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PHOSPHORUS MANAGEMENT TREATMENTS IN THE UPPER OCKLAWAHA RIVER BASIN (2001-2010)

by

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EXECUTIVE SUMMARY

Since 2001, the St. Johns River Water Management District (SJRWMD) has applied multiple treatments of liquid aluminum sulfate ($Al_2(SO4)_3$) in Emeralda Marsh Conservation Area (EMCA) and Lake Harris Conservation Area (LHCA). The purpose of these treatments was to reduce water column phosphorus (P) concentrations, which were elevated from former agricultural practices in both areas. Alum was utilized because of its ability to trap or bind P in a layer of flocculent material as it settles to the sediment.

Lake Harris Conservation Area and five areas within EMCA received surface water treatments with alum. Before each treatment, alum dosages were determined by jar tests on sediment and/or water samples. If insufficient alkalinity was present, lime slurry ($Ca(OH)_2$) or sodium aluminate ($Na_2Al_2O_4$) were used as buffers. In total, approximately 1,984 ha were treated with 5,462,497 L of alum and 443,344 L of buffer. The total application cost of the treatments was $1,368,845.

The effectiveness of each treatment was assessed from monthly water quality samples, which SJRWMD has collected in the restoration areas since 1994. Water quality parameters were compared from the average of samples taken two months before treatments and two months after treatments. Results showed that the treatment in Eustis Muck Farm had the highest percent reduction (97%) in average total phosphorus (TP-T). The first treatment in LHCA had the lowest TP-T reduction (44%). Pre-treatment, mean TP-T in EMCA and LHCA for the period of record ranged from 0.110 to 4.58 mg/L. Mean TP-T after treatment ranged from 0.051 to 0.504 mg/L in the short term (two months). Over all treatments, TP-T was reduced on average by 67%. Significant decreases in median soluble reactive phosphorus (SRP), total dissolved Kjeldahl nitrogen (TKN-D), total suspended solids (TSS), chlorophyll *a*, color, and dissolved organic carbon (DOC) occurred in most of the treatment areas. At several sites, improved water quality has persisted for many years and variabilities in TP concentrations were suppressed.

In all the areas except for Eustis Muck Farm and LHCA, the dose of alum applied was less than the dose recommended by the initial treatment designs. Under-dosing was caused by several factors. Heavy rains and leaking infrastructure increased water volumes in some areas, diluting the dosage. In the Lake Griffin Flow-Way, emergent vegetation significantly hindered the delivery of liquid alum to the water surface. Alum dosage also was miscalculated by not accounting for both water column P and sediment P concentrations.

Sediment biogeochemistry also appeared to affect the alum treatments. The amount of buffer needed to maintain pH and alkalinity in the treatment area was consistently less than the amount predicted by the jar tests. Preliminary jar tests with sediment-water slurries revealed that muck sediments provided a significant increase in alkalinity following alum dosing.

Project costs were analyzed and the cost per kg P sequestered was calculated. Application costs ranged from $87,210 to $278,060. Treatment designs, including jar tests, averaged $14,614. Treatment costs were driven by the amount of sediment work completed. Application costs typically varied because of the fluctuating expense of alum ($0.34/gal to $1.00/gal). The average cost/kg P removed from the water column was $164. This value does not include any sediment TP removal, since that is difficult to estimate.

Based on the methods and results of these eight alum treatments, several recommendations can be made:

- Areas with dense emergent and/or submerged vegetation should not be treated via a liquid alum barge application.
- Dosing calculations should include the chemical demand for alum within the water column and sediments for long-term nutrient management.
- Monitoring pH and alkalinity throughout the treatment prevents toxicity problems and *a priori* knowledge of the water column chemistry, such as DOC and SRP fraction can contribute to treatment success. However, due to the complexity of lake water chemistry, jar tests are vital for proper dosing.
- In shallow sites (<1 m), an accurate bathymetric map is essential for barge navigation.
- Frequent communication between chemical suppliers, barge applicators, and project managers is essential.
- Sediments have great influence on the buffering capacity of the system. The commonly held principle that the ratio of applied alum to sodium aluminate should be 2:1 was developed for soft water lakes, and this guideline may not be applicable to systems with higher acid neutralizing capacity.
- The dosing should be conducted as one event to create a broad "sweep" flocculation and to discourage microfloc formation.

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ACRONYMS AND ABBREVIATIONS

Location or Organization Acronyms

EMCA	Emeralda Marsh Conservation Area
ERD	Environmental Research and Design
FDEP	Florida Department of Environmental Protection
FWC	Florida Fish and Wildlife Conservation Commission
LHCA	Lake Harris Conservation Area
SJRWMD	St. Johns River Water Management District
UORB	Upper Ocklawaha River Basin

Technical Abbreviations

~	about
–	bound
:	ratio
/	per
↓	precipitate
%	percent
°C	degrees Celsius
90%	90th percentile
ac	acre(s)
Al	Aluminum
Al^{3+}	Aluminum ion
$Al(OH)_3$	Aluminum hydroxide
$AlPO_4$	Aluminum phosphate
Al_2O_3	Aluminum oxide
$Al_2(SO_4)_3$	Aluminum sulfate
ANC	Acid neutralizing capacity
Ca	Calcium
Ca^{2+}	Calcium ion
$CaCO_3$	Calcium carbonate
$Ca(OH_2)$	Hydrated lime or lime slurry
Chl-a	Chlorophyll *a*
cm	Centimeter
cm^{-1}	Per centimeter
DOQQ	Digital orthophoto quarter quad
DOC	Dissolved organic carbon
DOP	Dissolved organic phosphorus
DO	Dissolved oxygen
EC	Electrical conductivity
et al.	and others
Fe	Iron
g	gram

H^+	Hydrogen ion
H_2O	water
ha	hectare(s)
kg	kilogram
L	Liter
m	meter
m^{-2}	per $meter^2$
m^{-3}	per $meter^3$
meq	milli-equivalents
mg	milligram
Mg	Magnesium
Mg^{2+}	Magnesium ion
µg	micrograms
µmhos	micromhos
$Na_2Al_2O_4$	sodium aluminate
NGVD	National Geodetic Vertical Datum 1929 (NGVD 29)
NOM	Natural organic matter
OM	Organic matter
P-Al	Particulate aluminum
pH	Hydrogen ion concentration
PO_4	Phosphate
PP	Particulate phosphorus
P	Phosphorus
s_{-1}	per second
Si	Silica
SRP	Soluble reactive phosphorus or orthophosphate (PO_4^{-3})
SO_4	Sulfate
SO_4^{2-}	Sulfate ion
TKN-D	Total Kjeldahl nitrogen - dissolved
TP-D	Total dissolved phosphorus
TMDL	Total maximum daily load
TP-T	Total phosphorus
TOC	Total organic carbon
TSS	Total suspended solids
yr	year

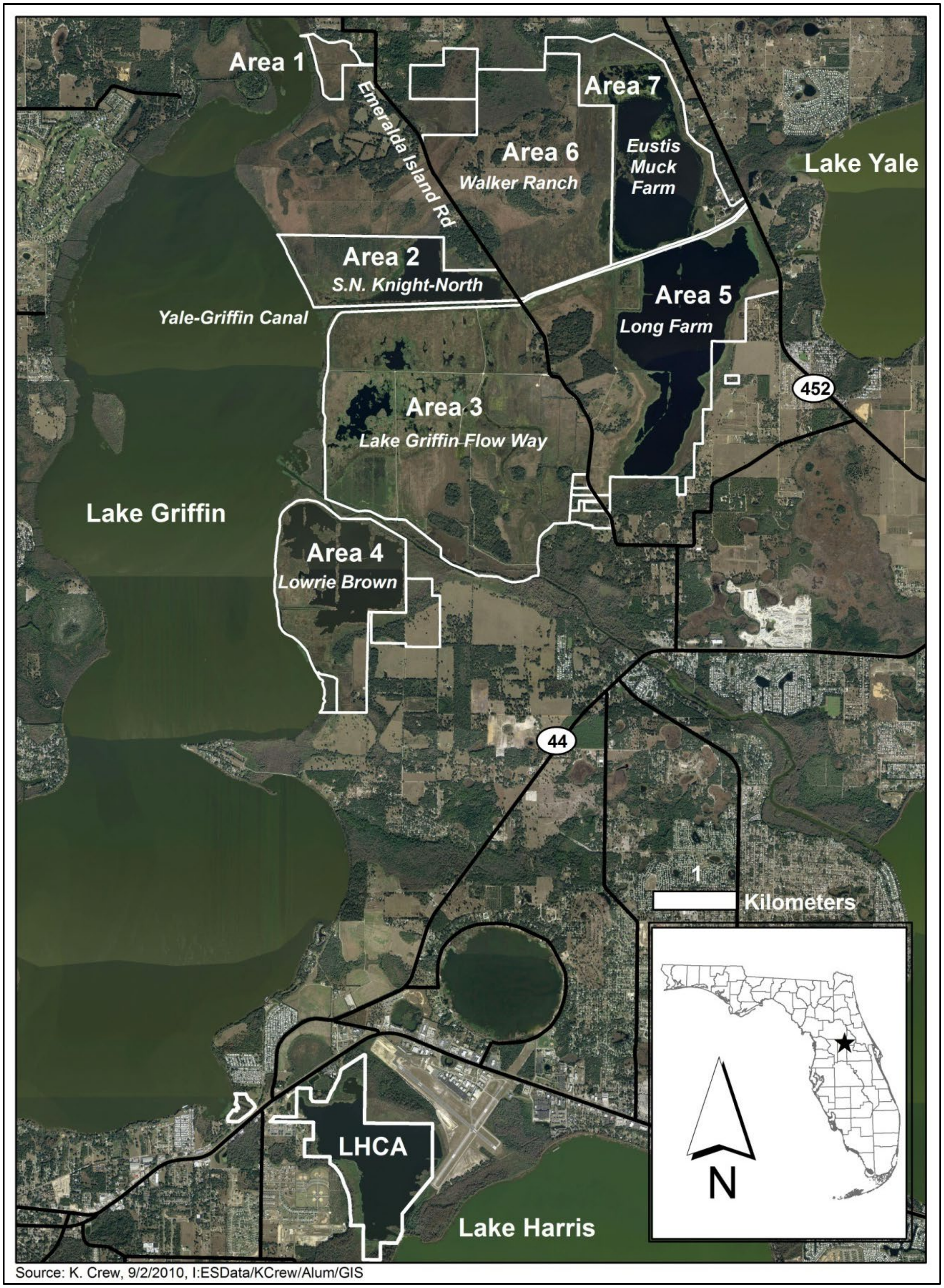
INTRODUCTION

Emeralda Marsh Conservation Area (EMCA) and Lake Harris Conservation Area (LHCA) are two of five restoration areas in the Upper Ocklawaha River Basin (UORB) that are managed by the St. Johns River Water Management District (SJRWMD). EMCA encompasses 2,630 ha and is located in northeast Lake County on the east side of Lake Griffin, one of the headwater lakes of the Ocklawaha River (Figure 1). The Yale-Griffin Canal, which runs east to west through the marsh, connects Lake Yale to Lake Griffin. LHCA comprises 194 ha and is located southwest of the Leesburg Airport, bordering the northwest side of Lake Harris (Figure 1).

Both EMCA and LHCA were once part of Emeralda Marsh, which was historically dominated by sawgrass, sedges, and water lilies, and comprised approximately 55% of the UORB's riparian wetlands. Before 1945, the wetlands south of Emeralda Marsh were still intact and contiguous with the forested uplands (Marburger and Godwin 1996). Much of the original marsh, however, was significantly altered between the early 1950s through the 1970s. Levees and canals were constructed in EMCA to convert most of the floodplain sawgrass marshes and wet prairies into arable land. The muck soils supported agriculture primarily vegetable crops and cattle pasture. In the early 1970s, LHCA, formerly Harris Bayou, was drained and diked for corn production. Intake and discharge pumps were installed through a railroad-grade levee between the farm and Lake Harris to regulate water levels.

The transformation of Emeralda Marsh into agricultural lands had direct impacts on the ecosystems' soils, hydrology, and vegetation, but one of the most significant impacts was the decline in Lake Griffin's water quality from increased nutrient loading. Phosphorus-rich fertilizers were applied to the already organic rich farm soils (muck), creating high-nutrient runoff into the adjacent lake. The elevated phosphorous (P) loads into Lake Griffin resulted in phytoplankton blooms that reduced water clarity and threatened important flora and fauna (Fulton 2016).

Beginning in the 1980s, initiatives were begun for restoring parts of Emeralda Marsh. After the enactment of legislation such as the Save Our Rivers Act (1981) and the Surface Water Improvement (SWIM) Act (1987), SJRWMD converted multiple floodplain muck farms into the EMCA and LHCA to reduce agricultural discharge to Lake Griffin and restore and protect floodplain and upland ecosystems (Fulton 1995).



Source: K. Crew, 9/2/2010, I:ESData/KCrew/Alum/GIS

Figure 1. EMCA (Areas 1-7) and LHCA boundaries (2004 DOQQ). EMCA is divided north to south by Emeralda Island Rd. The Yale-Griffin Canal divides EMCA from east to west.

Re-flooding the muck farms was required to restore wetland hydrology, but resulted in a flux of labile P from the soil to the overlying water column. An analysis of soils from EMCA confirmed that residual soil P presented a significant source of external loading to Lake Griffin (Reddy et al. 1997). The top 15-cm soil layer had a supply of labile P that could release for 30-140 years (Reddy et al. 1997). Treatment of excess P in EMCA and LHCA therefore was required to meet the Total Maximum Daily Load (TMDL) of 12,202 kg/yr for Lake Griffin.

SJRWMD chose to use aluminum sulfate ($Al_2(SO4)_3$), or alum, as a method for reducing excess nutrients in the restoration areas. Alum has been used in water purification for over 200 years (Cooke et al. 2005) and is preferred over other amendments due to its effectiveness, availability, permanence, low cost, and purity. Although various iron (Fe) and calcium (Ca)-based amendments have also been used for nutrient abatement, alum has had particular success in reducing soluble P in shallow lakes and wetlands (Cooke and Kennedy 1981; Welch et al. 1988; Bachand et al. 1999; Ann et al. 2000, Hoge 2003). Cooke et al. (2005) investigated alum applications on nine shallow lakes and basins, six of which were considered successful, averaging a 50% reduction in TP that lasted 5-11 years following alum treatment.

To date, eight surface alum applications have been implemented in the UORB. The Lake Griffin Flow-Way (LGFW) in EMCA was the first to receive treatment, followed by Lowrie Brown, Long Farm (treated twice), Eustis Muck Farm, S.N. Knight-North, and two treatments in LHCA (Figure 1). The purpose of this report is to present information concerning the chemistry of alum and phosphorus, methods of application, treatment results, and project costs related to each treatment.

PHOSPHORUS MANAGEMENT WITH ALUM

Water Column Chemistry

The coagulation and removal of dissolved and particulate P from the water column with alum involves several processes: charge neutralization, adsorption, enmeshment, and complexation/precipitation. When alum is added to water, the aluminum ion hydrolyzes to produce acid (H^+). If sufficient alkalinity is present, the acidity is neutralized and aluminum hydroxide ($Al(OH)_3$) coagulates (Harper et al. 1998) as shown below:

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$$

Aluminum hydroxide may carry a small positive charge due to polymeric forms of Al that are not completely neutralized. Negatively charged soluble reactive P (SRP, PO_4^{3-}) is therefore readily absorbed into its lattice. Once the charge is neutralized, the small, suspended particles stick to one another and form microflocs, which are not visible to the naked eye. If all the particles' charges have been neutralized, then collisions of the microfloc particles will cause them to adhere to one another to produce larger, visible flocs called pinflocs. The floc size continues to build through additional collisions and macroflocs are formed. Macrofloc will appear as tufts of cotton, separated by clear water. Because $Al(OH)_3$ flocculates to form large gelatinous particles, it can physically entrap particulate P as it settles to the sediment surface. Charge neutralization or entrapment (sweep flocculation) may occur simultaneously with either process dominating, depending on the water chemistry (Shin et al. 2008).

Although not a principle mechanism for P removal (Galarneau and Gehr 1997), alum can reduce dissolved P by forming $AlPO_4$ precipitate:

$$Al_2(SO_4)_3 + 14.3H_2O + 2PO_4^{3-} \rightarrow 2AlPO_4\downarrow + 3SO_4^{2-} + 14.3H_2O$$

The optimum pH range for $AlPO_4$ precipitation is 5.5 to 6.5. Al^{3+} also may form complexes with natural organic matter (NOM), which can precipitate and entrap colloidal material (Shin et al. 2008). NOM is comprised of the complex matrix of organic material present in natural waters, such as humic and fulvic acids (Srinivasan and Viraraghavan 2004). Usually quantified as dissolved organic carbon (DOC), this material can compete with P-species for Al bonding sites, decreasing alum's effectiveness in removing nutrients (Qualls et al. 2009). De Vincente et al. (2008a) found a stronger correlation between P removal and color than DOC, suggesting that humic acids might be largely responsible for the interaction.

pH is the most important parameter for proper coagulation performance because it affects coagulant solubility, the surface charges of colloids, NOM functional groups, dissolved-phase coagulant species, and floc particles (Pernitsky 2010). Surface charge strongly regulates which aluminum hydrolysis products will form (Cooke and Kennedy 1981, Cooke et al. 1993). Between pH 4 and 6, various soluble intermediates form. At pH levels above eight, solubility increases, potentially releasing phosphorus (Cooke et al. 1993). Between pH 6 and 8, hydrated and soluble Al^{3-} dominates (Cooke et al. 1993), $Al(OH)_3$ forms and P sorption and inactivation occur. Although alum is effective in the pH range of 4 to 7, Georgantas and Grigoropoulou (2006) encouraged a pH range of 5 to 6 to minimize residual Al and maximize the removal of soluble reactive phosphorus (SRP) and organic matter.

The process of manipulating pH to this desired range is dependent upon the water's alkalinity, or acid-neutralizing (buffering) capacity (ANC). Alum is acidic and consumes alkalinity. As alkalinity is consumed, pH values can become too low for effective coagulation and toxicities may occur. Alternatively, high alkalinity waters may require increased alum doses to lower pH to a level sufficient for effective coagulation (Pernitsky 2010).

Along with pH, the forms of P that are present in the water column may affect floc formation and P removal. Generally, $Al(OH)_3$ is most effective at sorbing inorganic forms of P. The removal of inorganic P depends primarily on reaction pH and P concentration (Cooke and Kennedy 1981). In general, a high inorganic P concentration (>1 mg P/L) and low pH would favor the formation of $AlPO_4$. Theoretically, under these conditions and in the presence of excess P, the removal of one mole of P as $AlPO_4$ would require one mole of Al.

It is generally accepted, however, that an Al-bound P molar ratio of 1.0 is unrealistically low because of competition for P from other ligands (Herrera Environmental Consultants 2003). At lower inorganic P concentrations (<1 mg P/L) and a pH range from 6.0-7.0, OH^- competes with

PO_4^{3-} for Al ions, favoring the formation of Al hydroxide-phosphates (Connor and Martin 1989). Under these conditions, maximum water column P removal efficiencies occur at even higher Al:P molar ratios. Maximum P removal from Cline's Pond water (0.43 mg SRP/L), which was found to be pH dependent, occurred at Al:P molar ratios ranging from 5.7:1 to 7.2:1 (Kennedy and Cooke 1982). Al:P molar ratios in excess of 525:1 were required to achieve 90 percent P removal from unfiltered Lake Mendota epilimnetic water (0.01 mg SRP/L) at pH 6.5 to 7.0 (Eisenreich et al. 1977).

Dissolved organic phosphates are less effectively removed by alum, presumably because of the complexity of their molecular structure and chemical characteristics. The efficiency of removal appears to be related more to the types of organic phosphates present than to treatment conditions. Certain blue-green algae produce phosphatase, an enzyme that can remove inorganic P from organic phosphates at rates sufficient to support elevated algae populations. Cooke et al. (1993) speculated that this could affect the long-term efficiency of alum treatments because P can be released from organic molecules.

Sediment Dynamics

Although the chemistry of the water column may affect an alum treatment's initial effectiveness, sediment biogeochemistry may dictate its longevity. In hypereutrophic lakes in Florida, internal recycling from the top layer of sediments can release a significant amount of bioavailable P to the water column (Steinman, et al. 2004). Managing the recycling of nutrients from the sediments to the water column with a stable alum floc is an important step in achieving long-term treatment success.

Ideally, an alum application creates a floc "blanket" that settles on the sediment surface. Reactive hydroxyls in the floc continue to bind labile P in the sediments above and below the blanket over time, increasing sediment TP (Narf 1985, Reitzel et al. 2005, Berkowitz et al. 2006). Two years after an alum application in Lake Möllen, Germany, pore water P concentration was 0.03 mg/L compared to 1.0-2.0 mg/L prior to application, indicating that surplus $Al(OH)_3$ in the upper 10 cm of sediment was still binding with P (Egemose et al. 2009).

