plausible that other artefacts, including uptake by macrophytes, phytoplankton and/or sediments may have attributed to some of the observed changes in nutrient concentrations in addition to those caused by WP-1™. Consequently, additional focused experimentation is required to confirm if settled WP-1™ will continue to remove addition P from the water column of natural waters as has been shown to be the case in agricultural swine lagoons (D. Akhurst unpub. data).

Table 3. Various N and P species concentrations in discharge water before and after WP-1™ application in STA-1W Test Cell #2 and comparison with the Class III FAC surface water quality criteria (FAC 62-304; FDEP 2010). (mg/L unless otherwise noted). Green = Reduction; Red = Increase.

Parameter	Method reference	Before WP-1™	1 Day After WP-1™	28 Days After WP-1™	1 Day % Change	28 Days % Change	Average % Change	FAC 62-304
TKN	EPA 351.2	2.330	2.140	2.070	8.2	11.2	0.9	
NO_x	EPA 300.0	0.035	0.037	0.094	5.4	59.5	83.8	$\leq$ 10
TP	EPA 365.4	0.037	0.033	0.034	10.9	8.1	2.9	$\leq$ 0.01
$TDPO_4$		0.014	0.012	0.011	14.3	21.4	6.5	
OPO_4		0.002	0.002	0.002	0	0	0	-
DOP		0.012	0.010	0.009	16.7	25	8.6	-
PP		0.023	0.021	0.023	8.7	0	9.4	-

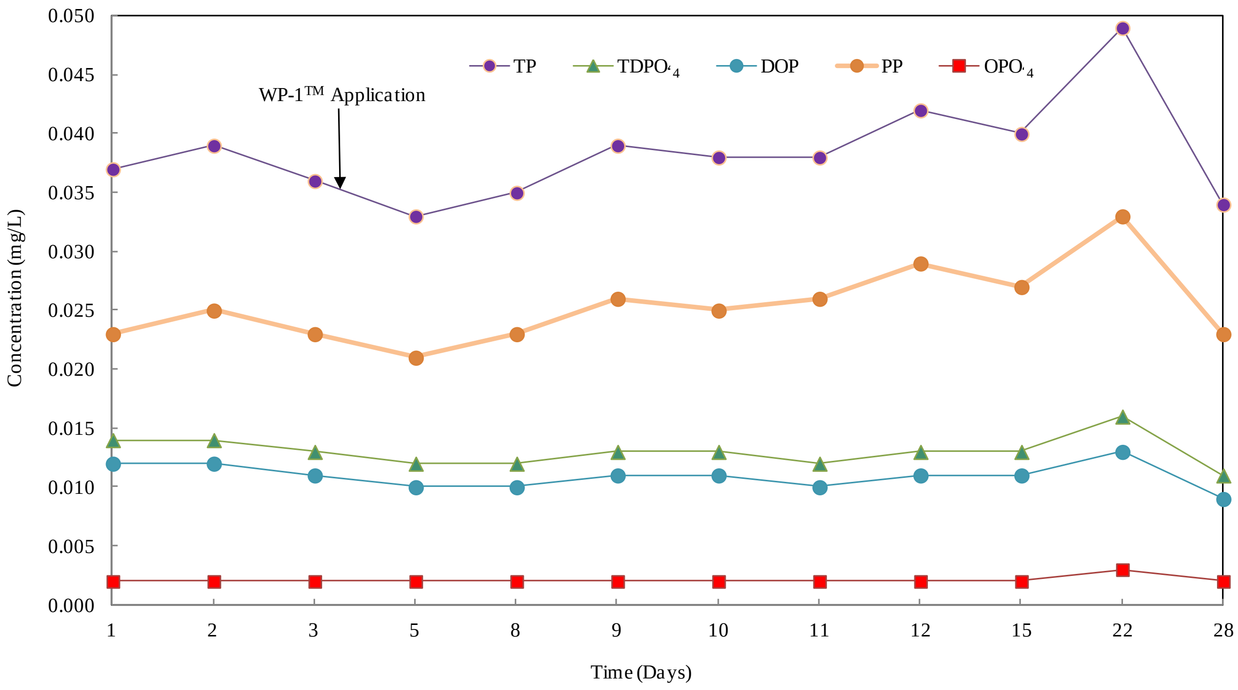

Fig. 6. Removal of various P species in SFWMD STA Test Cell #2 by WP-1™ adsorbent technology. Treatment Notes: STA Volume = 3,179,925 L (840,139 gallons); Day 1, 3, 5 are background control values. Dosage = 136.36 kg (300 lbs) of WP-1™ reagent was applied on Day 4.

The release of contaminants from WP-1^{TM} and physico-chemical changes during adsorption

The results from the test cell # 2 batch additions are given in Table 4 and Figure 6, as are the Florida Administrative Code Surface Water Quality Criteria (FAC 62-304). As was the case with the batch additions, bulk application of WP-1^{TM} did not result in the release of any element to the water column, in concentrations that would potentially compromise larger field applications (Table 4; Fig.7).

Table 4. Results of discharge water quality analysis (Cell # 2) before and after bulk WP-1^{TM} addition and comparison with the FAC surface water quality criteria (FAC 62-304; mg/L unless otherwise noted). Green = Reduction; Red = Increase.