The rate of sorption by the floc decreases over time, but sediment P inactivation continues until the sorption capacity of the alum floc is reached, which may take years (Egemose et al. 2009). The chemical stabilization of the floc, however, occurs more rapidly. Berkowitz et al. (2005) found that within three weeks after treatment, 20% of the amorphous Al:P solids in floc had crystallized into well-ordered gibbsite. X-ray diffraction suggested the formation of a second intermediate crystalline phase 150 days after application. By six months after treatment, 70% of the floc had crystallized into gibbsite and a linear decrease had occurred in its sorption capacity (Berkowitz et al. 2005). McLaughlin et al. (1981) demonstrated that newly formed Al colloids sorb one to two orders of magnitude more P than gibbsite.

At circumneutral pH values (pH 5 - 9), the crystalline structure of gibbsite is very stable. Its structure consists of stacked dioctahedral sheets of $Al(OH)_3$ held together by hydrogen bonds (Essington 2004). Aluminum complexes and polymers are inert to changes in redox conditions, so long as the pH remains circumneutral, then settled alum floc may persist in a relatively static state (Cooke and Kennedy 1981). Consistent Al:P ratios were found throughout sediment profiles 21 years after treatment (Rydin et al. 2000). The behavior of aluminum changes, however, below pH 5, possibly because of polymerization (Samaritan 1993). High primary production in shallow lakes can lead to pH > 9 in the water column, potentially solubilizing Al-P bonds (Egemose et al. 2009).

Physical disturbances also can affect an alum floc's P sorption capacity. Because of its low density in the first few weeks after treatment, floc can be easily resuspended in shallow lakes by wind events (Egemose et al. 2009). Resuspension of sediments substantially increased TP concentrations, but total soluble P concentration remained low in the water when alum was present in a sediment core study of Spring Lake, Michigan (Steinman et al. 2006). When floc is resuspended, it can bind additional dissolved P in the water column, essentially "re-treating" the water (Egemose et al. 2009). Upon settling, a noticeable improvement in water quality may be observed. If, however, the resuspension event coincides with high pH (>9) conditions, then Al-hydroxide dissolution and internal P recycling may occur (Van Hullebusch et al. 2003, Egemose et al. 2009).

Biological disturbances from benthic organisms and macrophytes (Welch and Schrieve 1994) can reduce the longevity of an alum treatment. Bioturbation can quickly bury the active floc layer, decreasing the chance of resuspension and the extent and duration of its effectiveness (Lewandowski et al. 2003). Elevated levels of aluminum were found 20 cm deep in the sediment of West Twin Lake, Ohio, nearly 16 years after treatment, suggesting substantial mixing of the floc over time (Welch and Cooke 1999).

Both emergent and submerged plants may decrease effectiveness by intercepting settling alum floc and preventing a uniform coating on the bottom. In addition, their roots penetrate below the sediment surface where they senesce and release P to the water through decomposition. In a survey of nine alum applications in shallow lakes, Cooke et al. (2005) found that treatment failure in three of the lakes was attributed to interference by an extensive coverage by submersed macrophytes. Macrophytes, however, provide the benefit of protecting the water surface from wind mixing.

Avoiding Toxicity Problems

Forming a stable alum floc layer is necessary to avoid potential risks to biota, such as significant decreases in water column pH and aluminum toxicity. If alum dosages are miscalculated or water chemistry is not measured properly, then a solid floc may not form and suspended aluminum in the water column could pose a risk to organisms. Colloidal solids (particles less than 0.01 mm in diameter) or microfloc, could also form, creating turbidity that might not settle for days or months. Gensemer and Playle (1999) suggested that freshwater algae and fish would be the most appropriate organisms to monitor during any application since they are most likely to be affected.

Cooke et al. (2005) suggested several water body conditions that should be present to avoid acute or chronic harmful effects to biota during an alum application. These conditions include an alkalinity above 75 mg/L (as $CaCO_3$), high levels of Si, Ca, and SO_4, and a low-energy environment that allows for the vertical settling of floc. A high concentration of total organic carbon (TOC) is also desirable because Al-NOM complexes are less toxic to organisms (Roy and Campbell 1997; Gensemer and Playle 1999).

In conditions where low alkalinity (<35 mg/L) is present and the addition of alum may reduce the pH to harmful levels (<6.0 by Class III standards, FDEP 2009), $Ca(OH)_2$, or hydrated lime, may be used as a buffering agent. Lime is inexpensive, easy to handle, and readily available. It contains approximately 22-30% percent calcium and has a neutralizing value or calcium carbonate equivalency of 136%. Another commonly used buffer is sodium aluminate ($Na_2Al_2O_4$), which is expensive and caustic (pH = 14), but provides additional aluminum for P sorption. Sodium aluminate has the same pH solubility curves and precipitation stoichiometry as alum (Osgood et al. 2004) and is commonly available in 32 to 45% solutions (9 – 12% as Al). In general, toxicity risks are minimal if alum is properly dosed and applied (Cooke and Kennedy 1981).

Dose Determination

Water Column Dosing

The method for determining alum dosage depends on whether the treatment objective is to remove P from the water column (precipitation) or to manage sediment P release (inactivation; Cooke et al. 2005). In the UORB, all alum treatments except for those in LGFW (Area 3) and Long Farm (Area 5) were designed for P precipitation. For this approach, the most common and effective method is a "jar test" in which surface water samples are treated with varying amounts of alum and buffers (if needed) until the desired level of total P (TP-T) is reached. In EMCA and LHCA, composite water samples were collected and treated with doses of alum and lime or sodium aluminate ranging from 5 - 30 mg Al/L (ERD 2001, 2002a, 2002b, 2003a, 2003b; MACTEC 2003, 2004; DB Environmental 2004, 2005).

Sediment Dosing

For long-term sediment inactivation, dosage may be determined by three different procedures (Cooke et al. 2005). The first procedure is similar to a jar test for precipitation but focuses on using the maximum dose while maintaining specific alkalinity and pH levels for environmental safety (Kennedy and Cooke 1982; Cooke et al. 2005). More recent calculation methods have centered on quantifying the internal loading of P from the sediment (Kennedy et al 1987) or from the mobile P in the upper layers of the sediment (Rydin and Welch 1999).

The second procedure involves estimating the internal recycling rates from the sediments using a mass balance equation. The internal recycling rate is multiplied by the number of years of expected treatment, giving a more accurate estimate of the proper alum dosage (Kennedy et al. 1987). Measuring the internal release of sediment P requires incubation studies with intact cores, an expensive and cumbersome task.

The third procedure is to measure the mass of mobile inorganic P in the upper layers of the sediment (Rydin and Welch 1999). After determining the "mobile" P in the top 4 cm of the sediment to be treated, they recommend dosing using a 100:1 (by weight) ratio of Al added: Al-P formation expected. This would potentially account for all the internal recycling from mobile P in the top 4 cm of the sediment and any migrating P from greater sediment depths.

This method was used to calculate dosage for the LGFW and Long Farm sediment treatments based on 10 cm-deep sediment cores. Quantifying the mobile P in the upper layers of the sediment largely depends on the extraction method used. In addition, determining the ratio of Al added:P_{mobile} for sediment treatment is largely in debate. Earlier work suggested that a 1:1 (Al:P_{mobile}) ratio was sufficient. Recent research suggests that much higher ratios may be required and that additional work will be necessary to understand proper sediment dosing techniques. In addition, the depth of the active sediment layer contributing to internal P recycling is unknown (James 2010) and may be influenced by many factors, such as bioturbation.

To determine P mobility, various sequential extraction schemes or P-fractionations can be conducted. No one extraction procedure has been widely accepted for dividing organic P into potentially mobile and more refractory forms (Rydin 2000). However, most of the fractionation schemes appear to utilize the bicarbonate dithionite extraction (BD-P). BD-extractable P fraction was a good predictor of total P release rates from sediment under anoxic conditions according to Nürnberg (1988). Rydin (2000) used the P fractionation scheme of Psenner and Puckso (1988) and determined that pools of loosely sorbed-P and Fe-P surface sediments were found to be fully mobile, and about 60% of the extractable organic-P pool was mobile. In contrast, Rydin (2000) considered Al-P, Ca-P and residual-P (calculated) permanently bound.

Mobile P may migrate upward in the sediment profile, increasing the molar Al requirement for long-term nutrient inactivation (Rydin et al. 2000, James 2005). Studies on alum-treated lake sediments reported molar ratios of Al-added: mobile P in the range of 4:1 to 115:1 (Rydin and Welch 1999, Reitzel et al. 2003, James 2005). Rydin et al. (2000) investigated six lakes in Washington that had long-term successful alum treatments and found a sediment Al:Al-P ratio of 11:1, by weight (9.6:1 molar). The sinking depth of the alum floc, the thickness of the active layer of sediment, and bacterially-mediated transformations of polyphosphates in the sediments also may account for higher ratio requirements (James 2005).

James (2007) used concentrations of redox-sensitive P (does not include any organic P) in the sediment to determine the quantity of alum (as Al) required using the Psenner and Puckso (1988) extraction method. In general, the Al:$P_{90\%}$ ratio (the concentration of aluminum required to bind 90% of the redox-sensitive P) approached ~100:1 for sediments with redox-sensitive P concentrations less than 1.0 mg P/g. As the redox sensitive P concentration increased above 1.0, the Al:$P_{90\%}$ declined exponentially, approaching 20:1 at very high P concentrations.

Additional work by James (2011) recommended a dosing scheme so that Al:P ratios were the concentration of alum (as Al) required to bind 90% of the BD extractable P. In one example, the concentration of Al required to bind 90% of the BD-extractable P was ~22.8 mg/g, resulting in an Al:$P_{90\%}$ of 170:1 (i.e., 22.8 mg Al/g required to bind 0.134 mg P/g). Sediment with a much higher BD-extractable P concentration of 2.0 mg/g only required a ratio of ~ 20:1 for a 90% inactivation. James hypothesized that a lower stoichiometric ratio is needed because there is more P relative to other constituents to compete for binding sites on the alum floc and found a negative nonlinear relationship between the redox sensitive P concentration and the Al:P ratio for sediment collected in Half Moon Lake in Wisconsin.

Huser and Pilgram (2014) evaluated how the amount of added Al, relative to mobile P, affects the conversion of mobile P to Al-P. They studied 300 subsamples of 35 sediment cores taken from 20 lakes in the upper Midwest. The sediment mobile P content ranged from 0.04 to 2.8 g m^{-2} cm^{-1}, which is a rather large range of mobile P. Even with differences in sediment composition, the conversion of mobile P to Al-P appeared to be mechanistically similar across lakes, following a Langmuir type adsorption relationship for Al-P formation. They developed the AlMobP (pretreatment mobile sediment P and the amount of Al necessary to form a known mass of Al-P) dosing model, which covers a wide range of sediment mobile P content, sediment types, and potential Al doses, potentially providing a flexible method to weigh the costs of application versus reduced internal loading.

Lewandowski and others (2003) suggested that repeated additions of small amounts of Al salts to the sediment surface is a more effective technique than a single addition of the same amount of Al salt because the new floc layer not only retains P liberated from underlying old sediment, but also draws P out of the overlying fresh sediment that settles over the alum over time. de Vicente et al. (2008b) suggested targeting readily available inorganic P and most iron-bound inorganic P in the first dose. The second dose would target the organic P-pool that would be mineralized in a three- to ten-year period.

Repeated additions of small amounts of alum, however, would need to be dosed sufficiently to overcome the absorptive capacity of the water column, unless a deep-water application was used. Van Hullebusch and others (2003) used solid alum product to bypass the water column and provide a low dose to the sediments of Lake Courtille, France. However, this effort was unsuccessful due to high primary productivity in the water column and subsequent organic matter sedimentation.

ALUM APPLICATIONS IN THE UORB

Application Methods

SJRWMD used liquid alum because of its low cost, ease and speed of delivery, and excellent floc formation (Jernelöv 1971, Cooke et al. 1993). In addition to liquid alum, alum residual was used in one treatment. A by-product of the drinking water industry, alum residual has been used extensively in the Lake Apopka Basin for reducing P flux from organic soils (Hoge 2003). Residual was spread in Area 4 using a manure spreader at a rate of 14.6 metric wet tons/ha.

For the liquid alum treatments, chemicals were off-loaded from 5,000-gallon tractor-trailer tankers and transported onsite by barges. In the LGFW application, alum was dispersed across the water surface from a small barge with a large diameter hose with a fire nozzle and a high velocity pump due to the presence of heavy vegetation. Spraying with a hose from an airboat allowed access to shallower areas in two instances (LGFW and Lowrie Brown), but did not provide the physical mixing from a propeller that encourages floc formation. In Lowrie Brown, Long Farm, and LHCA, alum was dispersed through a manifold mounted on a small barge. For sites S.N. Knight North, Eustis Muck Farm, and the second application at LHCA, the alum was dispersed by a large multi-thousand-gallon barge with a manifold system that could distribute alum and a buffering agent simultaneously.

For each treatment, the alum was supplied by General Chemical Corporation (Tampa, FL) and delivered primarily by McKenzie Tanker Lines (Tampa, FL). The alum was environmental grade, low-iron aluminum sulfate with a 4.4% Al content. Each tanker held approximately 17,034 L of alum. Chemical Lime Company (Nichols, FL) supplied lime, while Kemira Chemical, Inc. (Savannah, GA) and Thatcher Chemical (Deland, FL) supplied the sodium aluminate.

The buffering agents, if needed, were also delivered in liquid form. Hydrated lime ($Ca(OH_2)$) was delivered in a pre-mixed slurry (typically around 40% solid, pH=12.4 at 25°C), which allowed for easier handling and prevented inhalation problems. At 40% solids, the mixture weighed approximately 1.2 kg/L, with the lime portion weighing 0.5 kg/L. Constant agitation was necessary to avoid settling of the lime. The sodium aluminate weighed approximately 1.4 kg/L and contained approximately 10.38% Al^{+3}.

Assessing Treatment Effectiveness

In previous studies, alum treatment effectiveness was determined using changes in average TP-T concentration, sediment P release rates, and the water body’s trophic status index (Welch and Cooke, 1999). In the UORB, post-treatment sediment samples were not collected, so TP-T and other water quality parameters were a primary focus of before and after treatment comparisons. To assess the short-term effectiveness of each treatment, the average of water quality parameters from two months before and two months after treatment were compared. The percent change was calculated to describe how the alum application affected P levels in the water column.

Lake Griffin Flow-Way (Area 3)

Site Description

The Lake Griffin Flow-Way (LGFW) was a wetland on the former S.N. Knight farm designed to treat circulated surface water from Lake Griffin. The site was divided into three cells that covered 456 ha when water levels are at 18.3 m (60 ft) National Geodetic Vertical Datum 1929 (NGVD2929). Water entered Q cell from Lake Griffin and then was routed through T cell, Z cell, or both (Figure 2). Dense cattail (*Typha latifolia*) dominated the site, which was generally 0.6 to 0.9 m in depth at normal operating stage. Most of the LGFW is underlain by Everglades and Oklawaha muck soils (Soil Survey Staff 2009). Everglades muck is a very deep, very poorly drained organic soil with 0 to 20 cm muck over mucky peat. Oklawaha muck is a deep, very poorly drained organic soil with 0 to 23 cm muck over mucky peat, sandy loam, sandy clay, and clay.

Initial LGFW operations were started after the property was reflooded in 1994, but existing farm intake and discharge pumps were inadequate for proper flow-through the area. In 1995, new culverts and pumps were installed, increasing flows from 0.9 - 1.1 m^3s^{-1} to 2.3 - 2.6 m^3s^{-1}. Between November 1995 and 1997, LGFW was maintained as a deep marsh system (up to a mean depth of 5.3 feet deep) at 17.8 m (58.5 ft NGVD29, Appendix A). Intake water from Lake Griffin was used (Figure 2). Although P discharges from LGFW (21.5 metric tons over 3.29 years) were below FDEP thresholds, bottom sediments were continually resuspended and aquatic vegetation failed to develop in the deep water (>1 m).

A significant drawdown was initiated in November 1997 to allow for further infrastructure improvements and vegetation planting. Water elevation was lowered to a mean depth of 0.09 meters (53 ft NGVD29) and wetland macrophytes were planted such as spikerush (*Eleocharis interstincta*), spatterdock (*Nuphar advena*), maidencane (*Panicum hemitomon*), pickerelweed (*Pontederia cordata*) and duck potato (*Sagittaria lancifolia*). By November 1999, the drawdown was complete and LGFW was operated as a shallow marsh system with water levels at 16.8-17.1 m (55-56 ft) NGVD29. Starting in May 2000, stage was again lowered to 15.8-16.2 m (52-53 ft) NGVD29 to accommodate construction projects. Additional culverts were installed and a north-south levee was built up to create a separate east pond flow-way (K cell, Figure 2).

Figure 2. Lake Griffin Flow-Way and connection structures.

The long-term restoration plan for LGFW was to reconnect the wetlands hydrologically to Lake Griffin. However, water column TP levels in LGFW were consistently high (>3 mg TP/L) ever since the property was initially reflooded. A target level of approximately 0.2 mg/L was necessary for reconnection to the lake. It was suspected that residual labile phosphorus within the sediments was fluxing into the overlying water column. In 2001, a chemical treatment design was completed that called for a liquid alum application to inactivate sediment P (ERD 2001). Flow-through operations were suspended in April 2001 in anticipation of the alum treatment.

Treatment Design and Application

Although iron and calcium-based amendments were discussed in the design study, an aluminum-based amendment was recommended because of the anoxic and slightly acidic nature of LGFW sediments (Reddy et al. 1997; ERD 2001). The design included the use of both alum and lime (in slurry form) to maximize floc formation (ERD 2001).

To determine the alum dosage needed for sediment P inactivation, 18 sediment samples were analyzed for bulk density, TP-T, Al, Ca, Fe, moisture, and organic content (ERD 2001). A fractionation procedure (Chang and Jackson 1957) was performed to determine the Fe-bound P, Al-bound P, and saloid-bound P (the sum of soluble P and readily exchangeable sediment P). Saloid-bound P is considered to be available at all times. Fe-bound P is relatively stable under aerobic conditions, while unstable under anaerobic conditions. Al-bound P is considered to be stable under all conditions. Available P (saloid and Fe-bound P) in the top 10 cm of sediment was determined based on an Al:P molar ratio of 1:1 and an excess factor of 4.0 (Table 1). This means that to form $AlPO_4$ precipitate, one mole of Al^{3+} would be needed to remove one mole of PO_4^{-3}, but to counter competition from other cations, up to four moles of Al may be required (ERD 2001). Isopleth contours of alum application rates were drawn based on total sediment available P (Figure 3).

Table 1. Available P content in LGFW sediments (top 10 cm) and amount of alum required for inactivation (ERD 2001). *4:1 Al:P ratio.

	Available phosphorus		Alum required		
Cell	G	Moles	moles*	kg	L
Q	1,519,433	49,014	196,056	5,294	90,392
T	2,458,020	79,291	317,164	8,563	146,227
Z	1,896,155	61,166	244,665	6,606	112,802
All Cells	5,873,608	189,471	757,885	20,463	349,421

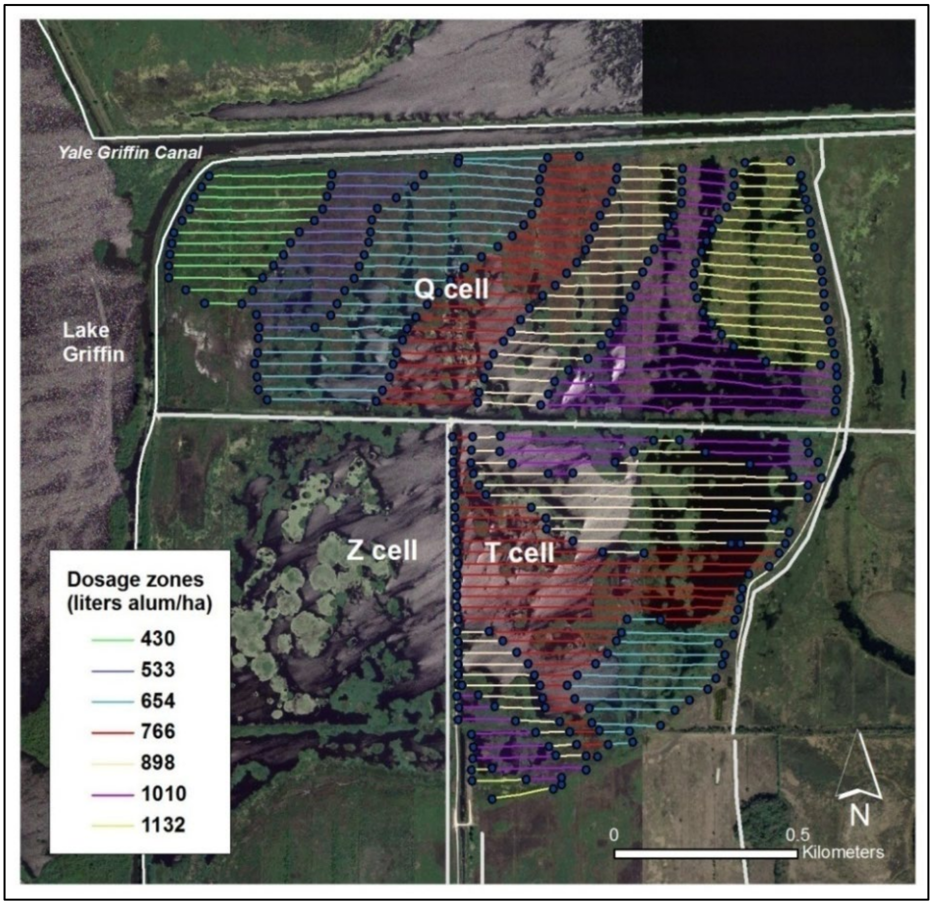


Figure 3. Isopleth map of alum dosage zones and barge pathways in Area 3.

To allow access for the application equipment, pathways were cleared through the vegetation with a "cookie cutter" (Figure 4a) perpendicular to the direction of flow at 100' intervals in Q cell and T cell (Figure 4b) at a cost of $60,000. Paths were not cut in Z cell because it was mostly open water with submerged vegetation.

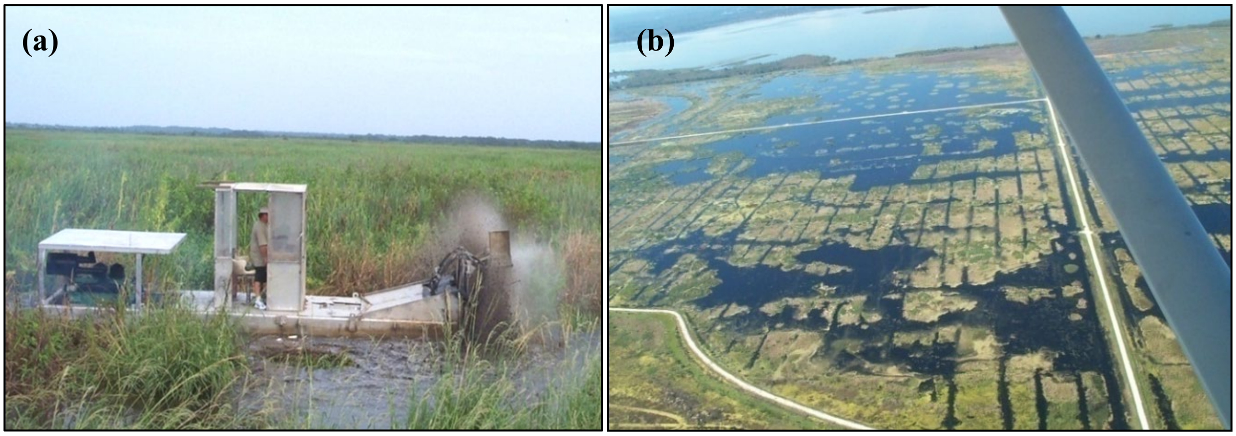


Figure 4. (a) "Cookie cutter" clearing paths through vegetation for barge access. (b) Aerial image showing paths cut every 30 m in cells Q and T.

Between November 26, 2001, and March 28, 2002, a total of 419,045 L of liquid alum and 23,848 L of lime slurry ($Ca(OH)_2$) were applied in LGFW by Environmental Research and Design (ERD). For applications in areas deeper than 0.75 m, a floating barge was pulled by a pontoon boat (Figure 5). The alum was dispersed over a distance of 15 m from the barge by an adapted spray nozzle. Different concentrations of alum were applied across the cells based on sediment P concentrations (Figure 3). Latitude/longitude points were mapped for each dosage zone and path locations were identified in the Q and Z cells.

Figure 5. Alum tank being pulled on a floating barge behind a pontoon boat.

Lime applications were restricted to open water areas. Since alkalinities remained steady during application, the total amount of lime was lowered from approximately 54 metric tons to 15 metric tons. For the shallow areas, a Marsh Master^{TM} (Coast Machinery, Baton Rouge, Louisiana) was rented by ERD for $1,700 per week (Figure 6). The alum was applied via a hose connected to a 945 L tank on the back of the Marsh Master^{TM}. In total, 338 ha were treated by barge, 14 ha by airboat and 40 ha by Marsh Master^{TM}. The total cost for treating the Q, T and Z cells was $87,210 (Table 2).

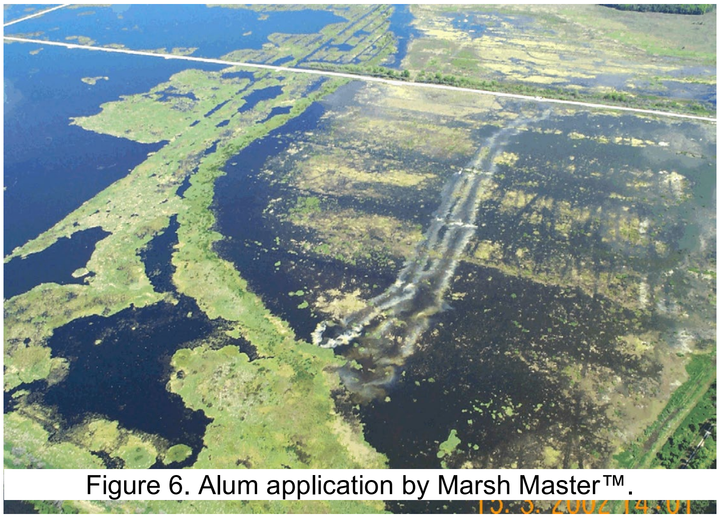


Figure 6. Alum application by Marsh Master™.

Table 2. Summary of surface alum applications in the UORB and their short-term effectiveness (±2 mo.). Does not include site preparation or treatment design.

Area	Dose Applied (mg Al/L)	Treatment Target	Application Dates	Alum (L)	Buffer (L)	Area Treated (ha)	Total Application Cost ($)	% change TP-T	Cost/kg TP removed ($)
LGFW-Q cell	3.2	Sediment	11/26/2001 - 12/10/2001	419,045	23,848 (ls)	393	87,210	-58	275
LGFW-Z cell	10.3	Sediment	12/28/2002 - 3/26/2002					-59	
LGFW-T cell	6.6	Sediment	12/13/2001 - 3/28/2002					-57	
Lowrie Brown	9.3	Water Column	09/16/2002 - 11/14/2002	374,755	---	220	90,755	-72	550
Long Farm -1	9.5	WC and Sediment	01/28/2003 - 05/05/2003	868,752	255,515 (ls)	333	224,500	-92	13
Long Farm - 2	9.7	WC and Sediment	12/30/2004 - 01/27/2005	592,190	112,317 (sa)	372	197,774	-60	53
Eustis Muck Farm	20.7	Water Column	11/13/2003 - 11/20/2003	1,396,374	22,849 (sa)	223	278,060	-97	38
SN Knight North	12.6	Water Column	12/15/2004 - 12/17/2004	331,496	---	97	90,000	-53	1857
LHCA-1	26.9	Water Column	05/21/2008 - 06/13/2008	624,192	---	166	189,682	-44	137
LHCA-2	28.6	WC and Sediment	8/25/2010 – 9/2/2010	821,624	28,815 (sa)	166	210,863	-62	83
Total	---		---	**5,462,497**	**443,344**	**1,984**	**1,368,844**		

ls = lime slurry; sa = sodium aluminate; wc = water column

Following the completion of treatment within the LGFW, high P measurements indicated that the 14-ha retention pond (U pond) southeast of the T cell (Figure 2) also needed treatment. Approximately 34,069 L of alum was sprayed by airboat and Marsh Master^{TM} over U pond between April 2 and 4, at a cost of $9,340. Due to a breakdown of the Marsh Master^{TM}, most of the application was completed by airboat with a 945 L alum tank. The alum tankers could not reach the U pond, so a truck with a 1900 L tank was used to move alum to the airboat. SJRWMD supplied an airboat and two staff members. ERD supplied two personnel, a Marsh Master^{TM}, tanks, hoses, spray nozzles, and fuel.

Results

In Q cell, TP-T decreased by 58% in the two months following treatment (Table 3). Chlorophyll *a* (Chl-a), color, DOC, TOC, TSS and other P species also showed decreases in the first two months after treatment.

Table 3. Mean water column parameters in LGFW, Q cell two months before and two months after alum was applied. All units are mg/L, except for color (cpu), electrical conductivity (EC; μmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	111.5	118.0	6
Al-T	n/a	0.036	n/a
Chl-a	28.1	11.9	-58
Color	75	63	-17
DOC	23.7	19.7	-17
DOP	0.034	0.033	-3
EC	321.7	367.5	14
pH	7.14	7.19	1
Secchi	1.10	1.78	61
SRP	0.103	0.027	-73
TKN-D	1.756	1.615	-8
TOC	26.6	20.0	-25
TP-D	0.137	0.060	-56
TP-T	0.205	0.087	-58
TSS	7.8	5.5	-29

In Z cell, SRP, TP-T and TP-D decreased 59% and 80%, respectively two months after treatment (Table 4). Secchi depth and TSS did not dramatically change in the short-term after treatment.

Table 4. Mean water column parameters in LGFW, Z cell two months before and two months after alum was applied. All units are mg/L, except for color (cpu), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	n/a	152.1	n/a
Al-T	n/a	0.140	n/a
Chl-a	52.1	34.2	-34
Color	80	65	-19
DOC	n/a	32.8	n/a
DOP	0.049	0.024	-51
EC	441.3	481.2	9
pH	7.07	7.09	0
Secchi	0.60	0.63	4
SRP	0.110	0.009	-92
TKN-D	2.331	2.251	-3
TOC	n/a	34.0	n/a
TP-D	0.159	0.033	-80
TP-T	0.290	0.118	-59
TSS	12.0	11.5	-4

In the two months after treatment in T cell, TP-T, TP-D and SRP decreased by 57%, 63%, and 74%, respectively (Table 5). In all three cells, pH remained circumneutral.

Table 5. Mean water column parameters in LGFW, T cell two months before and two months after alum was applied. All units are mg/L, except for color (cpu), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	n/a	129.5	n/a
Al-T	n/a	0.046	n/a
Chl-a	13.5	13.6	1
Color	80	70	-13
DOC	n/a	23.0	n/a
DOP	0.048	0.039	-19
EC	373.2	397.4	6
pH	6.87	7.12	4
Secchi	1.40	1.50	7
SRP	0.196	0.052	-74
TKN-D	2.121	2.023	-5
TOC	n/a	26.2	n/a
TP-D	0.244	0.091	-63
TP-T	0.276	0.118	-57
TSS	5.0	3.5	-30

Water quality data from Q, Z and T cell (1994 to 2008) illustrates how nutrient levels fluctuated during different operating stages of the LGFW (Figures 7-9). Decreases in P beginning in 1995 were likely a result of the change of intake water from the Yale-Griffin Canal to Lake Griffin. The dramatic increase in water column P from 1997 to 1999 was possibly correlated to the LGFW drawdown in which low water levels, decreased inflows and turbulence from construction activities led to more highly concentrated nutrients. Samples were only collected three times during the drawdown because of difficult access to the sampling locations. The sharp P decrease in 1999 occurred during resumption of LGFW operations. Phosphorus levels in all three cells decreased toward the end of treatment in January 2002, but increased to over 0.70 mg/L by October 2003.

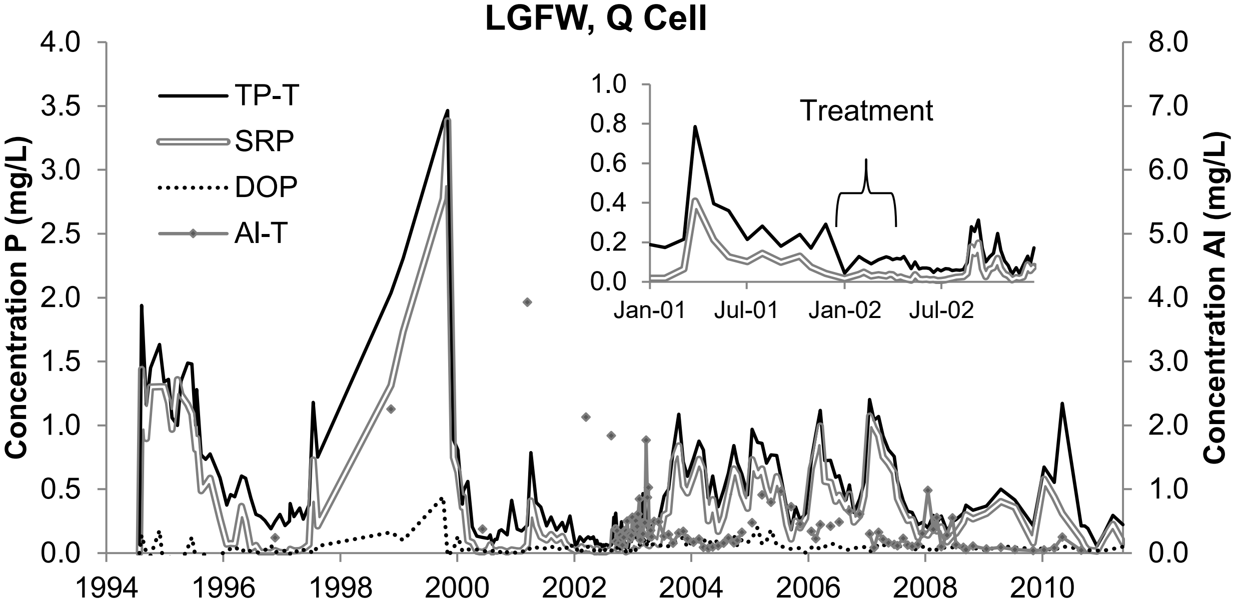


Figure 7. Water column P and total aluminum (Al-T) from 1994 to 2010 in LGFW, Q cell. Alum was applied from 11/26/2001 to 12/10/2001.

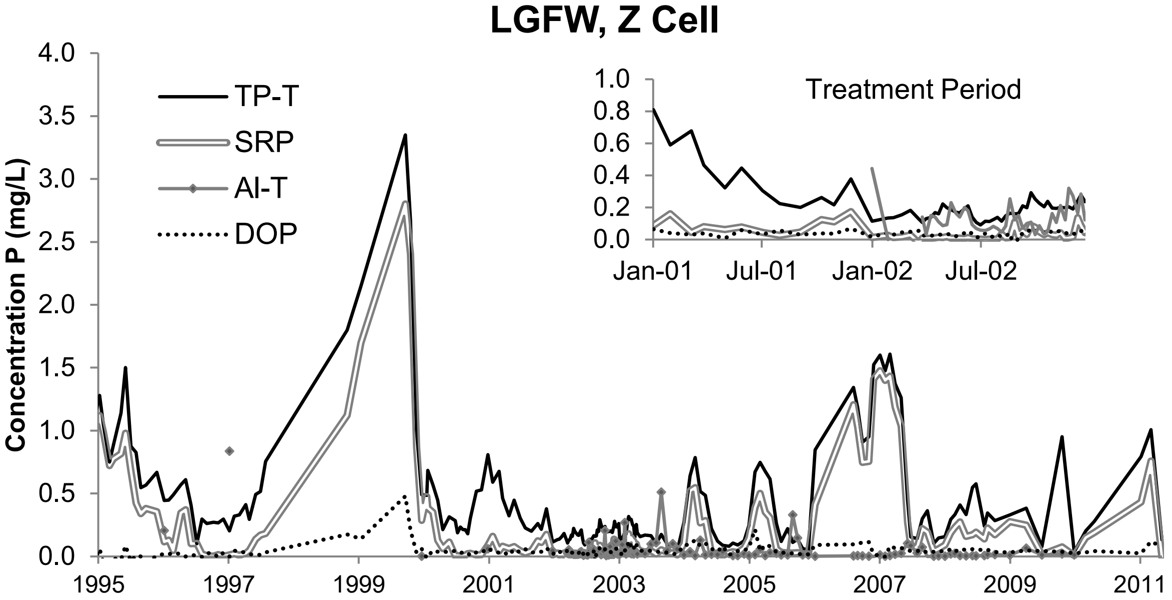


Figure 8. Water column P and Al-T from 1995 to 2011 in LGFW, Z cell. Alum was applied from 12/28/2001 to 3/26/2002.

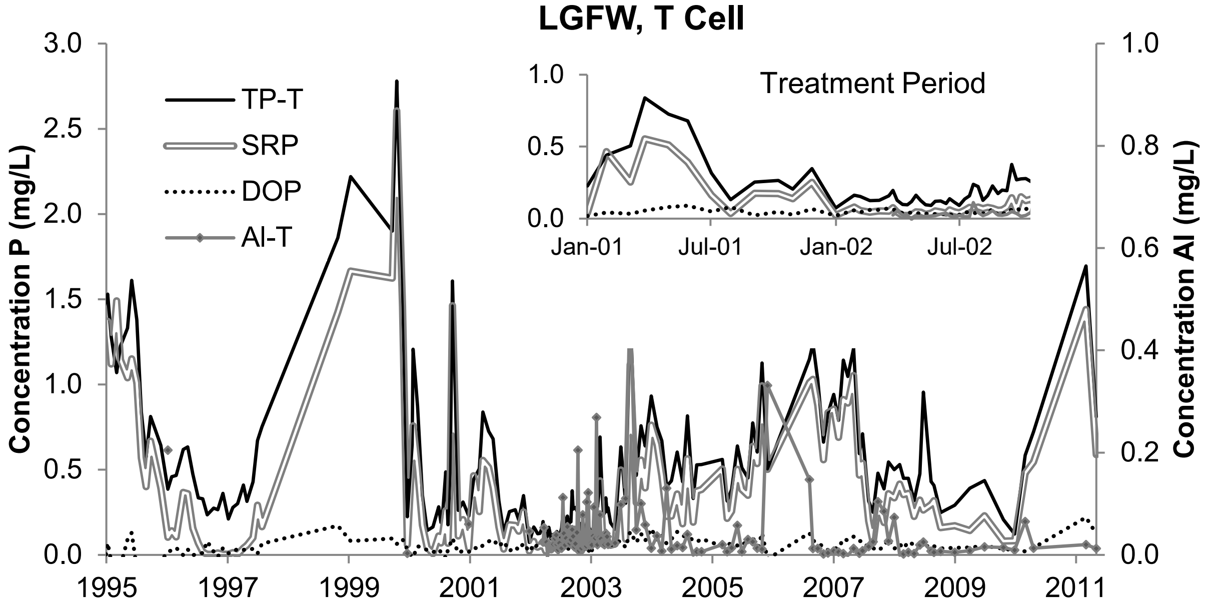


Figure 9. Water column P and total aluminum (Al-T) from 1995 to 2011 in LGFW, T cell. Alum was applied from 12/13/2001 to 3/28/2002.

The treatment in U pond resulted in short-term decreases in chlorophyll *a*, TSS, TP-T, TP-D, DOP and SRP, and an increase in Secchi depth (Table 6).

Table 6. Mean water column parameters in the U pond of the Lake Griffin Flow-Way two months before and two months after alum was applied. All units are mg/L, except for color (CPU), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	n/a	107.6	n/a
Chl-a	28.9	18.5	-36
Color	n/a	52.5	n/a
DOC	n/a	34.3	n/a
DOP	0.101	0.035	-65
EC	545.2	728.3	34
pH	6.73	6.57	-2
Secchi	0.53	0.71	36
SRP	0.568	0.008	-99
TKN-D	3.230	2.471	-23
TOC	n/a	35.6	n/a
TP-D	0.669	0.043	-94
TP-T	0.760	0.099	-87
TSS	10.6	4.2	-60

The initial improvement in water quality after treatment in LGFW suggested that alum was effective in “sweeping” the water column. After a few months, however, high (>0.200 mg/L) TP concentrations indicated that under-dosing had occurred and that P was continuing to flux from the sediments. Although the treatment was designed for sediment inactivation, the prescribed alum dose did not consider the amount of aluminum that would first bind with P in the water column. A large portion of the alum adhered to vegetation during the application, so the remaining amount that made it through the water column was likely insufficient to treat the sediments.

The problems created by emergent vegetation in LGFW were numerous. Alum that adhered to vegetation was difficult to remove, even when using water from a fire hose pumped from a water tank mounted on an airboat. Water levels were held high to facilitate barge movement, but with the increased stage, large stands of cattails became uprooted and formed floating islands, which depending on the wind direction, caused logistic and possible water quality issues. The vegetation might have physically disrupted the formation of a stable floc layer, as well as released P after their decomposition (Welch and Schrieve 1994, Welch and Cooke 1999, Malecki-Brown et al. 2007).

Additional sources of error in the treatment process include disturbed vegetation and sediments from the Marsh Master^{TM}. Although using an airboat required more time than the Marsh Master^{TM} because of its smaller tank, it created less physical disturbance in the treatment sites (see Figure 6). Spraying alum directly from the tanker trucks with a fire hose worked well in the canals and pump basins near the levees. Levee access, however, was problematic. Parking an alum tanker on the edge of a levee led to the partial collapse of the levee and navigating narrow turns proved difficult. Extensive roadwork was necessary to provide wide areas for safe turns. Nevertheless, by mid-2016, water column TP levels had decreased to levels acceptable where reconnection to Lake Griffin would not prove harmful (~0.2 mg/L). Consequently, reconnection was accomplished in 2017 and TP levels have remained below 0.2 mg/L since that time.