Parameter	Before WP-1^{TM}	1 Day After WP-1^{TM}	28 Days After WP-1^{TM}	1 Day % Change	28 Days % Change	Average % Change	FAC 62-304
Alkalinity	266	247	249	7.1	6.4	0	≥ 20
Aluminum	24	36	49	50	102	27.8	≤ 1.5
Calcium (dissolved)	91	61	87	37.1	4.4	5.6	-
Calcium (total)	91	67	89	26.4	2.2	3.8	-
Color (PCU)	117	110	105	6.0	10.2	0	-
Conductivity (mS)	1.055	1.020	1.063	3.3	0.8	1.4	≤ 1.28
Dissolved oxygen	6.0	6.03	2.17	0.5	63.8	16.1	≥ 5
Hardness	330	320	313	3.0	5.2	1.5	-
Iron	42	40	40	4.8	4.8	23	≤ 1.0
Magnesium	25	41	23	60.9	8	14.6	-
pH	8.0	8.72	8.31	8.3	3.7	0.5	6.0 – 8.5
Potassium	9.7	10	9	3	7.2	0	-
Sodium	86	88	92	2.3	6.5	6.5	-
Sulfate	69	68	65	1.4	5.8	0.9	-
TSS	3	20	3	666	0	61.3	-

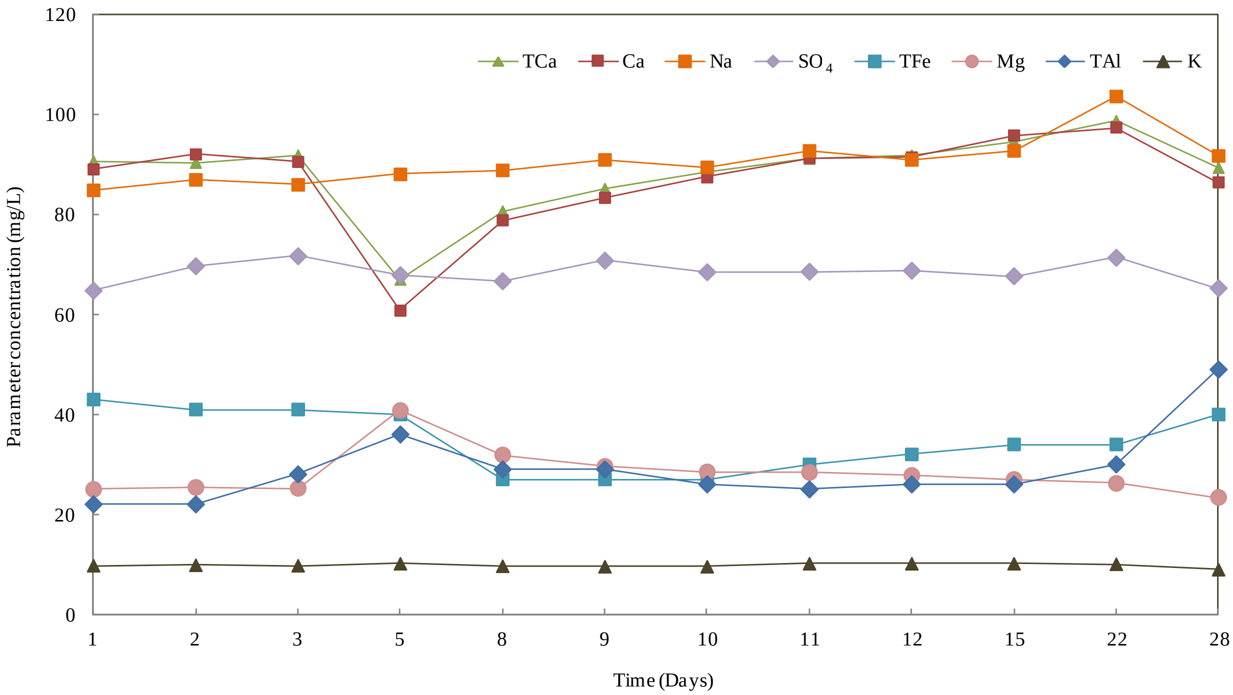

Fig. 7. Concentrations of analytes of interest in SFWMD STA Test Cell #2 discharge water before and after bulk application of WP-1^{TM}. Treatment Notes: Day 1, 2, 3 are background control values. Dosage = 136.36 kg (300 lbs) of WP-1^{TM} reagent was applied on Day 4. Constant flow = 204 gal/min.

Effect on pH

Results indicate that addition of WP-1^{TM} from STA Cell #2, as anticipated increased discharge pH from 8.00 ± 0.04 (background) to 8.72 (Day 4; Fig. 8) before decreasing rapidly back to pre-treatment levels (pH ~7.8 – 7.9) over the next 48 hr period (Fig. 8). No adjustment of pH was employed during this bulk application. The results of pH monitoring confirm other observations (e.g. N and P concentrations; Fig. 6) made during this experiment that WP-1^{TM}, under these flow through conditions, did not exude a significant influence on water column chemistry much beyond 48 hr after application.