Lowrie Brown (Area 4)

Site Description

Lowrie Brown Cattle Ranch was purchased and reflooded by SJRWMD in 1991. After re-flooding, Lowrie Brown (308 ha) contained approximately 51 ha of shallow marsh vegetation and 166 ha of open water (0.9 m deep or greater). Oklawaha muck soils cover most of the area. The muck overlays peat, sandy loam, and sandy clay layers. Iberia sandy clay covers the southern and western portions of the property (Soil Survey Staff 2009). The Iberia series is poorly drained and very slowly permeable.

Treatment Design and Application

The purpose for treating Lowrie Brown was to reduce TP concentrations in the water column to 0.050 mg TP-T/L prior to dewatering for the construction of Phase II of the Lake Griffin Flow-Way (Figure 2). Following water quality and sediment monitoring, ERD (2002a) recommended an alum dosage of 10 mg Al/L in the northeast and northwest cells, and 15 mg Al/L in the south cell (Figure 2). Lime was not required as a buffering agent due to acceptable alkalinity results during the laboratory jar tests.

Between September 16 and October 14, 2002, a total of 374,755 L of alum was applied by ERD at a total cost of $90,755 (Table 2). A SJRWMD-operated airboat treated 40 ha of shallow vegetated area. The deeper area (167 ha) was treated using a boat/barge system, which injected alum at a controlled rate into a continuously pumping stream of surface water (Figure 10). The alum was mixed in a ratio of 1 part alum to 10 parts surface water prior to spraying it on the water surface (ERD 2002a). Due to low water levels in the southern portion of the project area, the SJRWMD Department of Operations and Land Resources treated nine ha with 14.6 wet metric tons/ha of alum residual utilizing SJRWMD-owned manure spreaders.

Figure 10. Aerial view of Lowrie Brown alum application. Lake Griffin visible in upper left corner.

To allow access by tanker trucks, the east levee was built up with lime rock out to the open water, a distance of 610 m. The tankers then had to back down the entire length of the road. Frequent rains affected the access levee and caused several work stoppages. Old fence posts and tree stumps at or just below the surface of the water also hindered barge movement in the area. The majority of the posts and stumps were flagged, but one submerged log caused the barge to capsize while full, spilling approximately 2,839 L of alum. A small (approximately 20 m^2) localized mortality of snails and other mollusks was noted the following day. After heavy rains, water levels increased from 17.7 m (58 ft) NGVD29 (mean depth of 2.58 feet) to 17.9 m (58.6 ft) NGVD29, thus diluting the actual average dosage to 9.3 mg Al/L.

Results

After the alum treatment in LB, water transparency dramatically increased and P concentrations decreased (Table 7, Figure 11). TP-D, TP-T and SRP decreased by 72%, 61%, and 63%, respectively two months after treatment.

Table 7. Mean water column parameters in Lowrie Brown, two months before and two months after alum was applied. All units are mg/L, except for color (CPU), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	115.4	93.2	-19
Al-T	n/a	0.182	n/a
Chl-a	32.5	17.0	-48
Color	73	45	-39
DOC	30.8	23.8	-23
DOP	0.040	0.016	-60
EC	446.8	442.0	-1
pH	7.74	6.74	-13
Secchi	0.25	0.74	190

SRP	0.025	0.009	-63
TKN-D	3.096	2.176	-30
TOC	31.1	25.0	-20
TP-D	0.065	0.025	-61
TP-T	0.228	0.063	-72
TSS	52.8	7.6	-86

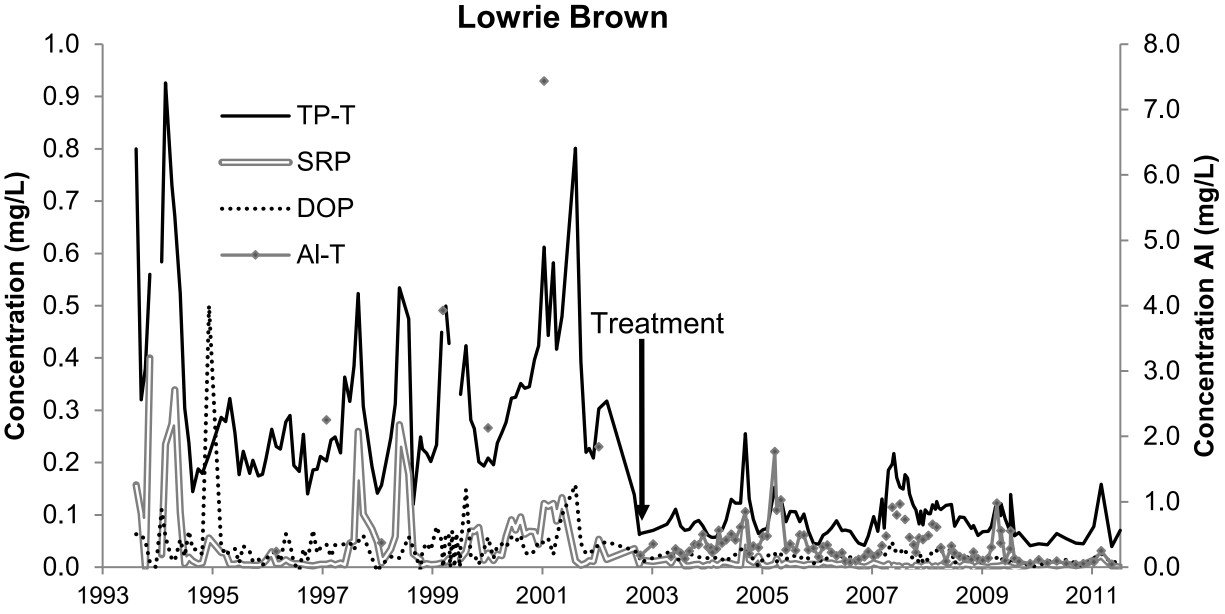


Figure 11. Water column P and Al-T concentrations in Lowrie Brown from 1993 to 2011. Alum was applied between September 16 and October 14, 2002.

At low stage, sample locations in Lowrie Brown are difficult to reach without disturbing the sediments, even with an airboat. The Al-T spikes in Lowrie Brown (>2 mg/L) possibly resulted from resuspended sediments during sample collections or during wind events. If resuspension was occurring during sampling events, then TP values during low stage may have been overestimated. Although Al-T values reached up to 7.4 mg/L before treatment and 1.8 mg/L after treatment, Class III water quality standards use dissolved aluminum (Al-D) as a measure for toxicity concern. Al-D after treatment comprised 3% of Al-T and only exceeded the criteria (0.085 mg/L) once by 0.001 mg/L.

Lowrie Brown was not dosed for sediment inactivation, but the alum treatment significantly decreased median water column TP concentrations in the long term. External loading from the basin, however, was not reduced after treatment. TP-T concentrations frequently over 0.100 mg/L might be attributed to nearby cattle pastures. LB was dosed to treat the water column for dewatering prior to construction of Phase II of the Lake Griffin Flow-Way. However, improved lake water quality negated the need for the LGFW and the area was reconnected to Lake Griffin in August 2007.

Long Farm (Area 5)

Site Description

Long Farm (535 ha) was purchased by the SJRWMD in 1992. Unlike the other muck farms in EMCA, which were flooded after a fallow period, Long Farm was flooded as bare soil (Everglades and Oklawaha muck). The water elevation was within 0.3 m of Lake Griffin in 1993 and to lake level in 1995 (57.3 ft mean stage). This produced mean water elevations of approximately 2.8 ft. Due to the deep flooding, wetland vegetation became limited to the shoreline (Marburger 1999).

Before water levels in Long Farm could be lowered to allow vegetation plantings, TP levels had to be reduced. The goal of the alum application was to reduce water column TP to less than 0.075 mg/L and to inactivate sediment P. Preceding the first alum and lime treatment in 2003, water quality was poor with Secchi readings of less than 0.5 m. SRP comprised 94% of TP-T concentrations with a median concentration of 3.22 mg/L.

Treatment Design and Application

The initial design included 30 sediment samples, which were analyzed for moisture content, organic content, sediment density, total nitrogen, and TP (ERD 2002b). The modified Chang and Jackson procedure, as proposed by Peterson and Corey (1966), was used for P fractionation. Saloid and Fe-bound P were considered potentially available P, while aluminum-bound P was considered stable and unavailable. The suggested excess molar ratio was 5:1 to encourage the formation of Al:P bonds within the sediments. The available sediment P in the top 10 cm equated to 7,235 kg of P or 233,222 moles of available P to be inactivated.

The composite water sample for the jar test contained 5.05 mg TP/L, with SRP comprising 95% of the TP measured. In addition to treating the sediments, 570,227 moles of P would need to be treated within the water column. A total of 800,925 L of alum was therefore required to treat LF at a water elevation of 17.4 m (57.0 ft NGVD29) (mean water depth of 2.4 ft) at an average total dose of 12.7 mg Al/L.

The first alum treatment was applied between January 28 and May 5, 2003. Approximately 868,752 L of liquid alum (51 tankers) and 255,515 L of lime slurry (15 tankers) were applied by barge to 350 ha. In the time between the signing of the contract and the completion of the application, however, heavy rains and a leaky culvert increased the stage in Long Farm from 17.4 m to 17.9 m (57.0 ft to 58.7 ft), adding 2,804 ha/m of water. The actual dosage was therefore diluted to only 9.5 mg Al/L. However, rapid water quality improvements were documented during the application period (Figure 12). Application delays and schedule adjustments were made because of public access for duck hunting season, road repair, project extensions in Lowrie Brown, and equipment breakdowns. The total cost was $224,500 (Table 2).

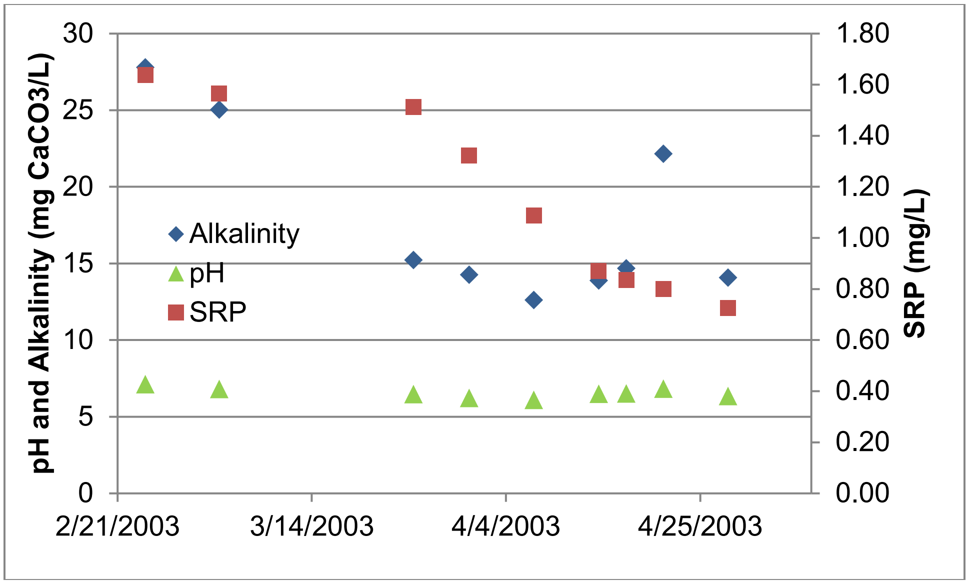


Figure 12. Average water quality results (from 5 sites) during alum application. Samples were collected and analyzed by Environmental Research and Design, Inc.

By the summer of 2004, water column concentrations up to 2.0 mg TP/L indicated that a second alum treatment was required. Sediment samples were taken from 10 of the original 30 sample sites. Sediment TP should have increased after the first alum treatment from Al:P solids that settled from the water column (Narf 1985, Reitzel et al. 2005). However, the TP sediment measurements for 2002 and 2004 were 3,707 ± 954 µg TP/cm^3 dry and 396 ± 107 µg TP/cm^3 dry, respectively (DBE 2004). Even though two different laboratories were used in 2002 and 2004, the same fractionation sequence of Peterson and Corey (1966) was used. The reasons for the unexpected decrease in sediment TP after treatment are unknown.

On a mass basis, it was calculated that Long Farm sediments contained 2,380 kg (76,800 moles) of readily labile P (DBE 2004). Because of an extremely low alkalinity value (24 mg $CaCO_3$/L) in the sample water, lime and sodium aluminate were examined as buffering agents for the second application. Liquid sodium aluminate (32-45% solutions) contains 9-12% Al, so it is very effective in removing TP while maintaining alkalinity.

Analyses of Long Farm raw water also revealed a relationship between TP and color (r^2=0.82, DBE 2005). Because high concentrations of DOC (a main source of color) can interfere with P removal by alum (Qualls et al. 2009), a dosage of 20 mg Al/L (10 mg Al/L alum and 10 mg Al/L sodium aluminate) was recommended following jar tests (DBE 2004: Figure 13). Combining the water column TP mass of 174,000 moles and the “available” sediment P mass of 76,800 moles, a total of 250,800 moles of P would need to be immobilized by 4,140,000 moles Al at a ratio of 16.5:1. The sediments contained a high percentage of volatile solids (mean = 59.8%), which are a rough estimate of the amount of organic matter present in the solid fraction of sediments (DBE 2004). A higher ratio was recommended because decomposable organic P was not included in the extractions, possibly underestimating the labile sediment P fraction.

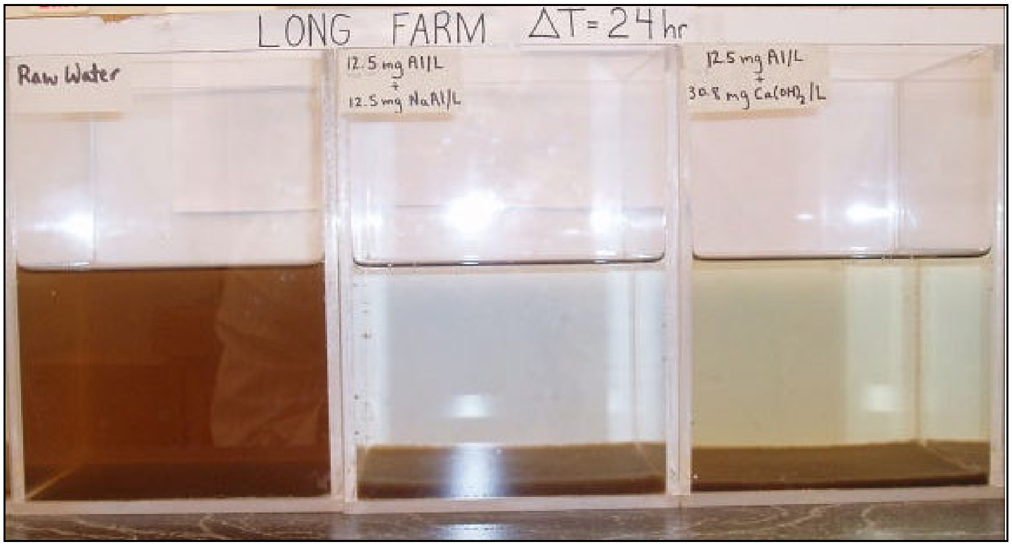


Figure 13. Long Farm raw water (un-amended), 12.5 mg Al/L as alum + 12.5 mg Al/L as (NaAl) treatment, and 12.5 mg Al/L as alum + 30.8 mg lime Ca(OH)2/L treatment after 24 hours of settling in the jar tests. Photo courtesy of DB Environmental.

Between December 30, 2004, and January 27, 2005, approximately 592,190 L of alum and 112,317 L of sodium aluminate were applied at a total cost of $197,773.74 (Table 2). To ensure an even coverage of chemical, the area was divided into 11 sections, each of which was treated three times. Because of unexpected high-water levels, the actual alum dosage was diluted to 9.7 mg Al/L (6.55 mg Al/L from alum, 3.22 mg Al/L from sodium aluminate), instead of the recommended 20 mg Al/L (DBE 2005). During the second application, daily SRP, pH, and alkalinity measurements were taken since SRP was approximately 95% of the TP-T and the low alkalinity levels were potentially dangerous (Figure 14). The results from these measurements could be attained within 24 hours and guide application decisions on a daily basis. The results showed a steady decline of SRP and alkalinity.

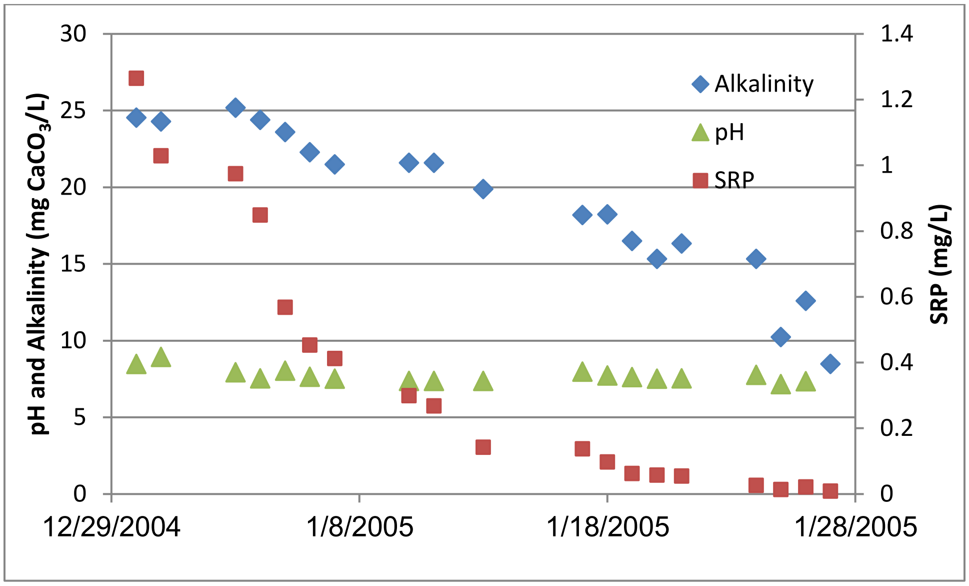


Figure 14. Average water quality results (from 2 sites) during alum application. Samples were collected and analyzed by Environmental Research and Design, Inc.

Results

Two months after the first alum treatment, TP-T, TP-D, and SRP were reduced by approximately 94% on average (Table 8). Secchi depth greatly improved and chlorophyll *a* and TSS decreased. Five months after the first treatment, however, TP-T increased from a low of 0.31 mg/L to over 1.0 mg/L (Figure 15).

Table 8. Mean water column parameters in Long Farm, two months before and two months after the first alum treatment. All units are mg/L, except for color (CPU), electrical conductivity (EC; μmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	16.2	13.9	-14
Al-T	0.063	0.592	840
Chl-a	7.0	14.0	99
Color	325	n/a	n/a
DOC	49.4	36.1	-27
DOP	-0.100	0.128	-229
EC	307.7	385.9	25
pH	6.35	6.73	6
Secchi	0.60	1.02	69
SRP	4.566	0.160	-96
TKN-D	3.547	2.268	-36
TOC	49.5	37.1	-25
TP-D	4.466	0.288	-94
TP-T	4.580	0.365	-92
TSS	6.8	5.8	-15

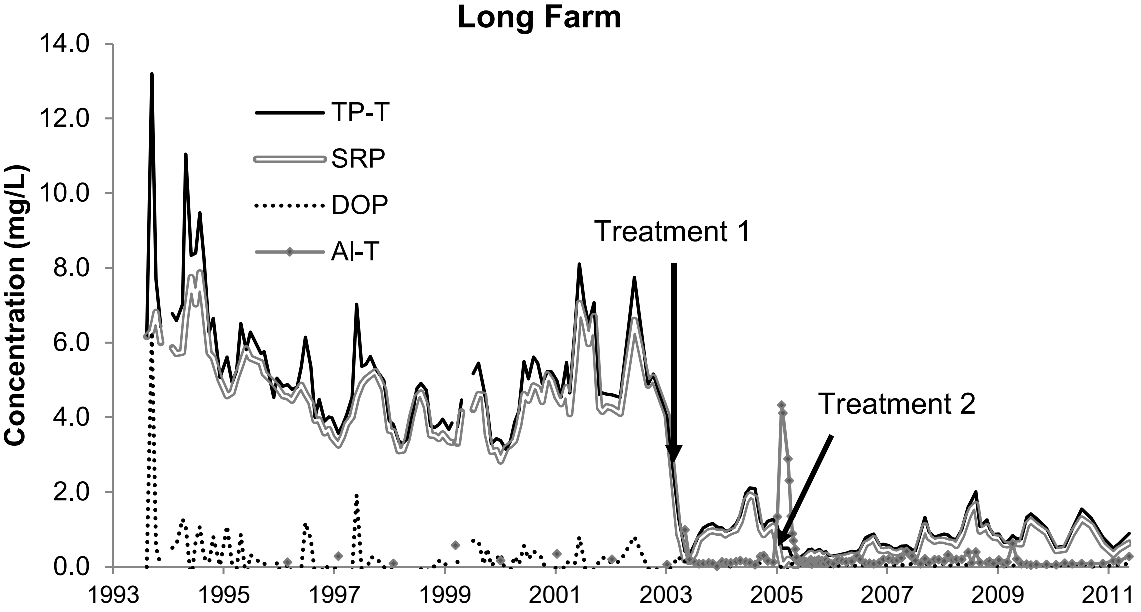


Figure 15. Water column P and Al-T in Long Farm from 1993 to 2011. Alum was applied from 1/28/2003 to 5/5/2003 and 12/31/2004 to 1/27/2005.