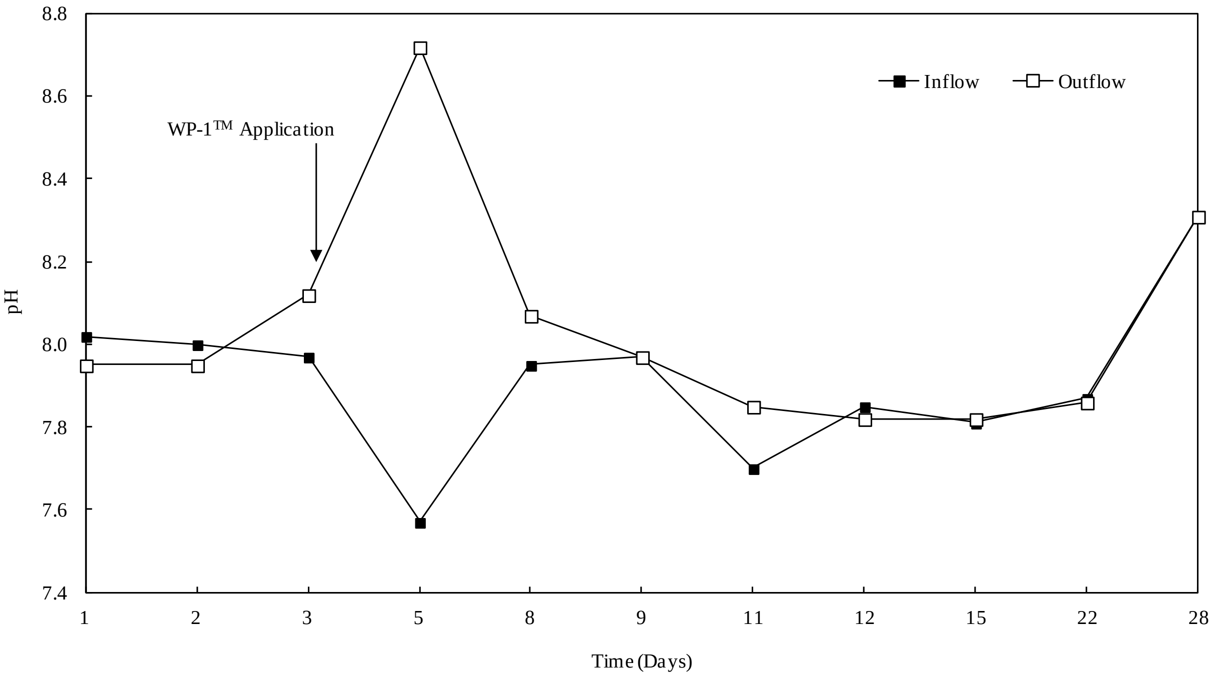

Fig. 8. The effect of WP-1^{TM} applications (Day 4) on pH in SFWMD STA-1W, Test Cell #2.

Implications for management

Waters of the SFWMD are currently affected by two major water quality problems relevant to the finding of this study: (*1*) SFWMD must address legacy nutrients and the high nutrient loadings existing/entering District waterways that (*2*) result in the occurrence of excessive growth and blooms of potentially toxic nuisance algae and aquatic macrophytes. Both occurrences pose serious threats to ecosystem sustainability, human health and regional economic by rendering aquatic systems unsuitable for recreational and commercial use.

This investigation demonstrated that WP-1^{TM} is effective at immobilising soluble P and N in the water column, using a batch additional approach, although additional testing is recommended to confirm the “true” efficiency of this remediation technology. Further testing should, where possible, seek to include treatment replication and a full cycle experimental controls to improve the validity of the results. Modification and monitoring of system pH post WP-1^{TM} application appears to be a pre-requisite for treatment in low alkalinity natural waters. It is clear that WP-1^{TM} could serve as an innovative water treatment technology for removing both N and P from natural waters and is worthy of further investigation.

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References

Akhurst, D. J., Jones, G. B. Clark, M. and McConchie, D. M. (2006). Phosphate removal from aqueous solutions using neutralised bauxite refinery residues (Bauxsol^{TM}). *Environmental Chemistry* **3**, 65-74.

Akhurst, D. J., Jones, G. B. and McConchie, D. M. (2004). The application of sediment capping agents on phosphorus speciation and mobility in a sub-tropical dunal lake. *Marine and Freshwater Research* **55**, 715-725.

Altundogan, H. S. and. Tumen, F. (2003). Removal of phosphate from aqueous solutions by using bauxite II: the activation study. *Journal of Chemical Technology and Biotechnology* **78**(7), 824-833.

Kopatek, J., Borovec, J., Hejzlar, J., Ulrich, K. U., Norton, S. A. and Amirbahman, A. (2006). Aluminum control of phosphorus sorption by lake sediments. *Environmental Science and Technology* **40**(14), 4455-4459.

Florida Department of Environmental Protection [FDEP] (2001). Total maximum daily loads for total phosphorus Lake Okeechobee, Florida. Submitted to US Environmental Protection Agency Region IV, Atlanta (GA). pp 47.

Florida Department of Environmental Protection [FDEP] (2010). Surface water quality standards, Florida Administrative Code Chapter 62-304. pp. 30-46. http://www.dep.state.fl.us/legal/Rules/shared/62-304/62-302.pdf Accessed 1/5/2012.

Furse, J. B. and Fox, D. D. (1994). Economic Fishery Valuation of Five Vegetation Communities in Lake Okeechobee, Florida. *Proceedings of the South-eastern Association of the Fish and Wildlife Agencies* **48**, 575-591.

James, R. T., Jones, B. L. and Smith, V. H. (1995). Historical Trends in the Lake Okeechobee Ecosystem II. Nutrient Budgets. *Archiv fur Hydrobiologie Monographische Beitrage* **107**, 25-47.

James, R. T. and Pollman, C. D. (2011). Sediment and nutrient management solutions to improve the water quality of Lake Okeechobee. *Lake and Reservoir Management* **27**, 28-40.

Liu, G. R., Ye, C. S., He, J. H., Qian, Q. and Jiang, H. (2009). Lake sediment treatment with aluminium, iron, calcium and nitrate additives to reduce phosphorus release. *Journal of Zhejiang University: Science* **10**(9), 1367-1373.

Mullan, A., Quinn, J. P. and McGrath, J. W. (2002). Phosphate removal from wastewater: a novel approach. *Engineering life Science* **2**, 63-66.

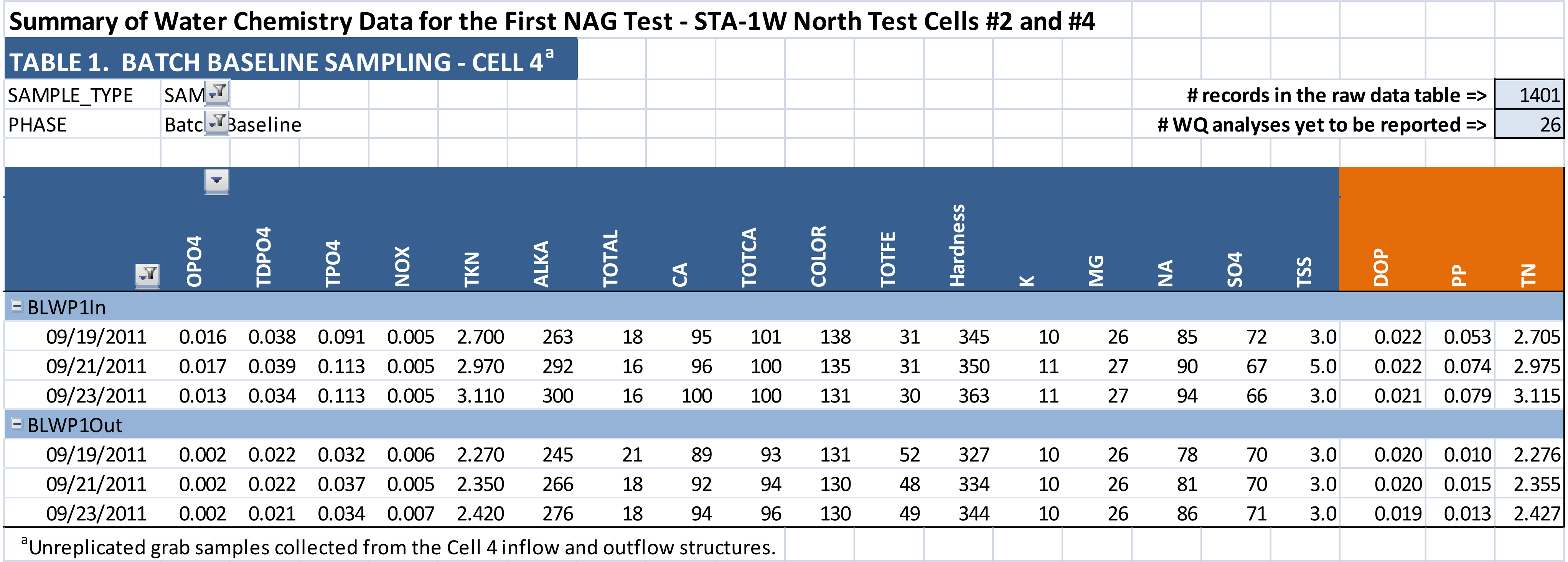
Subramanian, S. and Arnot, T. C. (2001). In *2nd International Conference on Recovery of Phosphate from Sewage and Animal Wastes*, Holland, NL, 12-13 March).

U.S. Environmental Protection Agency [USEPA] (1994). Test method for evaluating solid waste, physical/chemical methods (SW 846 Method 1312), 3rd Edition. Environmental Protection Agency, national Center for Environmental Publications, Cincinnati, OH. www.eap.gov/osw/hazard/testmethods/sw846/pdfs/1312.pdf Accessed: 5/21/2011.

U.S. Environmental Protection Agency [USEPA] (1996), Test method for evaluating solid waste, physical/chemical methods (SW 846 Method 1311), 3rd Edition. Environmental Protection Agency, National Center for Environmental Publications, Cincinnati, OH. www.eap.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf Accessed: 5/21/2011.

Webster, I. T., Ford, W. P. and Hancock, G. (2001). Phosphate dynamics in Australian lowland rivers. *Australian Journal of Marine and Freshwater Research* **52**, 127-137.

Zhang, J., James, R. T., Ritter, G. and Sharfstein, B. (2007). South Florida Environmental Plan, Chapter 10: Lake Okeechobee Protection Program – State of the Lake and Watershed. South Florida Water Management District, pp 1-67.