Following the second application, TP-T, TP-D, and SRP were reduced by 85%, on average (Table 9). Daily SRP measurements during the application showed that 89% of bioavailable P was removed within the first two weeks of treatment (Figure 16). Alkalinity was below the Class III standard of 20 mg/L in weeks three and four of the treatment, but has rebounded over time.

Table 9. Mean water column parameters in Long Farm, two months before and two months after the second alum treatment. All units are mg/L, except for color (CPU), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Al-D	0.098	0.142	45
Alkalinity	22.7	8.2	-64
Al-T	0.141	4.222	2897
Chl-a	11.3	9.7	-14
Color	n/a	n/a	n/a
DOC	35.7	21.9	-39
EC	186.9	280.7	50
pH	6.63	6.89	4
Secchi	0.59	0.58	-2
SRP	1.035	0.035	-97
TKN-D	2.075	1.313	-37
TOC	35.7	26.4	-26
TP-D	1.206	0.027	-98
TP-T	1.244	0.504	-60
TSS	2.0	4.3	113

In February 2005, one month after the second treatment, SRP target concentrations were met (0.031 mg/L), so discharge pumping began. Within a week, however, pumping was stopped because subsequent laboratory results revealed that particulate P (PP) and particulate Al (P-Al) concentrations had increased dramatically (Figure 16). This increase suggested that either alum floc had become resuspended or that a microfloc had formed because of insufficient dosage for sweep flocculation. Since Long Farm is generally deeper than the other treatment sites, microfloc formation was suspected. The suspended floc gradually settled out of the water column over three months.

Within two months after the increase in Al-T, Al-D increased over 300% (Figure 17). Studies have shown that floc resuspension and higher pH (9-11) can lead to a release of Al-D in the water column prior to floc stabilization (Egemose et al. 2009). Since high levels of Al-P were in the water column already, an apparent release from Al-P to Al-D occurred. Inexplicably, pH did not increase over 8.5 until 3 weeks (weekly sampling) after the Al-D increase (Figure 17). Chlorophyll *a* increased in conjunction with pH beginning in late March suggesting that an algal bloom instigated the increased pH due to carbon dioxide removal by growing algae (Figure 18). Between April and mid-May, pH remained over 8.85. During this event, TP-T decreased from a median concentration of 0.48 mg/L in March to 0.26 mg/L in May, suggesting a “re-treatment” of the water column from the suspended floc or a settling of the microfloc. By late May, pH levels had dropped to <8.0, Al-D levels were < 0.100 mg/L, and chlorophyll-a levels were down to 50 mg/m^3 from a high of 325 mg/m^3. Al-D levels over 0.100 mg/L were measured only one time in July 2006 (0.164 mg/L) within Long Farm since this solitary event.

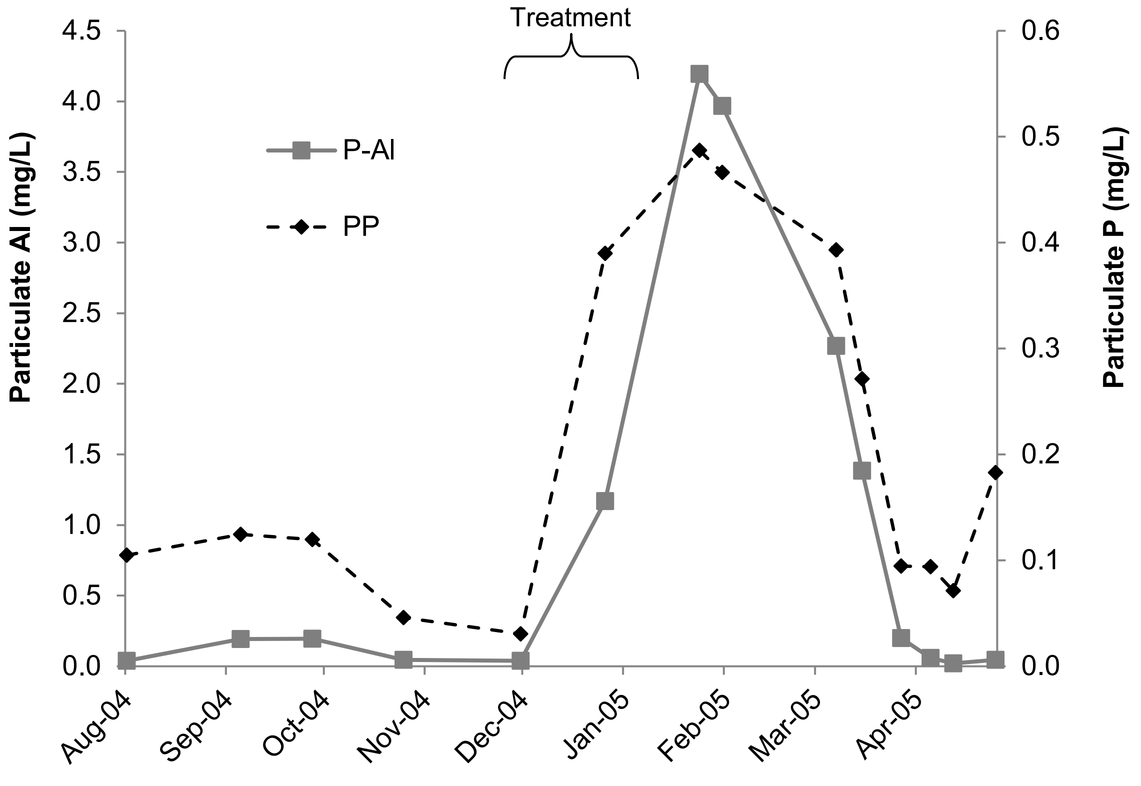


Figure 16. Particulate P (PP) and particulate Al (P-Al) in Long Farm before and after the second alum treatment. The sharp increase in particulates suggest the presence of a microfloc.

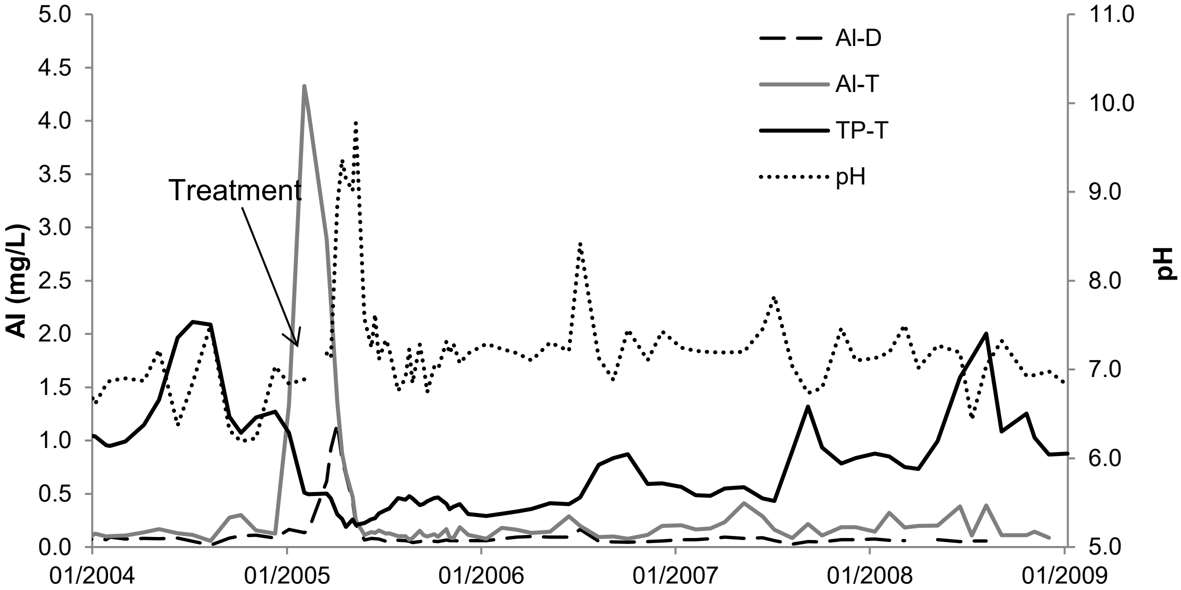


Figure 17. Al-D, TP-T and pH in Long Farm after the second alum treatment.

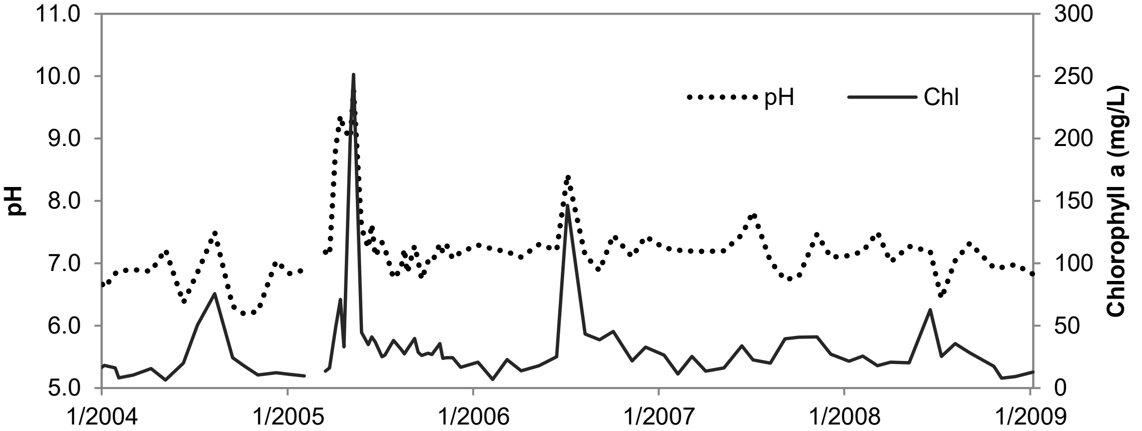


Figure 18. Chlorophyll *a* vs. pH in Long Farm from January 2004 to January 2009.

Although heavy rains and leaking structures increased the volume of water to be treated and diluted the alum dosage, TP-T concentrations were reduced by 86% in total after the two treatments. Possibly contributing to the effectiveness of the treatments was that approximately 90% of the phosphorus was SRP with small fractions of DOP and PP. However, high levels of DOC and color might have interfered with alum effectiveness, as suggested by the jar tests. Spreading the second application over three separate events for each of the 11 treatment areas, compounded with the already low dose, possibly caused microfloc formation. This may have been avoided with a single application. In addition, both applications were delayed by various issues including access problems, scheduling conflicts, and hunting access.

Four sediment cores were collected in Long Farm on September 9, 2010, to measure total aluminum (Al-T) concentrations at 5 cm increments. Alum floc layers were not visible. The surface layer (0-5 cm) had an average Al-T of 3,275 mg/kg dry weight (dw), which is slightly higher than the average Al-T from (0-15 cm) samples taken from nearby untreated SJRWMD properties in 1998. Average Al-T concentration was 2,192 mg/kg (dw, n=12) in Cell E of the Lake Apopka Marsh Flow-Way and 2,952 mg Al/kg (dw, n=88) in the recently flooded North Shore Restoration Area of Lake Apopka. The concentration of Al-T decreased in the profile, suggesting that alum floc was still present in the 0-5 cm depth range (Figure 19). Additional sampling of Long Farm sediments should include sectioning the core into 1 cm slices for more accurate assessments of accretion and burial.

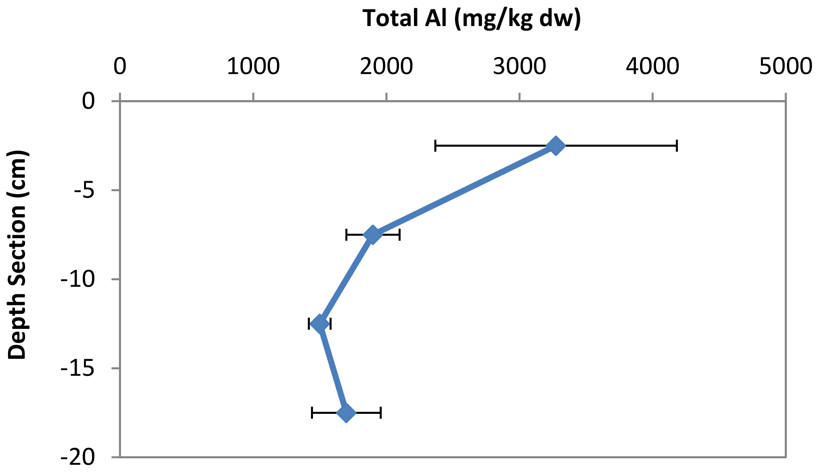


Figure 19. Average sediment total aluminum concentration from four Long Farm cores (sectioned every 5 cm).

Eustis Muck Farm (Area 7)

Site Description

Eustis Muck Farm comprises approximately 239 ha of former row-crop agriculture. It was purchased in 1993 and flooded to lake level in 1994. The Florida Fish and Wildlife Commission (FWC) and SJRWMD planted native vegetation such as eelgrass (*Vallisneria americana*) and giant bulrush (*Scirpus californicus*), but hydrilla and water hyacinth now occupy much of the shoreline. Most of Eustis Muck Farm soils are Everglades muck (Soil Survey Staff 2009). The northwest and southeast shores consist of Emeralda fine sand, Pomello sand, Myakka sand, and Placid sand (Soil Survey Staff 2009).

Treatment Design and Application

In January 2004, water depths had to be lowered from 2.1 m to 1.5 m to create storage for sediment disposal from a canal dredging project. Elevated P concentrations in Area 7 (2 to 3 mg/L TP) precluded any pumping event. The treatment goal in Eustis Muck Farm was to reduce TP concentrations to 0.50 mg/L or lower. Sediment P inactivation was not considered since the objective of this project was to reduce TP in the water column only. The initial design recommended an alum dose of 18 mg Al/L and a buffering agent (lime at 16 mg/L; ERD 2003a). An additional design to investigate the use of sodium aluminate recommended a ratio of 20:1 (by volume) alum to sodium aluminate (MACTEC 2003). Using sodium aluminate was considered more efficient than lime because of its ability to provide additional aluminum for P sorption (MACTEC 2003).

Because of a dispute concerning a SJRWMD easement to the site, the SJRWMD constructed a new access road to the property along the Yale-Griffin Canal. Approximately 1,396,374 L (82 tankers) of alum and 22,849 L of sodium aluminate (2 tankers) were applied between November 13 and November 20, 2003. Cold overnight temperatures caused the sodium aluminate to become highly viscous, which made handling difficult until temperatures warmed during the day.

Sweetwater Technology Division (Aitkin, MN) provided the barge system. Two boom arms extended from each side of the barge and had numerous hoses that reached the water surface (Figure 20a). The alum and sodium aluminate were delivered through alternative hoses, therefore ensuring an even distribution in an 18.2 m wide swath (Figure 20b). A global positioning system (GPS) controlled the boat movement, while a computer-integrated sonar continually adjusted the dosing. The total cost was $278,061.10 (Table 2). Post-alum data did not include samples collected after dredging activities began in June 2005.

Figure 20. (a) Alum delivery system from Sweetwater Technology. Liquid alum was injected in a swath from hoses attached to each boom arm. (b) Routes of the alum barge system (recorded by GPS). Each color represents a different day of application.

Results

Although Eustis Muck Farm was the most expensive barged alum treatment in the UORB because of the volume of water treated, the resulting short-term increase in water clarity (Figures 21a and b) and decrease in TP-T was significant. Mean SRP, TP-D and TP-T were reduced by 100%, 99% and 97%, respectively (Table 10, Figure 22). Decreases in TSS and DOC were evident in the increase in Secchi transparency (Table 10).

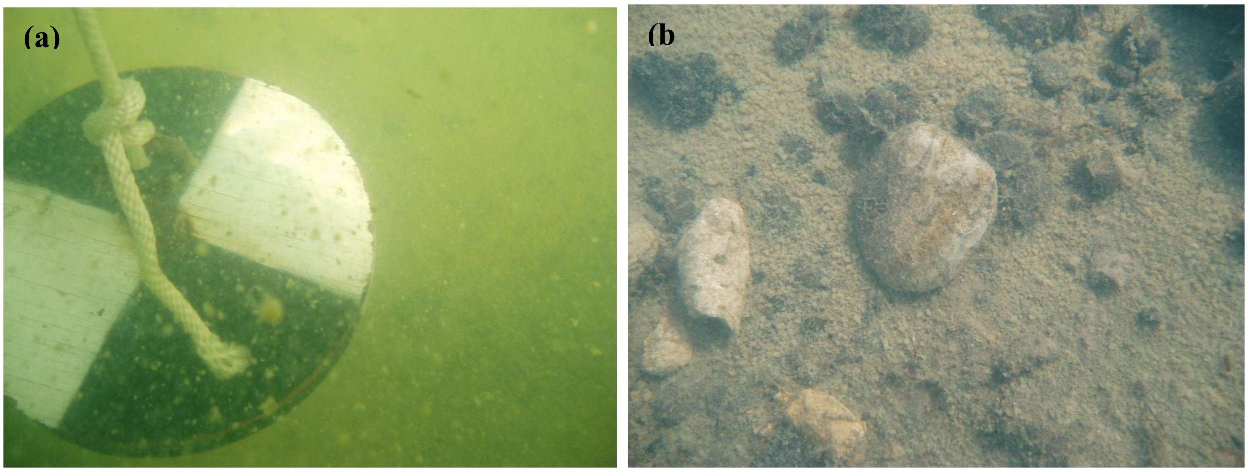


Figure 21. Underwater photograph of (a) floc formation and (b) water clarity following alum application.

Table 10. Mean water column parameters in Eustis Muck Farm, two months before and two months after the second alum treatment. All units are mg/L, except for color (CPU), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	73.1	9.2	-87
Al-T	0.198	0.486	146
Chl-a	69.3	16.2	-77
Color	80	n/a	n/a
DOC	41.8	24.7	-41
EC	305.6	409.4	34
pH	7.75	7.31	-6
Secchi	0.45	1.53	239
SRP	1.618	0.002	-100
TKN-D	2.332	1.475	-37
TOC	42.2	25.2	-40
TP-D	1.805	0.013	-99
TP-T	1.957	0.051	-97
TSS	12.5	5.3	-58

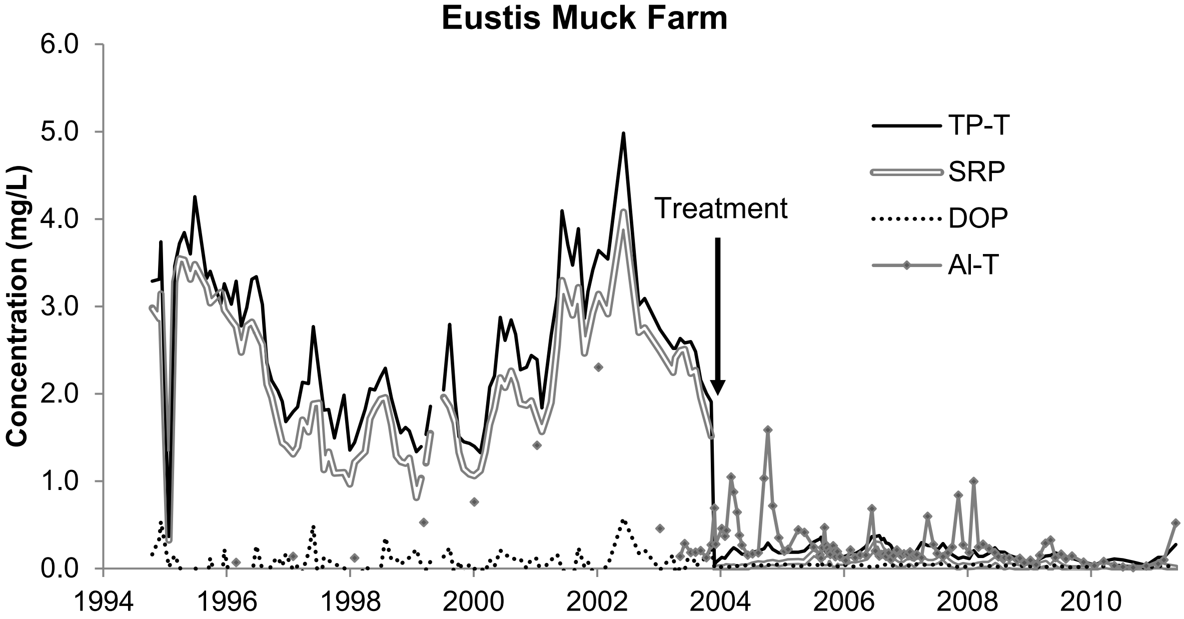


Figure 22. Water column P and Al concentrations for Eustis Muck Farm, 1994-2010. Alum was applied between November 13 and November 20, 2003.