Summary of Water Chemistry Data for the First NAG Test - STA-1W North Test Cells #2 and #4

TABLE 1. BATCH BASELINE SAMPLING - CELL 4[a]

SAMPLE_TYPE	SAM	**# records in the raw data table =>**	1401
PHASE	Batc Baseline	**# WQ analyses yet to be reported =>**	26

	OPO4	TDPO4	TPO4	NOX	TKN	ALKA	TOTAL	CA	TOTCA	COLOR	TOTFE	Hardness	K	MG	NA	SO4	TSS	DOP	PP	TN
⊟ BLWP1In																				
09/19/2011	0.016	0.038	0.091	0.005	2.700	263	18	95	101	138	31	345	10	26	85	72	3.0	0.022	0.053	2.705
09/21/2011	0.017	0.039	0.113	0.005	2.970	292	16	96	100	135	31	350	11	27	90	67	5.0	0.022	0.074	2.975
09/23/2011	0.013	0.034	0.113	0.005	3.110	300	16	100	100	131	30	363	11	27	94	66	3.0	0.021	0.079	3.115
⊟ BLWP1Out																				
09/19/2011	0.002	0.022	0.032	0.006	2.270	245	21	89	93	131	52	327	10	26	78	70	3.0	0.020	0.010	2.276
09/21/2011	0.002	0.022	0.037	0.005	2.350	266	18	92	94	130	48	334	10	26	81	70	3.0	0.020	0.015	2.355
09/23/2011	0.002	0.021	0.034	0.007	2.420	276	18	94	96	130	49	344	10	26	86	71	3.0	0.019	0.013	2.427

[a] Unreplicated grab samples collected from the Cell 4 inflow and outflow structures.

TABLE 2. BATCH TEST SAMPLING - CELL 4[b]

SAMPLE_TYPE SAM

PHASE Batc Test

Mean Values

	OPO4	TDPO4	TPO4	NOX	TKN	ALKA	TOTAL	CA	TOTCA	COLOR	TOTFE	Hardness	K	MG	NA	SO4	TSS	DOP	PP	TN
09/27/2011	0.002	0.020	0.031	0.030	2.240	254	34	85	85	116	48	317	10	26	79	63	3.0	0.018	0.012	2.270
09/28/2011	0.002	0.019	0.030	0.031	2.120	251	28	82	85	115	46	310	9	25	78	63	3.0	0.017	0.012	2.151
09/29/2011	0.002	0.019	0.030	0.032	2.220	256	28	81	84	114	44	313	9	27	78	63	3.0	0.017	0.011	2.252
09/30/2011	0.002	0.018	0.028	0.030	2.185	257	28	81	79	110	44	317	9	28	78	63	3.0	0.016	0.010	2.215
10/03/2011	0.002	0.016	0.024	0.019	2.135	254	26	78	79	107	32	315	9	29	79	67	3.0	0.014	0.009	2.154
10/04/2011	0.002	0.015	0.023	0.014	2.085	246	25	77	78	106	30	316	9	30	79	63	3.0	0.013	0.008	2.099
10/05/2011	0.002	0.016	0.023	0.014	2.020	246	29	77	79	105	30	318	9	31	79	69	3.0	0.014	0.007	2.034
10/06/2011	0.002	0.013	0.024	0.010	2.030	256	28	75	76	102	28	320	10	32	80	66	3.0	0.011	0.011	2.040
10/07/2011	0.002	0.013	0.021	0.009	1.965	257	26	74	75	103	26	320	10	33	79	65	3.0	0.011	0.008	1.974
10/10/2011	0.002	0.012	0.020	0.007	1.865	237	32	69	70	94	22	303	10	32	78	63	3.0	0.010	0.008	1.872
10/17/2011	0.002	0.010	0.018	0.005	2.020	227	21	65	66	90	20	298	10	33	82	64	3.0	0.008	0.008	2.025
10/24/2011	0.002	0.009	0.017	0.005	1.895	219	22	62	61	81	17	281	9	31	78	62	3.0	0.007	0.008	1.900
10/31/2011	0.002	0.006	0.016	0.010	1.845	191	31	54	57	72	21	247	8	27	70	55	3.0	0.004	0.010	1.855

[b] Mean values of two composite samples collected along a four-station transect oriented down the center of Cell 4. Each composite sample was created by combining two individual surface grab samples (station 1 combined with station 2 and station 3 combined with station 4).