Precision in dosing and application probably contributed to the effectiveness of the alum treatment in Eustis Muck Farm. Similar to Long Farm, the high percentage of P as SRP probably enabled significant reductions in water column TP-T. A short-term increase in Al-D, however, was observed after treatment during March 2004 (Figure 23). Between January and March 2004, chlorophyll *a* increased from 20 mg/L to 150 mg/m^3 and pH increased to 9.14. Simultaneously, Al-D rose from 50 µg Al/L to 460 µg Al/L before decreasing to 73 µg Al/L just two weeks later. This was a similar result to the Long Farm event with the exception of the pH increase coinciding with the increase in Al-D.

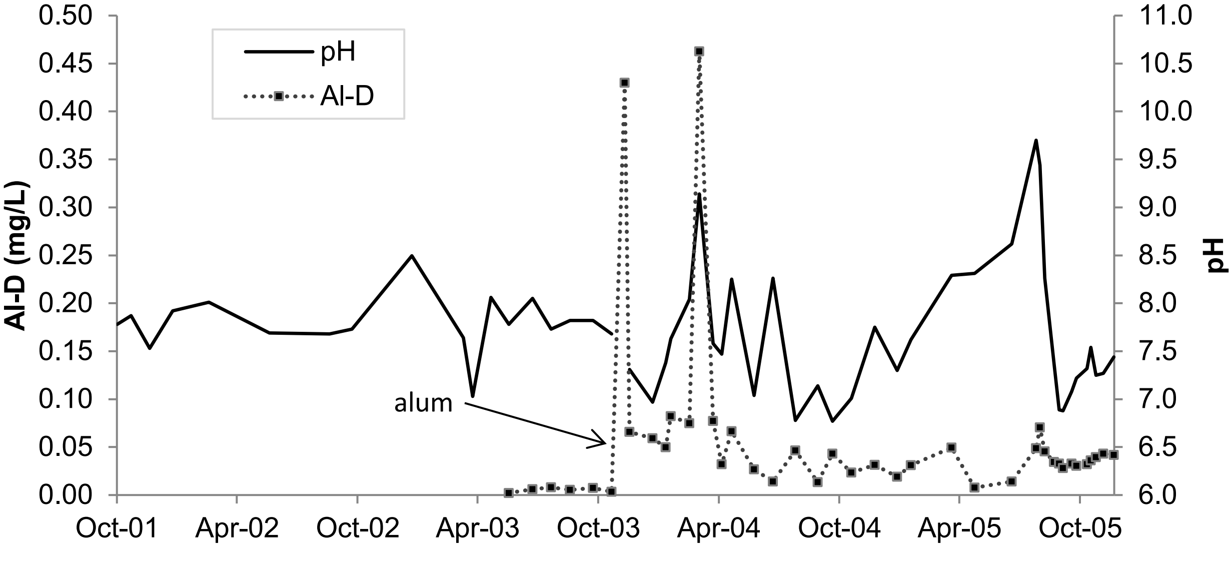


Figure 23. Dissolved aluminum (Al-D) and pH in Eustis Muck Farm during and after alum treatment

Eustis Muck Farm was the first alum application project that included an intensive (throughout the day) water sampling program at the time of application. During the first few hours of application, the pH values from the treated area were higher than expected at the planned dosage. The application was stopped and discussions with the contractor were intiated. It was discovered that the depth finder on the boat had not been calibrated to include the displacement of the boat in the water and was feeding insufficient chemical to the manifold system. This change in depth had not been important when the barge was working in 10 m of water in deeper lakes, but was vital in a 1-2 m system. The changes were made and the application was reinitiated.

Between December 31, 2003 and February 1, 2004, the water elevation was lowered from 17.97 m (58.96 ft) to 17.37 m (56.99 ft) NGVD29 (mean depth of 4.2 ft) to provide storage for the planned incoming dredge material. Based on pumping records, an estimated 133 kg TP was discharged to Lake Griffin during the drawdown, but approximately 3,267 kg TP was retained onsite because of the alum application, and not sent to Lake Griffin.

Dredging and disposal pumping was conducted by E.R. Jahna Industries (Lake Wales, FL). Approximately 206,400 m^3 of dredge material was deposited between August 2005 and June 2008. The influent water and sediment slurry was treated with 401,170 kg of alum (48%) and 10,540 kg acrylic polymer to promote settling (R. Mincey, pers. comm.). This was likely responsible for the aluminum concentration spikes that occurred during and after 2005.

S.N. Knight North (Area 2)

Site Description

S.N. Knight North (SNKN) was purchased by SJRWMD in 1991 and reflooded to lake level in 1992. SNKN contains approximately 174 ha of open water, submersed vegetation, shallow marsh, and wet prairie. *Hydrilla verticillata* colonized the open water areas (0.6 to 1.2 m depth) and displaced large areas of coontail (*Ceratophyllum demersum*) and southern naiad (*Najas guadalupensis*; Marburger and Godwin, 1996). Soil series include Everglades and Oklawaha mucks, Iberia sandy clay, and Emeralda fine sand (Soil Survey Staff 2009).

The restoration goal for SNKN was a permanent reconnection with Lake Griffin, which would require an alum treatment to reduce TP loading to the lake. Periodic connections existed, however, between SNKN and the Yale-Griffin Canal prior to treatment. A levee breech, likely caused by alligators, also enabled water to be exchanged from SNKN and the canal. Water quality results for SNKN therefore include possible contamination from the Yale-Griffin Canal, depending on the stage of Lake Griffin, seiche, rainfall differentials, and control structure release. SNKN was permanently reconnected to Lake Griffin and the Yale-Griffin Canal in August 2005.

Treatment Design and Application

The feasibility study conducted in June 2004 suggested a dosage of 18 mg Al/L to reduce water column TP concentration from peaks over 1.0 mg/L to 0.050 mg/L (MACTEC 2004). Since reconnection with Lake Griffin was imminent, the major concern was water column phosphorus, so sediment treatment was not included in this scope of work. Jar tests indicated sufficient alkalinity levels, so buffering agents were not recommended.

Application was delayed from the summer of 2004 until late in the year due to a series of hurricanes crossing the area. Between December 15 and 17, 2004, 331,496 L of alum was applied to 97 ha by Sweetwater Technologies using a barge (Figure 24). The total cost was $90,000 (Table 2). Before, during and after the application, a study was conducted to examine the movement of alum floc in Area 2. The goals of the study were to quantify initial floc distribution and movement, evaluate fish and benthic invertebrate communities before and after alum application, and quantify DO, pH, and SRP values at depths throughout the water profile and at the sediment-water interface (MACTEC 2005a and b).

Figure 24. Trail of liquid alum floc in S.N. Knight North.

During the application, one slight delay occurred during the treatment when a driver took a wrong turn through an open gate before dawn one morning. The driver attempted to turn around on a levee and nearly dropped the load into Cell Q of LGFW (Figure 25). A rescue by tow trucks averted the loss of any material.

Figure 25. Getting tow truck assistance after tanker slides off levee.

Results

Total phosphorus within the water column decreased 53% to 0.052, extremely close to the target of 0.050 mg TP/L, (Table 11).

Table 11. Mean water column parameters in SNKN, two months before and two months after alum was applied. All units are mg/L, except for color (CPU), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Al-D	0.009	0.027	218
Alkalinity	109.8	58.3	-47
Al-T	0.385	0.306	-20
Chl-a	49.7	27.0	-46
Color	n/a	30	n/a
DOC	21.2	15.9	-25
EC	293.9	382.5	30
pH	7.49	7.48	0
Secchi	0.43	0.58	35
SRP	0.007	0.005	-25
TKN-D	1.324	1.018	-23
TOC	22.2	16.4	-26
TP-D	0.024	0.010	-57
TP-T	0.110	0.052	-53
TSS	14.8	12.5	-15

Prior to the alum treatment, water quality measurements from 1994 to 2010 showed a dramatic reduction in P species in late 2002 (Figure 26). From the period when stage recorders were installed (August 2000) until treatment (2004), stage and TP-T were highly negatively correlated ($r^2=0.88$, $p=0.000$). The 2000-2002 drought therefore likely explains the peaks over 1.0 mg P/L and the subsequent decrease in concentrations when water levels rose again in 2003. In addition, several small breaches occurred in the south levee from alligator crawls and a leaky culvert from the Yale-Griffin Canal allowed Lake Griffin water to enter SNKN and dilute nutrient levels.

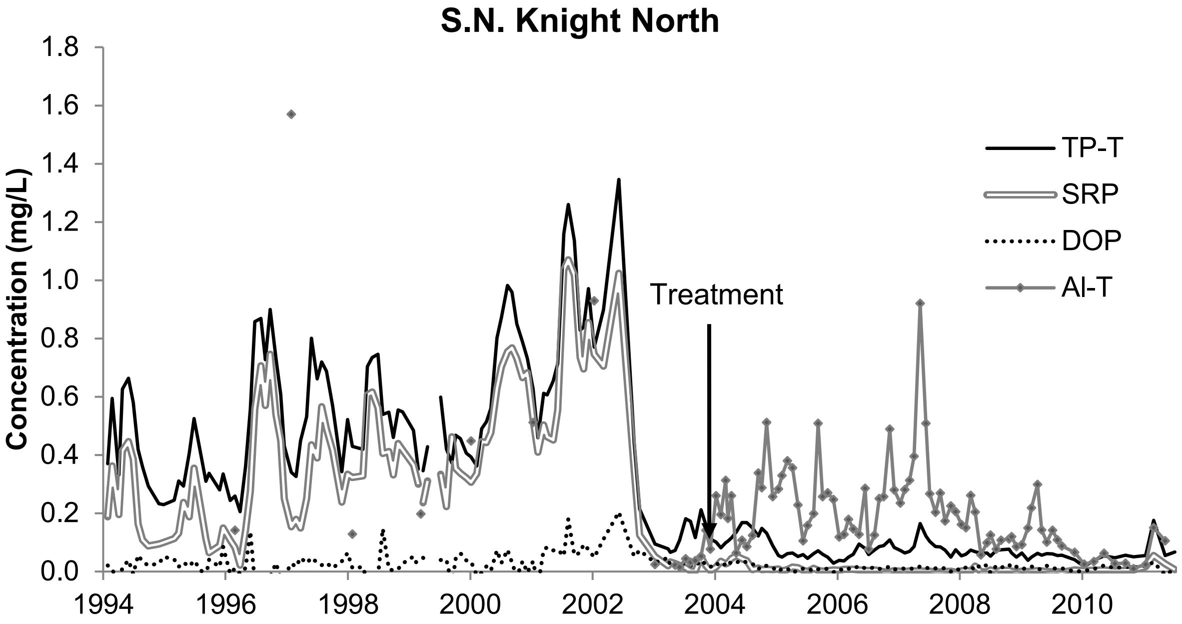


Figure 26. Water column P and Al in S.N. Knight North, 1994-2010. Alum was applied between December 15 and 17, 2004.

Results from the sediment monitoring study showed that floc movement decreased in the six months after treatment, possibly because of floc entombment. The resuspension of floc appeared to be a function primarily of water depth, rather than wind speed and fetch. Fish species were dominated by non-benthivorous centrarchids, decreasing the likelihood that bioturbation was a major factor in resuspension. Benthic invertebrate density and diversity appeared to be unchanged by alum application. Following application, water column chemistry (DO, pH, and conductivity) varied little with depth. Overall, the alum treatment resulted in no observed negative effects on the biota (MACTEC 2005a and b).

Accuracy in dosing and application contributed to the successful P reduction in SNKN. The manifold barge system enabled an even distribution of chemical across the water surface and the dose of 12.6 mg/L was sufficient for an effective sweep flocculation to occur. TP decreased to levels that allowed its reconnection to Lake Griffin in August 2005. Approximately 53 kg of TP was removed from the water column and trapped in the sediments.

Lake Harris Conservation Area

Site Description

Lake Harris Conservation Area (LHCA), formerly Harris Bayou, is immediately south of the Leesburg Municipal Airport and covers approximately 160 hectares of former row crop agriculture. LHCA is mostly open water with vegetation limited to shallow shoreline areas only. The dominant soil is Everglades muck (Soil Survey Staff 2009). At a stage of 59 ft (NGVD29 1929), the mean depth is less than one meter. In May 2008, a conveyance project was completed that enabled water flow between Lakes Griffin and Harris through LHCA. Prior to construction activities, TP-T in LHCA ranged from 0.214 to 3.10 mg/L, so surface water had to be treated to reduce nutrient loading to Lake Griffin.

Between 1994 and 2002, median TP-T in LHCA was 1.58 (±0.67) mg/L, but between 2003 and 2008, median TP-T was 0.46 (±0.17) mg/L. It is hypothesized that the significant decrease in median TP-T between these two time periods was the result of fluxes in stage. However, between 1993 and 2002, TP-T and stage were uncorrelated (Figure 27). The stage recorder in LHCA, however, was located in a ditch, which became exposed during the 2002 drought, possibly confounding stage measurements for 2001-2002. Stage and TP-T were significantly negatively correlated from June 2003 to November 2006, after the recorder was relocated.

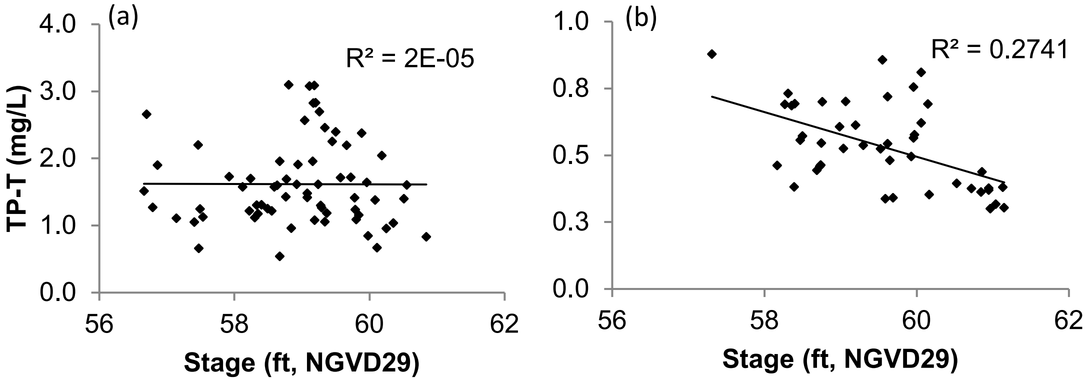


Figure 27. Stage vs. TP-T in LHCA between (a) 1994 and October, 2002 and (b) June 2003 and November 2006.

Treatment Design and Application

The treatment design completed in August 2003 recommended a dose of 25 mg Al/L alum for reducing water column TP to a range of 0.050-0.100 µg/L (ERD 2003b). However, the design did not include sediment inactivation because the original construction plan called for alum application followed by dewatering. Between May 21 and June 13, 2008, ERD applied 624,192 L (38 tankers) of liquid alum to LHCA using a spreader bar boom system on a small airboat hull towed behind a jon boat. Total cost was $189,681.74 (Table 2) and the actual dosage applied was 26.9 mg/L.

The median TP-T concentration the year after the first alum treatment was 0.26 mg/L. To operate the LHCA for flood protection, nutrient levels had to be further reduced to prevent high TP loads into Lake Griffin. In-house jar tests showed the best floc formation at 15 mg Al/L. At concentrations of 20 mg Al/L and above, however, the alkalinity dropped to less than 20 mg/L, indicating a need for a buffering agent. Sediment characterization was not completed, but a higher dose was planned to provide sediment treatment.

The second treatment was applied using the same barge/manifold system that was used on SNKN and EMF (Sweetwater Technologies 2010). Between August 25 and September 2, 2010, 48 tankers (821,624 L) of alum and 2 tankers of sodium aluminate (28,815 L) were applied at a cost of $210,863 (Table 2). The second treatment involved more logistical difficulties than the first treatment because of the deeper draft of the barge/manifold system. Shallow water depths in LHCA prevented the barge from filling its tanks with more than 5,600 L (1,500 gallons). Exposed tree stumps and an underwater levee were flagged prior to mobilization, but hidden high spots less than 0.75 m deep frequently caused the barge to become stuck. Leftover farm equipment (ropes, chains, etc.) became entangled in the propellers, which caused the barge to be inoperable for two days.

A localized mortality of mollusks and small (1-2 inch) American gizzard shad (*Dorosoma cepedianum*) occurred during the next to last day of treatment. Once the mortality was observed, the dosing was immediately decreased. At the time of the mortality, the water column pH had dropped to <4.5 directly behind the barge. Constant supervision of the water column pH and alkalinity prevented a larger mortality event.

Results

Two-months following the first treatment in LHCA, TP-T and TP-D decreased on average by 26%. Secchi improved by 57% (Table 12).

Table 12. Mean water column parameters in LHCA, two months before and two months after the first alum treatment. All units are mg/L, except for color (CPU), electrical conductivity (EC; µmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Alkalinity	146.5	85.4	-42
Al-T	0.230	0.457	99
Chl-a	225.9	162.3	-28
Color	100	85	-15
DOC	47.0	35.3	-25
EC	426.6	598.5	40
pH	7.76	7.95	2
Secchi	0.20	0.28	38
SRP	0.012	0.006	-52
TKN-D	2.627	2.266	-14
TOC	53.1	45.1	-15
TP-D	0.053	0.038	-28
TP-T	0.475	0.264	-44
TSS	65.9	44.8	-32

The second alum treatment resulted in 62% decrease in TP-T and 58% decrease in TP-D (Table 13). Although the bottom was visible immediately after treatment (within 1-6 hrs), Secchi depth increased only 26% in the first two months after treatment, but chlorophyll *a,* color and TSS decreased (Table 13).

Table 13. Mean water column parameters in LHCA, two months before and two months after the second alum treatment. All units are mg/L, except for color (CPU), electrical conductivity (EC; μmhos/cm), pH, and Secchi (m).

Analyte	Pre-alum	Post-alum	% Change
Al-D	0.092	0.103	12
Alkalinity	120.5	51.0	-58
Al-T	0.263	0.701	166
Chl-a	156.7	46.4	-70
Color	82	38	-54
DOC	26.9	15.1	-44
EC	357.0	675.4	89
pH	8.08	7.60	-6
Secchi	0.33	0.42	26
SRP	0.014	0.004	-69
TKN-D	1.643	1.023	-38
TOC	28.4	20.3	-29
TP-D	0.028	0.012	-58
TP-T	0.284	0.108	-62
TSS	38.8	23.3	-40

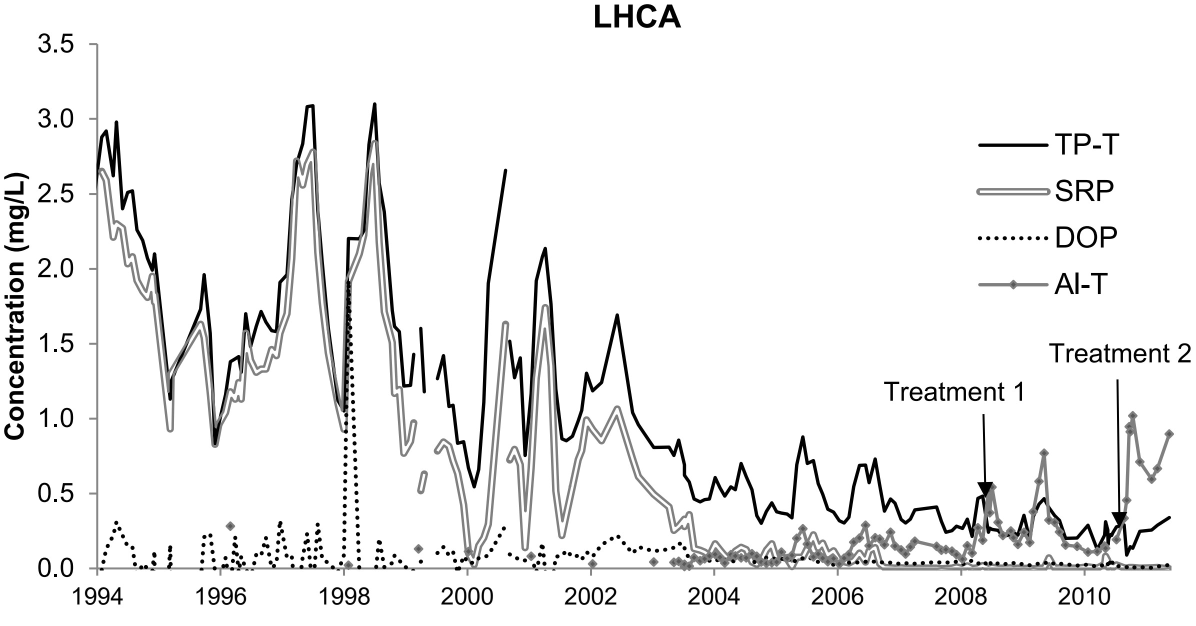


Figure 28. Water column P and Al in LHCA from 1994 to 2010. Alum was applied from May 21 to June 13, 2008 and from August 25 to September 2, 2010.

A drawdown in LHCA was not implemented before the first alum treatment, as called for in the initial design. The construction was conducted "in the wet." Therefore, the first alum application was conducted post construction and prior to reconnection. P concentrations spiked >0.200 mg/L in the spring of 2009 likely because of continual internal recycling (Figure 28). Following the second alum treatment, shallow water depths in LHCA (mean= 0.75m) resulted in frequent sediment resuspension (Figure 29). This is shown as elevated total aluminum concentrations persisted after treatment. Dissolved P was minimalized while particulate P that was bound in floc became prevalent.

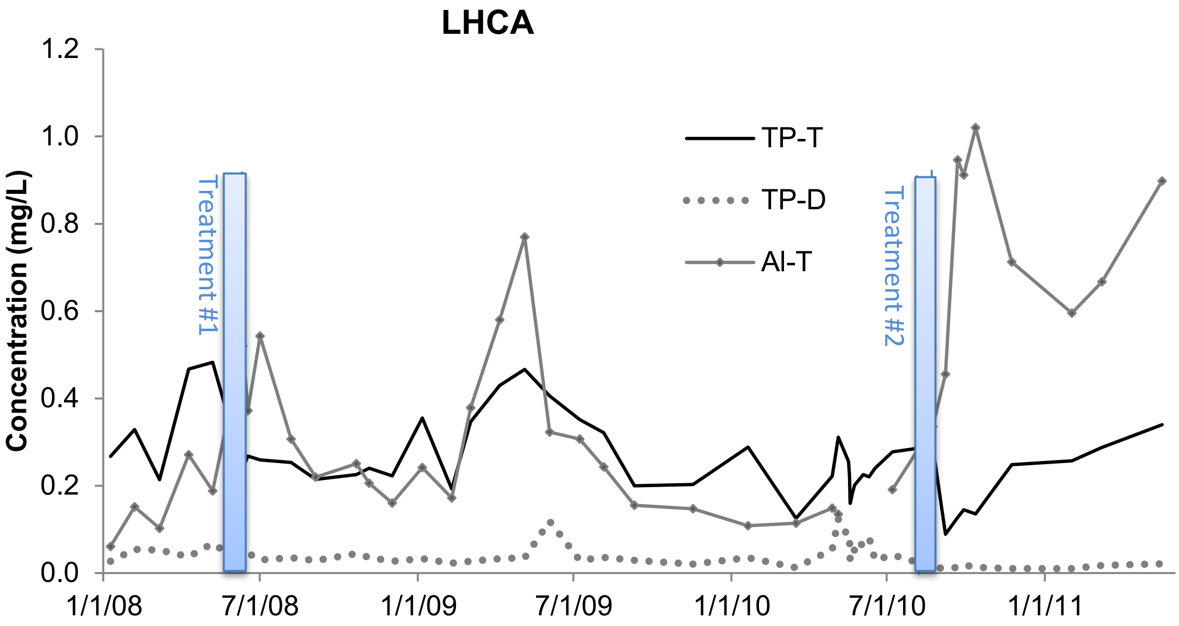


Figure 29. Water column P and Al in LHCA from 2008 to May 2011. Alum was applied from May 21 to June 13, 2008 and from August 25 to September 2, 2010.

DISCUSSION

Long-term Treatment Success

A two-month average before and after treatment was used to determine the "immediate" effect of alum on water column variables, or short-term effectiveness. Assessing long-term treatment effectiveness was more complicated. It was thought that a multi-year median for parameters before and after alum could be compared for a general assessment of long-term success.

Upon initial analysis, however, it was found that several water quality parameters (e.g. TP-T, TSS) were correlated (r^2>0.65) with stage because of volumetric dilution and concentration effects. To account for the effect of volume on water quality, pre-alum samples were only included in analyses if they were collected when stage was within the minimum and maximum stage observed after treatment. This filtering method ensured that all comparisons of before and after alum used data collected within the same range of stages.

Pre-alum data were also examined for other factors that might confound before and after comparisons. In LHCA, because of the significant, unexplained decrease in median TP-T, TP-D and SRP in LHCA after 2003 (Figure 28), only the five years directly preceding alum treatment were used in the before and after analyses. This more contemporary baseline for water quality data avoids an over-estimation of long-term nutrient reduction. Pre-alum data before the second treatment in LHCA included samples taken after the flow through test on May 24, 2010. Post-alum data included all water quality samples that either were taken after the last day of treatment, or in the case of prolonged treatments, when a significant decrease in TP-T first appeared. Post-alum data included samples until 2010, or when the area became hydrologically connected with Lake Griffin. Percent change in water quality after treatment was calculated using median values of pre-alum samples and post-alum samples. A Kruskal-Wallis test (Minitab ^{TM}) was used to find significant differences (α=0.05).

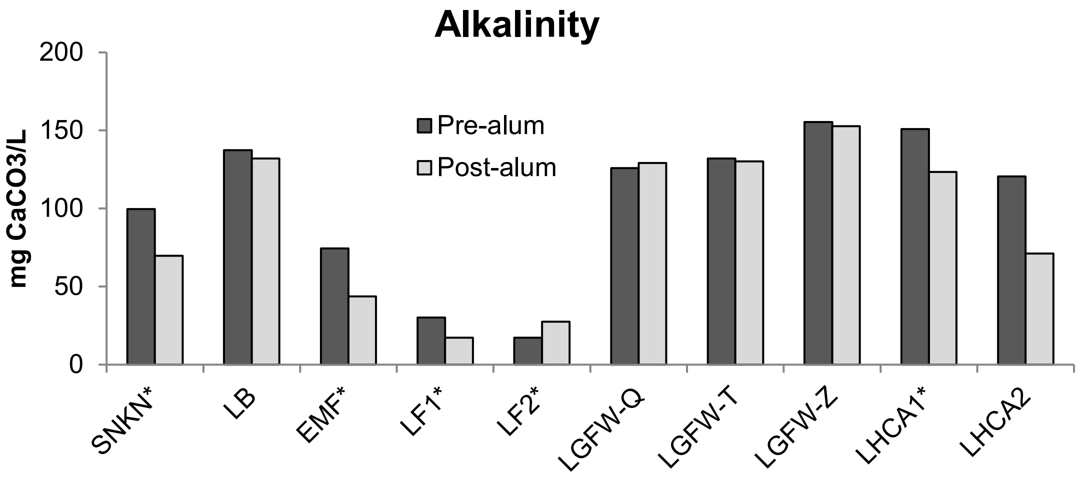
In the long-term, post-treatment TP-T was significantly reduced in all areas except for Q cell in LGFW (Table 14). SRP decreased significantly after treatment in all areas except for Q, T and Z cells. Water transparency, as measured by Secchi depth, increased significantly in most of the areas while chlorophyll *a* and TSS decreased significantly (Figure 30).

Table 14. Percent change in total phosphorus, soluble reactive phosphorus, and Secchi depth over long term following alum application.

	Total Phosphorus (mg/L)			SRP (mg/L)			Secchi Depth (m)		
Site	Pre-alum	Post-alum	% Change	Pre-alum	Post-alum	% Change	Pre-alum	Post-alum	% Change
LGFW-Q	0.215	0.257	20	0.071	0.151	112	0.80	1.08	34*
LGFW-T	0.429	0.287	-33*	0.207	0.140	-32	0.60	0.7	17
LGFW-Z	0.447	0.199	-55*	0.062	0.052	-16	0.25	0.7	180*
SNKN	0.160	0.055	-66*	0.037	0.007	-82*	0.65	0.6	-8
LB	0.323	0.082	-75*	0.053	0.005	-90*	0.22	0.6	173*
EMF	2.190	0.187	-91*	1.830	0.031	-98*	0.28	0.55	96*
LF-1	3.402	1.072	-68*	3.222	0.932	-71*	0.43	0.6	41
LF-2	1.072	0.466	-56*	0.932	0.328	-65*	0.60	0.5	-17
LHCA-1	0.532	0.260	-51*	0.112	0.003	-98*	0.25	0.33	33*
LHCA-2	0.225	0.135	-42*	0.016	0.006	-62	0.39	0.35	-5

* denotes significance

Overall, rapid initial water quality gains were generally tempered by a new steady state. As explained by Huser et al. (2011), although this may seem to represent a decrease in effectiveness, it more likely represents the water body "recovering" from the alum treatment.


Alkalinity
mg CaCO3/L
200
150
100
50
0
■ Pre-alum
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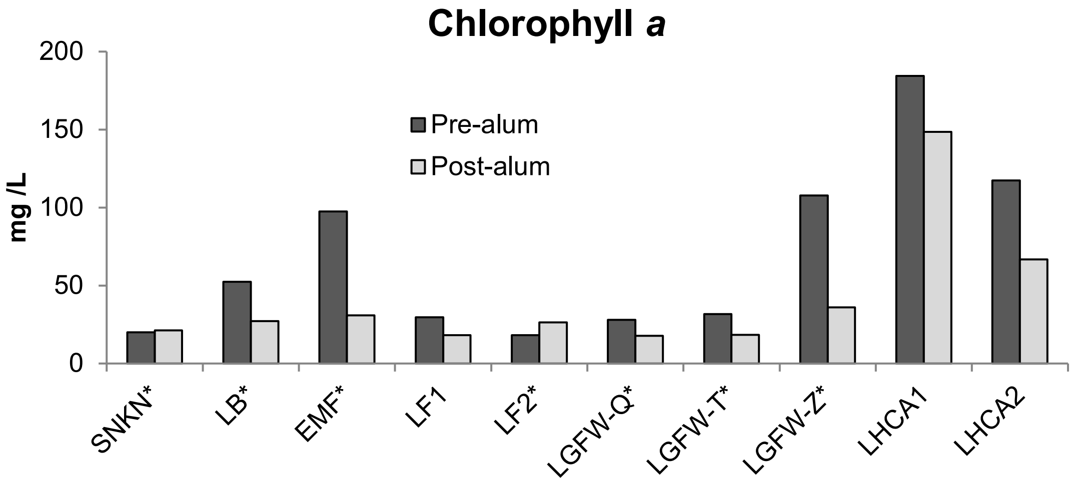
SNKN*
LB
EMF*
LF1*
LF2*
LGFW-Q
LGFW-T
LGFW-Z
LHCA1*
LHCA2


Chlorophyll a
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SNKN*
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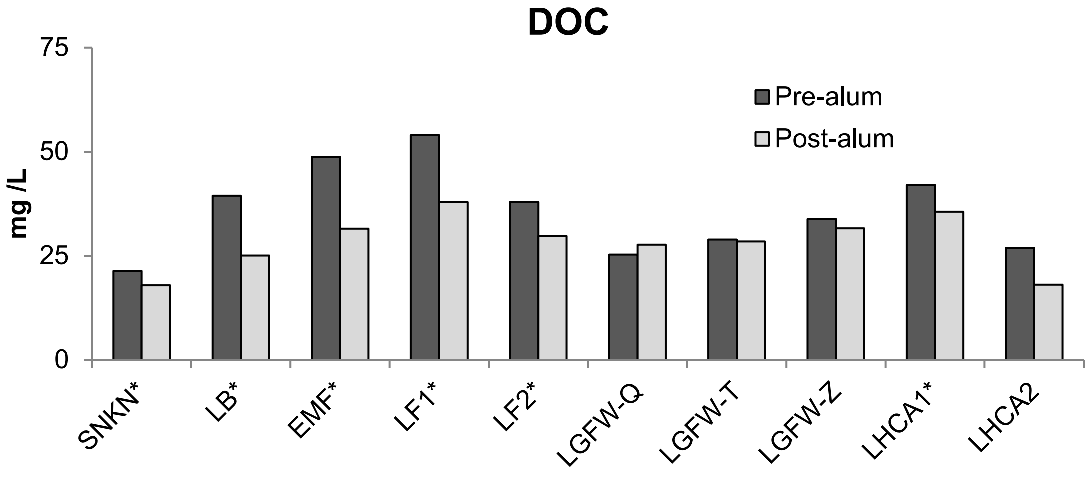
LGFW-Z*
LHCA1
LHCA2


DOC
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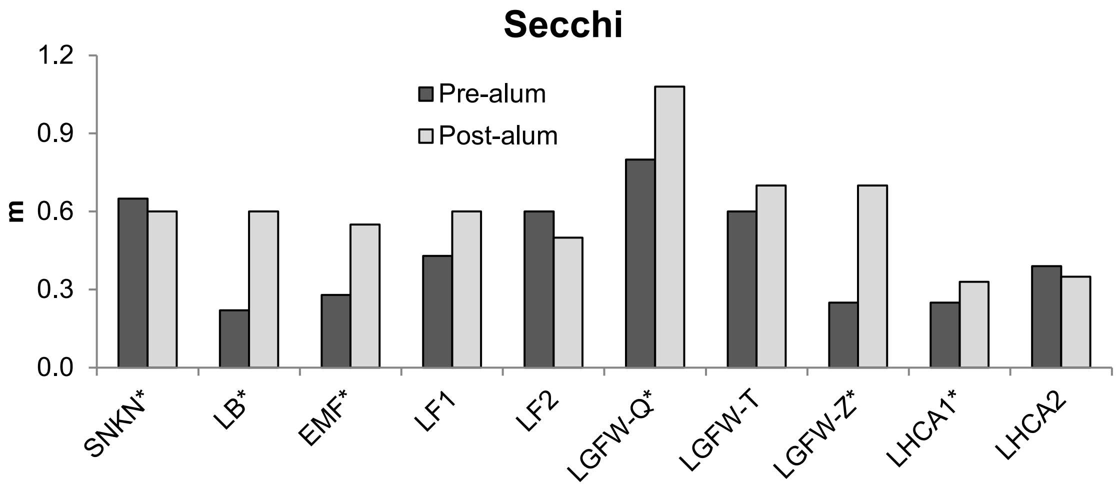
LHCA2


Secchi
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SNKN*
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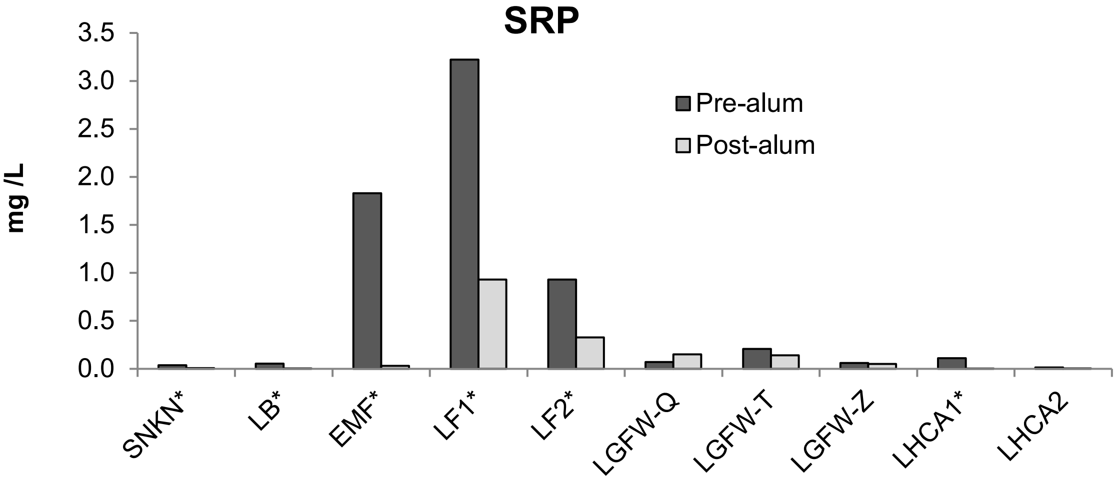
LHCA1*
LHCA2


SRP
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SNKN*
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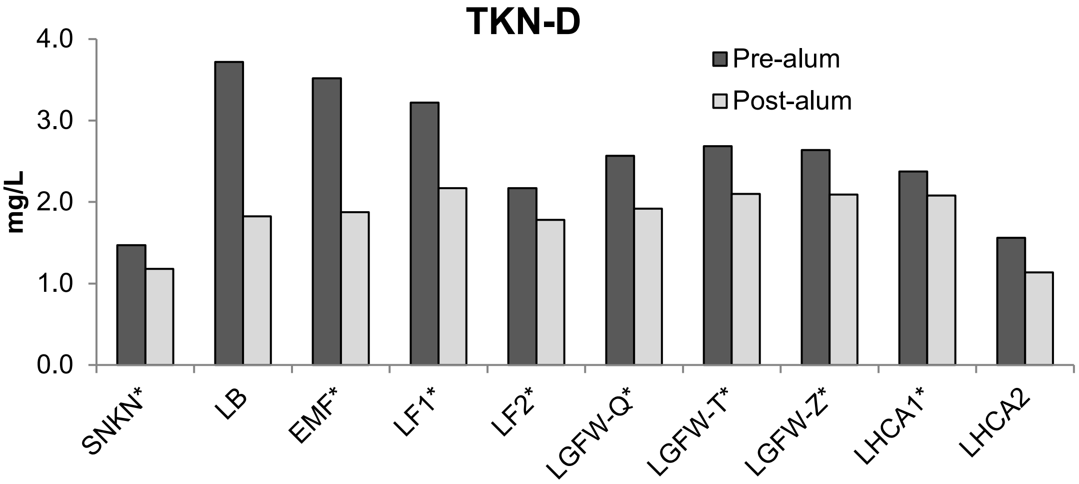
EMF*
LF1*
LF2*
LGFW-Q
LGFW-T
LGFW-Z
LHCA1*
LHCA2


TKN-D
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□ Post-alum
SNKN*
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LF1*
LF2*
LGFW-Q*
LGFW-T*
LGFW-Z*
LHCA1*
LHCA2

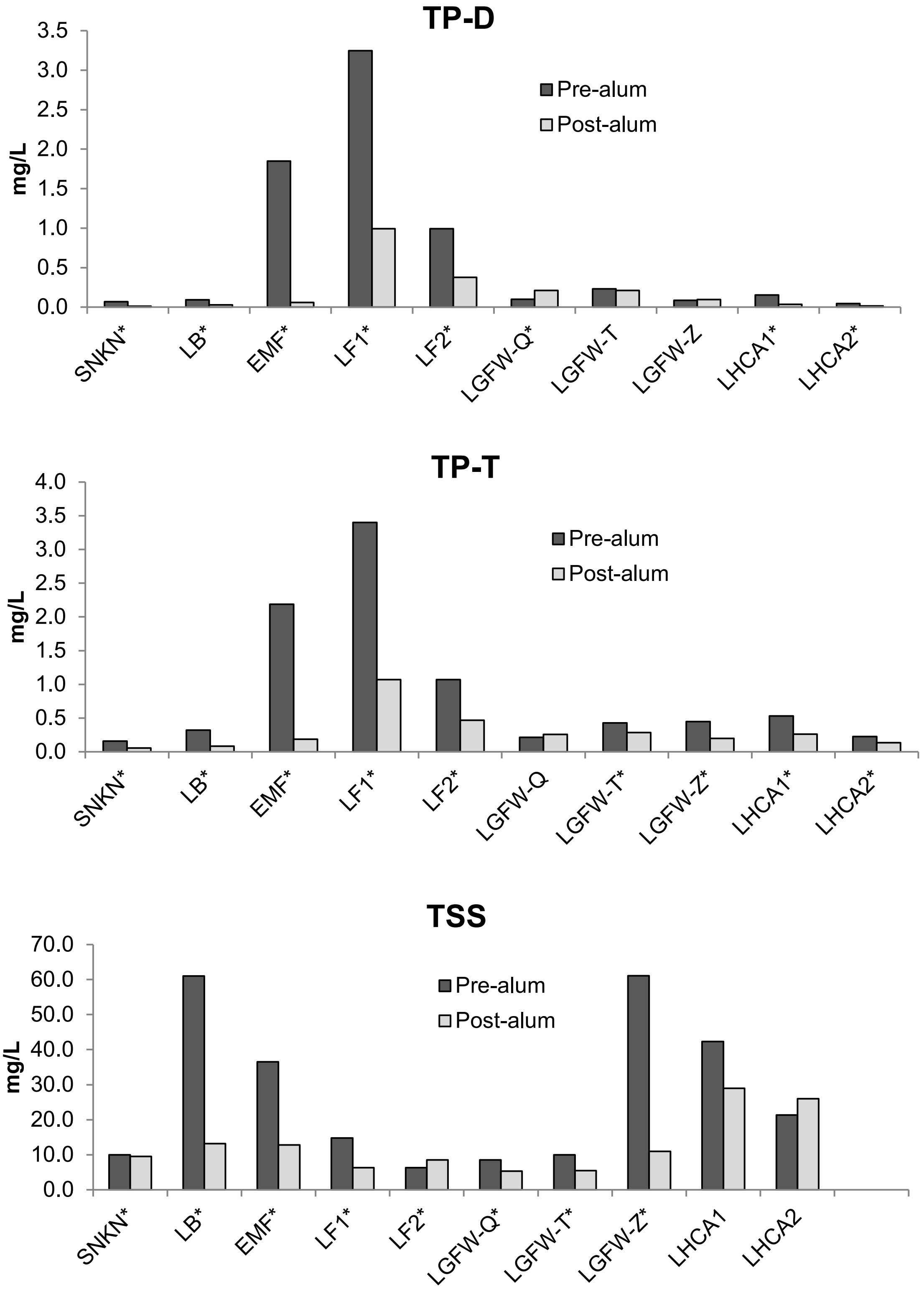

Figure 30. Multi-year median water quality parameters in EMCA areas and LHCA before and after alum treatment. Asterisk (*) denotes significance. SNKN - S.N. Knight North; LB - Lowrie Brown; EMF - Eustis Muck Farm; LF - Long Farm; LGFW - Lake Griffin Flow-Way; LHCA - Lake Harris Conservation Area.