Field Data for the First NAG Batch Test - North Test Cell #4

Date	Time	Statio	DO (mg/l	Temp (°C	pH (s.u.)	Cond (m
09/27/11	-	1	6.30	27.35	7.97	0.973
09/27/11	-	3	3.10	27.36	8.00	0.973
09/28/11	9:25	1	-	27.64	8.12	0.968
09/28/11	9:29	2	-	27.70	8.15	0.969
09/28/11	9:31	3	-	27.70	8.18	0.969
09/28/11	9:34	4	-	27.70	8.18	0.968
09/29/11	8:54	1	-	28.05	8.29	0.969
09/29/11	8:57	2	-	28.08	8.23	0.971
09/29/11	9:00	3	-	28.14	8.29	0.969
09/29/11	9:04	4	-	28.15	8.30	0.969
09/30/11	9:00	1	5.09	28.96	8.33	0.986
09/30/11	9:02	2	5.34	28.99	8.34	0.980
09/30/11	9:04	3	5.49	28.99	8.34	0.986
09/30/11	9:06	4	5.77	29.00	8.36	0.978
10/03/11	9:15	1	5.70	27.00	8.27	0.986
10/03/11	9:18	2	6.25	27.13	8.32	0.989
10/03/11	9:19	3	6.50	27.20	8.33	0.986
10/03/11	9:21	4	6.34	27.23	8.31	0.990
10/04/11	9:07	1	6.23	26.70	8.38	0.985
10/04/11	9:09	2	6.21	26.61	8.38	0.990
10/04/11	9:11	3	6.80	26.67	8.39	0.951
10/04/11	9:13	4	5.80	26.68	8.32	0.986
10/05/11	10:07	1	6.70	26.34	8.46	0.992
10/05/11	10:13	2	6.80	26.45	8.46	0.973
10/05/11	10:16	3	6.64	26.47	8.45	0.985
10/05/11	10:18	4	6.46	26.50	8.50	0.985
10/06/11	9:19	1	6.66	25.58	8.50	0.993
10/06/11	9:21	2	7.10	25.69	8.51	0.989
10/06/11	9:23	3	7.20	25.71	8.52	0.991
10/06/11	9:25	4	7.19	25.78	8.52	0.993
10/07/11	9:45	1	6.99	25.98	8.54	0.990
10/07/11	9:47	2	7.08	26.07	8.56	0.994
10/07/11	9:50	3	7.01	26.11	8.56	0.984
10/07/11	9:52	4	6.68	26.13	8.53	0.996
10/10/11	9:21	1	7.87	25.31	8.44	0.952
10/10/11	9:23	2	7.86	25.28	8.44	0.952
10/10/11	9:25	3	7.15	25.25	8.38	0.954
10/10/11	9:28	4	7.93	25.31	8.44	0.954
10/17/11	9:18	1	4.99	24.92	8.23	0.957
10/17/11	9:20	2	5.38	24.91	8.26	0.957
10/17/11	9:22	3	5.49	24.91	8.27	0.956
10/17/11	9:24	4	5.56	24.90	8.28	0.956
10/24/11	9:40	1	4.04	22.08	8.43	0.924
10/24/11	9:44	2	4.20	22.21	8.43	0.923
10/24/11	9:48	3	4.29	22.26	8.43	0.924
10/24/11	9:53	4	4.35	22.30	8.43	0.924
10/31/11	8:55	1	1.72	23.38	8.31	0.852
10/31/11	8:58	2	1.96	23.38	8.33	0.853
10/31/11	9:00	3	2.13	23.36	8.34	0.852
10/31/11	9:02	4	2.15	23.36	8.34	0.852

TABLE 3. BULK BASELINE SAMPLING - CELL 2[c]

	SAM
PHASE	Bulk aseline

	OPO4	TDPO4	TPO4	NOX	TKN	ALKA	TOTAL	CA	TOTCA	COLOR	TOTFE	Hardness	K	MG	NA	SO4	TSS	DOP	PP	TN
BLBulkIn																				
10/03/2011	0.008	0.028	0.065	0.009	2.520	281	18	97	98	133	27	345	10	25	90	68	3.0	0.020	0.037	2.529
10/04/2011	0.008	0.024	0.066	0.006	2.510	272	18	97	97	130	26	346	10	25	89	72	3.0	0.016	0.042	2.516
10/05/2011	0.002	0.014	0.037	0.037	2.320	264	45	91	89	118	54	333	10	26	87	72	6.0	0.012	0.023	2.357
BLBulkOut																				
10/03/2011	0.002	0.014	0.037	0.034	2.390	270	22	89	91	117	43	325	10	25	85	65	3.0	0.012	0.023	2.424
10/04/2011	0.002	0.014	0.039	0.033	2.300	262	22	92	90	115	41	335	10	25	87	70	3.0	0.012	0.025	2.333
10/05/2011	0.002	0.013	0.036	0.038	2.300	266	28	91	92	118	41	330	10	25	86	72	3.0	0.011	0.023	2.338

[c] Unreplicated grab samples collected from the Cell 2 inflow and outflow structures.

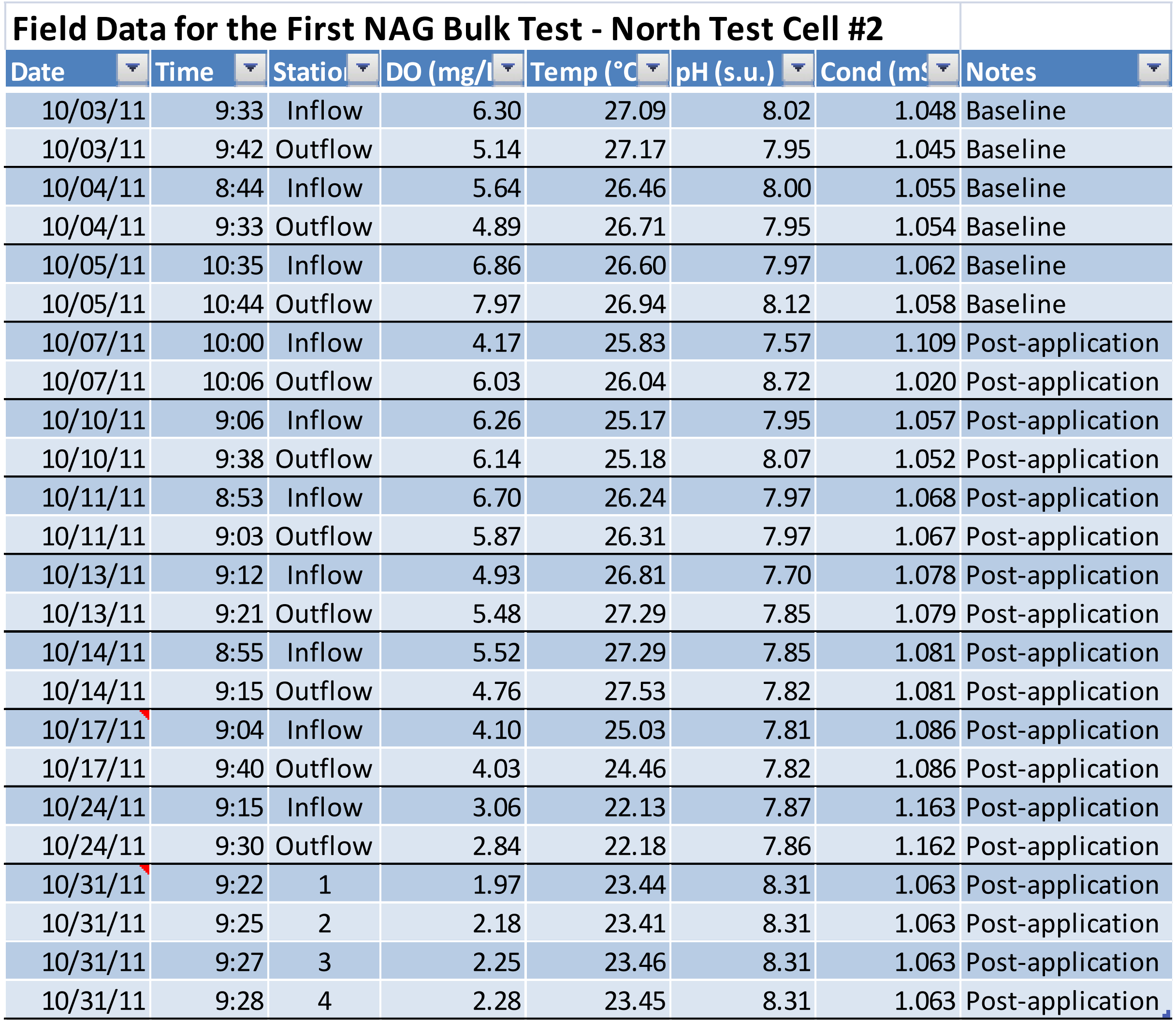
TABLE 4. BULK TEST SAMPLING - CELL 2[d]

SAMPLE_TYPE SAM

PHASE Bulk est

Mean Values	OPO4	TDPO4	TPO4	NOX	TKN	ALKA	TOTAL	CA	TOTCA	COLOR	TOTFE	Hardness	K	MG	NA	SO4	TSS	DOP	PP	TN
BulkWP1In																				
10/07/2011	0.006	0.023	0.058	0.011	2.350	280	17	97	97	129	23	347	10	26	90	70	3.0	0.017	0.035	2.361
10/10/2011	0.014	0.028	0.064	0.019	2.360	277	19	96	96	126	23	343	10	25	92	68	3.0	0.014	0.036	2.379
10/11/2011	0.012	0.027	0.061	0.011	2.480	276	21	95	96	128	22	339	9	25	89	72	3.0	0.015	0.034	2.491
10/12/2011	0.013	0.030	0.055	0.025	2.420	278	17	96	96	128	20	343	10	25	91	70	3.0	0.017	0.025	2.445
10/13/2011	0.007	0.022	0.066	0.025	2.440	269	20	96	96	126	31	347	10	26	90	68	3.0	0.015	0.044	2.465
10/14/2011	0.007	0.021	0.072	0.005	2.560	271	20	98	97	128	28	350	10	26	91	69	3.0	0.014	0.051	2.565
10/17/2011	0.007	0.020	0.061	0.012	2.540	277	18	96	96	128	22	348	10	26	93	68	3.0	0.013	0.041	2.552
10/24/2011	0.039	0.016	0.087	0.005	2.920	300	17	102	104	120	27	365	10	27	112	75	3.0	-0.023	0.071	2.925
10/31/2011	0.002	0.011	0.036	0.089	2.100	249	51	86	89	105	41	311	9	23	91	65	3.0	0.009	0.025	2.189
BulkWP1Out																				
10/07/2011	0.002	0.012	0.033	0.037	2.140	247	36	61	67	110	40	320	10	41	88	68	20.0	0.010	0.021	2.177
10/10/2011	0.002	0.012	0.035	0.070	2.230	261	29	79	81	117	27	328	10	32	89	67	3.0	0.010	0.023	2.300
10/11/2011	0.002	0.013	0.039	0.060	2.420	267	29	83	85	119	27	330	10	30	91	71	3.0	0.011	0.026	2.480
10/12/2011	0.002	0.013	0.038	0.059	2.380	274	26	88	89	122	27	336	10	29	90	69	3.0	0.011	0.025	2.439
10/13/2011	0.002	0.012	0.038	0.056	2.320	266	25	91	91	122	30	345	10	28	93	69	3.0	0.010	0.026	2.376
10/14/2011	0.002	0.013	0.042	0.039	2.480	268	26	92	92	125	32	343	10	28	91	69	3.0	0.011	0.029	2.519
10/17/2011	0.002	0.013	0.040	0.046	2.320	275	26	96	95	126	34	351	10	27	93	68	3.0	0.011	0.027	2.366
10/24/2011	0.003	0.016	0.049	0.118	2.430	286	30	98	99	121	34	351	10	26	104	71	3.0	0.013	0.033	2.548
10/31/2011	0.002	0.011	0.034	0.094	2.070	249	49	87	89	105	40	313	9	23	92	65	3.0	0.009	0.023	2.164

[d] Unreplicated grab samples collected at the Cell 2 inflow and outflow structures from 10/07/2011 through 10/24/2011; on 10/31/2011 samples were collected at four statior along a transect oriented down the center of Cell 2. Composite samples were created by combining surface grab samples from station 1 + station 2 and station 3 + station



Field Data for the First NAG Bulk Test - North Test Cell #2

Date	Time	Statio	DO (mg/l	Temp (°C	pH (s.u.)	Cond (m	Notes
10/03/11	9:33	Inflow	6.30	27.09	8.02	1.048	Baseline
10/03/11	9:42	Outflow	5.14	27.17	7.95	1.045	Baseline
10/04/11	8:44	Inflow	5.64	26.46	8.00	1.055	Baseline
10/04/11	9:33	Outflow	4.89	26.71	7.95	1.054	Baseline
10/05/11	10:35	Inflow	6.86	26.60	7.97	1.062	Baseline
10/05/11	10:44	Outflow	7.97	26.94	8.12	1.058	Baseline
10/07/11	10:00	Inflow	4.17	25.83	7.57	1.109	Post-application
10/07/11	10:06	Outflow	6.03	26.04	8.72	1.020	Post-application
10/10/11	9:06	Inflow	6.26	25.17	7.95	1.057	Post-application
10/10/11	9:38	Outflow	6.14	25.18	8.07	1.052	Post-application
10/11/11	8:53	Inflow	6.70	26.24	7.97	1.068	Post-application
10/11/11	9:03	Outflow	5.87	26.31	7.97	1.067	Post-application
10/13/11	9:12	Inflow	4.93	26.81	7.70	1.078	Post-application
10/13/11	9:21	Outflow	5.48	27.29	7.85	1.079	Post-application
10/14/11	8:55	Inflow	5.52	27.29	7.85	1.081	Post-application
10/14/11	9:15	Outflow	4.76	27.53	7.82	1.081	Post-application
10/17/11	9:04	Inflow	4.10	25.03	7.81	1.086	Post-application
10/17/11	9:40	Outflow	4.03	24.46	7.82	1.086	Post-application
10/24/11	9:15	Inflow	3.06	22.13	7.87	1.163	Post-application
10/24/11	9:30	Outflow	2.84	22.18	7.86	1.162	Post-application
10/31/11	9:22	1	1.97	23.44	8.31	1.063	Post-application
10/31/11	9:25	2	2.18	23.41	8.31	1.063	Post-application
10/31/11	9:27	3	2.25	23.46	8.31	1.063	Post-application
10/31/11	9:28	4	2.28	23.45	8.31	1.063	Post-application

Summary Water Chemistry Data for WP-1 Treatments of the Blue Heron Pond

1. Before Treatment water samples for the second WP-1 application were collected prior to the addition of the algaecide and WP-1.

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FIRST WP-1 APPLICATION

APPLICATION FIRST

PARAMETER CODES

PARAMETERS TIME & STATION	TPO4	TDPO4	OPO4	DOP	PP	CA	TOTCA	Hardness	TOTAL	TOTFE	K	MG	NA
BEFORE TREATMENT													
WP1-1	0.230	0.108	0.080	0.028	0.122	73	76	207	35	292	11	6	17
WP1-2	0.232	0.107	0.077	0.030	0.125	73	75	208	32	303	11	6	17
AFTER TREATMENT													
WP1-1	0.199	0.041	0.021	0.020	0.158	36	39	233	620	122	12	35	16
WP1-2	0.199	0.038	0.020	0.018	0.161	37	38	239	636	121	12	35	16

% DIFFERENCE BETWEEN BEFORE AND AFTER TREATMENT SAMPLES*

	TPO4	TDPO4	OPO4	DOP	PP	CA	TOTCA	Hardness	TOTAL	TOTFE	K	MG	NA
	-14%	-63%	-74%	-34%	29%	-50%	-49%	14%	1775%	-59%	11%	483%	-6%
	↓	↓	↓	↓	↑	↓	↓	↑	↑	↓	↑	↑	↓

SECOND WP-1 APPLICATION + ALGAECIDE

APPLICATION SECOND

PARAMETERS TIME & STATION	TPO4	TDPO4	OPO4	DOP	PP	CA	TOTCA	Hardness	TOTAL	TOTFE	K	MG	NA
BEFORE TREATMENT													
WP1-1	0.166	0.023	0.002	0.021	0.143	31	31	245	160	61	13	41	18
WP1-2	0.168	0.024	0.002	0.022	0.144	31	31	245	162	64	13	41	18
AFTER TREATMENT													
WP1-1	0.089	0.016	0.002	0.014	0.073	18	19	273	116	31	12	55	25
WP1-2	0.083	0.017	0.002	0.015	0.066	17	18	273	109	27	12	56	25

% DIFFERENCE BETWEEN BEFORE AND AFTER TREATMENT SAMPLES*

	TPO4	TDPO4	OPO4	DOP	PP	CA	TOTCA	Hardness	TOTAL	TOTFE	K	MG	NA
	-49%	-30%	0%	-33%	-52%	-43%	-40%	11%	-30%	-54%	-7%	37%	40%
	↓	↓	↑	↓	↓	↓	↓	↑	↓	↓	↓	↑	↑

* % difference = {[average(AFTER)-average(BEFORE)]/average(BEFORE)}*100