Water Quality Effects on Phosphorus Removal Efficiency

Dosing

We hypothesized that several physical and chemical factors might have influenced the short and long-term effectiveness of each alum treatment. In the short-term, unanticipated under dosing of alum might have led to decreased treatment effectiveness. The LGFW and Long Farm were the only sites designed for long-term sediment P inactivation (Table 15). The treatment design for LGFW, however, did not consider the large chemical demand for alum within the water column. It is likely that only a portion of the alum that was applied reached the sediments after either being intercepted by vegetation or flocculated in the water column. In Long Farm, heavy rains occurred during delays in the alum application leading to higher water levels, thus diluting the dosage.

Table 15. Recommended (Rec.) and applied sediment and water column dosages of alum in Lake Griffin Flow-Way (LGFW), Lowrie Brown (LB), Long Farm (LF), Eustis Muck Farm (EMF), S.N. Knight North (SNKN), and Lake Harris Conservation Area (LHCA).

Area	Rec. sediment Al:P ratio	Rec. sediment dose (g/m^2)	Actual sediment dose applied (g/m^2)	Rec. water column dose (mg Al/L)	Rec. total dose (mg Al/L)	Actual total dose applied (mg Al/L)
LGFW	4:1	5.4	7.0	0	N/A	6.1
LB	---	---	---	10-15	10-15	9.3
LF-1	5:1	9.5	7.2	4.2	12.7	9.5
LF-2	16.5:1	9.1	0	14	20	9.7
EMF	---	---	---	18	18	20.7
SNKN	---	---	---	18	18	12.6
LHCA 1	---	---	---	25	25	26.9
LHCA 2	N/A	19.6	15.8	15	32	28.6

The magnitude of the dose also affected the rate and size of floc formation. Applications that created large-particle flocs were more effective at completely “sweeping” or capturing suspended phosphorus particles than smaller particle floc. In Long Farm, dividing the already diluted dose over three separate applications to improve coverage created a microfloc which stayed suspended for months. This finding concurs with studies using alum for potable water treatment, which recommend dosing in excess of the required amount to encourage a large floc that settles rapidly and removes suspended particles by enmeshment (Pernitsky 2010).

In the long-term, numerous biogeochemical processes in both the water column and sediments likely affected treatment P removal efficiency. Identifying sources of variability in the percent TP-T reduction was complex because alum dosages were not constant across each treatment.

Reductions in internal recycling from P sorption by floc were not included in this treatment analyses. Post-alum, median water column TP-T would therefore be an underestimation of treatment success at sites where total dosing exceeded dosing required for the water column.

P Composition

Each area's unique water column chemistry, such as the composition of P species, might have affected flocculation and P removal after treatment (Eisenreich et al. 1977). Because of its reactivity, SRP typically is easier to remove with alum than DOP. The areas with the highest percentage of P as SRP, pre-treatment, were Eustis Muck Farm and Long Farm (Figure 31). These two areas also had the highest percent TP-T reduction after treatment (92% and 68%, respectively). Lowrie Brown, however, had the highest pre-treatment percentage of DOP (18%), but still had a 66% reduction in TP-T after alum.

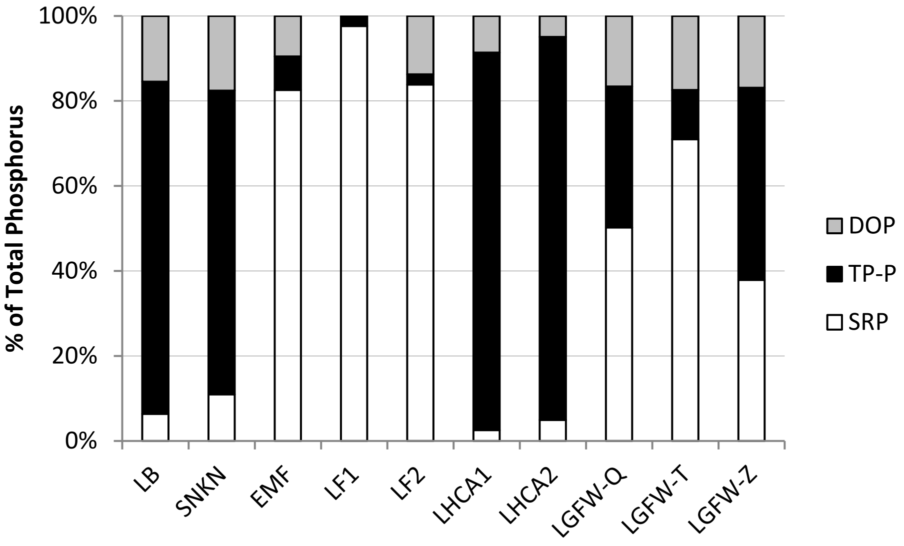

Figure 31. Percentage of median TP-T as DOP, TP-P (particulate P) and SRP, before treatment with alum. Lowrie Brown (LB), S.N. Knight North (SNKN), Eustis Muck Farm (EMF), Long Farm (LF), Lake Harris Conservation Area (LHCA) and Lake Griffin Flow-Way (LGFW, Q,T and Z cells).

Dissolved Organic Carbon

High concentrations of DOC have been shown to affect P removal with alum (Shin et al. 2008; Qualls et al. 2009). In a lab experiment using water from the Everglades, alum effectiveness was decreased with high (60 mg/L) concentrations of DOC (Qualls et al. 2009). High DOC (49 mg/L) in Long Farm and a low applied dosage (8.3 mg Al/L) possibly decreased the effectiveness of the first alum treatment. Average pre-treatment DOC in Eustis Muck Farm was 55 mg/L, but the rapid increase in transparency after treatment suggests that NOM was successfully removed with the sweep flocculation (Cooke et al. 2005). Precision in alum dosing and application in Eustis Muck Farm likely compensated for inhibitory effects of DOC. In Qualls et al. (2009), a dose of 16 mg Al/L in high DOC water reduced TP-T to 0.010 mg/L. A dose of 19.7 mg/Al L in Eustis Muck Farm was sufficient to reduce TP-T by 94% and DOC by 30% (Figure 31).

Along with raw water DOC concentration, the ratio of alum dose to DOC has been investigated for its effect on treatment. Srinivasan and Viraraghavan (2004) suggested an alum/DOC ratio (alum in mg/L:DOC in mg/L) of at least 7.3:1 to minimize residual aluminum from incomplete coagulation. When they measured an alum/DOC ratio of 5.3:1 in a pilot-scale water treatment plant, total aluminum values were high and most (88%) of the total aluminum was in particulate form, suggesting incomplete coagulation. All of the treatments, except in LGFW and the two treatments in Long Farm, were above Srinivasan and Viraraghavan's (2004) suggested alum/DOC ratio of 7.3:1 (Figure 32). An increase in particulate P, however, was only measured following the second application at Long Farm (Figure 16). An increase in residual (particulate) Al was measured in four of the sites (SNKN, EMF, LF2, and LHCA), which were among the treatments considered the most successful.

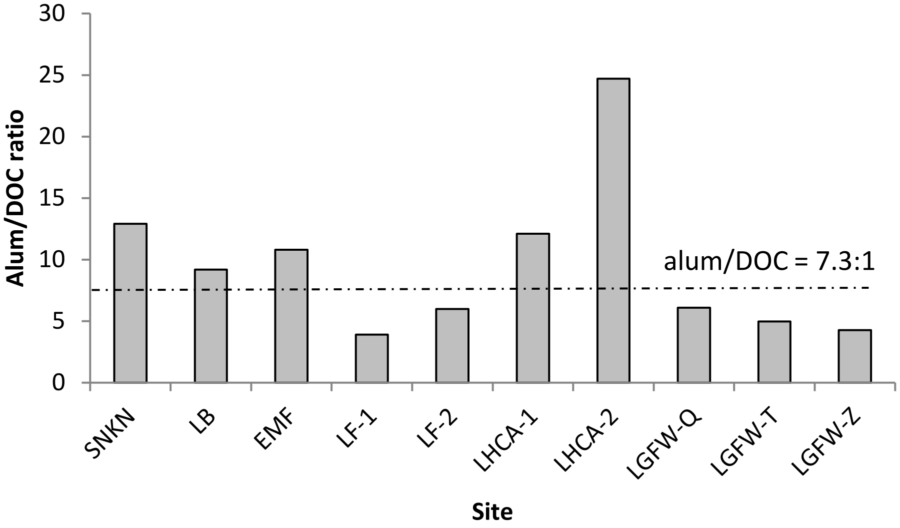

Figure 32. Alum/DOC ratio before treatment in each area. The dotted line is the suggested minimum ratio by Srinivasan and Viraraghavan (2004). S.N. Knight North (SNKN), Lowrie Brown (LB), Eustis Muck Farm (EMF), Long Farm (LF), Lake Harris Conservation Area (LHCA), and Lake Griffin Flow-Way (LGFW, Q, T and Z cells).

Sediment Buffering

Water quality results from the alum treatments revealed discrepancies between the predicted (in jar tests) and actual buffering capacities of each site. In every case where buffering was recommended, less chemical was required to maintain alkalinity and pH than predicted. Previous research on the acid neutralizing capacity (ANC) of lake sediments on lake pH has demonstrated several chemical and biological processes in the sediments that can neutralize inputs of acidity to the water column (Oliver and Kelso 1983, Baker et al. 1985, Cook et al. 1986, Perry et al. 1986). Neutralization can be rapid with equilibrium being reached within 24 hours (Baker et al. 1985).

Sediment buffering may occur through several mechanisms, including mineral dissolution, cation exchange, precipitation of humic acids, nitrification, and sulfate reduction (Baker et al. 1985). In several Florida lakes, cation exchange (Ca^{2+}, Mg^{2+}, and soil OM) was a dominant neutralizing mechanism in well-mixed sediments (Brezonik and Perry 1983, Perry et al. 1986). Calculated areal buffering capacities from ion exchange range from 5.5 to 149 meq/m^2/cm (Perry et. 1986). Perry et al. (1986) and Baker et al. (1985) found that ANC attributable to ion-exchange was strongly related to organic content.

Because of the high cost per gallon of sodium aluminate ($2.00/gallon), accurately predicting the buffering capacity in a treatment area is important. Generally, one gallon of sodium aluminate will buffer two gallons of alum (Sweetwater Technologies 2010). For the second LHCA treatment, the application of 82,629 L of sodium aluminate (20% Al_2O_3) was calculated for a 10:1 alum/sodium aluminate ratio. The larger ratio was based on previous SJRWMD experience with buffering materials. Similar to the other treatments, pH, and alkalinity readings behind the barge during the treatment suggested that the amount of buffering agent could be decreased, so only 28,815 L was applied.

Observations of the barge stirring up sediment in the shallow water indicated that ANC processes might be increasing the potential for cation exchange, which could contribute to higher alkalinities (Figure 33). To test this hypothesis, a jar test experiment was performed using four different amounts of sediment. Similar muck sediments (0-10cm) were collected from an untreated restored wetland in the North Shore Restoration Area of Lake Apopka. Each jar had 0g, 50g, 150g or 250g sediment and all received 25 mg Al/L. The results showed a significant increase in both alkalinity ($p=0.020$, $\alpha=0.05$) and pH ($p=0.023$) with increased amounts of sediment (Figure 34).

Figure 33. A plume of sediment (dark color) being suspended behind the barge during an application at Lake Harris Conservation Area.

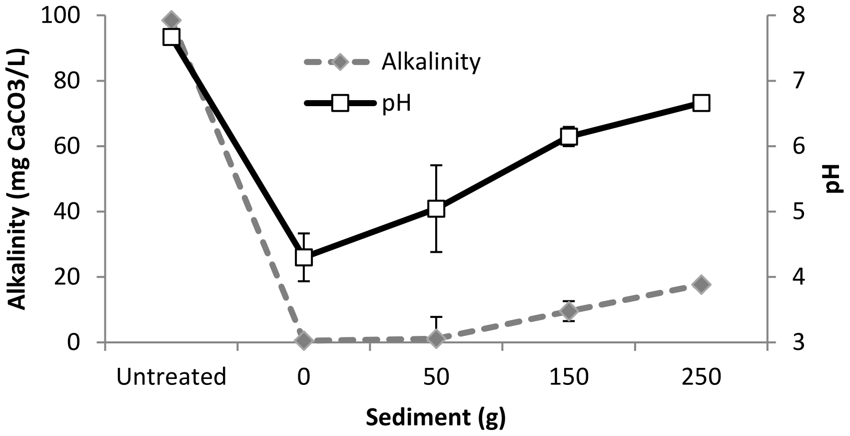

Figure 34. Jar test results showing increases in pH and alkalinity with increased sediment (n=12). Error bars are ± 1 standard deviation.

The results of the jar test experiment demonstrated the contribution of sediment biogeochemistry to alum applications. Dosing should therefore consider the effect of sediment buffering in shallow restoration areas or lakes that might be prone to resuspension.

Project Costs

Since the first whole-lake alum treatments in the 1970s, costs have decreased due to improved technology. In 1977, a barge treatment on Medical Lake, WA cost $1,520/ha (Cooke et al. 2005). In 2002, a large, high-speed barge, guided by a computerized dose and navigation system cost approximately $838/ha (Connor and Martin 1989). This system only required 0.06 worker days/ha (Eberhardt 1990). The average cost to treat one hectare in the UORB was $690 (Table 2).

The treatment designs averaged $14,614 (Table 16). The first design for LGFW was the most expensive because of costs associated with a literature review, assessment of various chemicals, sediment incubation, and evaluation of applications methods. Designs for the two Long Farm treatments contained sediment sampling and water column analysis. They averaged $22,266. Two jar test designs were completed for Eustis Muck Farm, which increased the cost. The initial design designated lime as the buffering agent, while the second design investigated sodium aluminate, which was the chosen buffer. The cost of treatment design for the second LHCA application was conducted by General Chemical at no cost. Since this time, the SJRWMD has purchased a jar test kit so that future jar tests can be completed in-house. Overall, as the vendors and SJRWMD staff became more familiar with information needs, procedures, and chemicals, the cost of planning the treatments fell drastically.

The extensive site preparation needed for the LGFW treatment of the Q, T, and Z cells cost $60,000. Pathways were cut every 100’ to allow chemical application in the Q cell and part of the T cell. All cells required extensive road and levee work to allow tanker access. However, that cost was not included in these calculations since these improvements were needed for future restoration efforts.

The cost to remove one kg P from the water column was calculated using water volumes from stage at the start of treatment and TP-T measurements one month prior to treatment and one month after treatment. The first treatment in Long Farm was the most cost-effective treatment at $13/kg P removed. This is due to the lower cost of treating higher TP concentrations. In addition, these values are based on the cost at the time of treatment, which often depended on the price of the chemical. They are not adjusted for present value. For example, in 2004, alum cost $0.34/gallon, but rose to $1.00/gallon in 2009. In 2010, the price was down to $0.51/gallon.

Table 16. Contractual treatment cost per ha and kg P removed. Does not include SJRWMD personnel. Lake Griffin Flow-Way (LGFW, Q, T, and Z cells), Lowrie Brown (LB), Long Farm (LF), Eustis Muck Farm (EMF), S.N. Knight North (SNKN), and Lake Harris Conservation Area (LHCA).

Area	Site Prep[+] ($)	Treatment design ($)	Application cost ($)	Water column P removed (kg)	Cost/kg P removed ($)
LGFW-Q	50,000	44,415	87,210	197	275
LGFW-T	10,000			153	
LGFW-Z				346	
LB		6,621	90,755	177	550
LF-1		31,622[*]	224,500	19,462	13
LF-2		12,910	197,774	3,995	53
EMF		9,163	278,060	7,646	38
SNKN		8,396	90,000	53	1,857
LHCA-1		3,783	189,682	1411	137
LHCA-2		0	210,863	2,536	83
Total		*116,910*	*1,368,844*	*35,976*	
Average		**14,614**	**171,112**	**4,497**	**376**

[+] Includes cutting of pathways, does not include levee improvement, which was already scheduled to be completed

[*] Portion of contract covering three sites

The extremely high cost of treatment in SNKN is likely due to large reductions in TP just prior to treatment and contamination of the site with off-site water post treatment. This site was still considered a success with a 53% reduction in TP. Although not measured, sediment treatment was likely achieved to some extent due to the overdosing of the water column. Jar test data indicated that a water column concentration of 50 µg TP/L could be achieved with the addition of 5 mg Al/L (MACTEC 2004). Since optimum aluminum hydroxide floc formation takes place at pH between 5.5 and 6.5, a dosage of 18 mg Al/L was recommended. This fit well with the planned budget and maintaining the alkalinity, while possibly treating the sediments.

The mean and median P removal cost (per kg) for EMCA and LHCA alum treatments was $376 and $110, respectively, which is similar to other nutrient removal projects implemented by the SJRWMD (Table 17). However, this is likely a very conservative value since the sediment treatment has not been included in the TP removal quantities.

Looking at other SJRWMD nutrient removal projects, the cost of TP removal from the Lake Apopka Marsh Flow-Way from 2004-2014 averaged $115/kg, excluding capital. The harvest of gizzard shad in Lake Griffin and Lake Apopka cost approximately $112/kg of TP removed in 2012. A temporary alum injection project that operated 272 days in 2005 reduced potential P loading offsite by over 1.5 metric tons at a cost of $196/kg (Hoge et al. 2006).

Table 17. Costs of various nutrient management practices.

Citation	**Year**	**Nutrient Management Practice**	**Pre [TP] mg/L**	**Post [TP] mg/L**	**$/kg**
Hoge et al. 2006	2005	Alum injection system[1]	0.347	0.157	196
SJRWMD	2012	Gizzard shad removal[2]	n/a	n/a	112
SJRWMD	2012	Gizzard shad removal[3]	n/a	n/a	31
SJRWMD	2014	Marsh Flow-Way[4]	0.12	0.09	242
SJRWMD	2014	Marsh Flow-Way[5]	0.12	0.09	115
This publication	2001-2010	Mean of barge alum applications	0.110 – 4.580	0.051-0.504	376
		Median of barge alum applications			110

[1] Includes capital and operating costs, not amortized

[2] Includes only costs for commercial harvest, P removal in biomass only

[3] Includes only costs for commercial harvest, P removal in biomass plus reduction in P recycling

[4] Includes operating costs plus capital costs over 11-year period

[5] Includes only operating costs over 11 years

SUMMARY AND RECOMMENDATIONS

A total of 5,462,497 L alum, 279,363 L lime and 163,981 L sodium aluminate were applied in the UORB for nutrient management from 2001-2010 (Table 2). Except for the Q and T cell in LGFW, all of the liquid alum treatments in EMCA and LHCA resulted in significant decreases in TP-T. Across all of the treatment areas, mean TP-T was reduced by approximately 67%.

Other water quality parameters also showed improvements after treatments (Figure 31). Water clarity improved as measured by increases in Secchi depth, and decreases in turbidity, color, TSS, DOC, and chlorophyll *a*.

Other than the localized mortality of mollusks after the barge spill in Lowrie Brown and a small number of snail and small (1-2 inch) American gizzard shad (*Dorosoma cepedianum*) mortalities at LHCA during the second treatment, no mortalities were observed in any of the sites following alum treatment.

Class III surface water standards for Florida require a pH above 6.0 and alkalinity above 20 mg/L (as $CaCO_3$; FDEP 2009). Field-measured pH in EMCA and LHCA was below 6.0 only ten times between 2000 and 2009. Four measurements of pH<6.0 occurred in LGFW after the alum treatment, and six occurred in Long Farm and LHCA before alum was applied. Alkalinity was below 20 mg/L in 3% of all site samples taken from 1998 to 2009.

According to the National Ambient Water Quality Criteria, acid soluble Al in a pH of 6.5 to 9.0 may cause acute toxicity effects at 0.750 mg/L and chronic effects at 0.087 mg/L (USEPA 1988). Acid-soluble aluminum is derived from a non-filtered water sample that is acidified to pH 1.5 to 2.0 prior to filtration through a 0.45-µm filter (USEPA 1988). Since filtration follows acidification, most forms of colloidal and polymeric Al, which are non-toxic, would be included in these measurements (Gensemer and Playle 1999). Since these recommendations may be dated and insufficient, Gensemer and Playle (1999) advise that monitoring for acute toxicity in and near the mixing zones is vital. The SJRWMD did not measure acid soluble Al at any of the sites, however during the period of record for all the sites, 4% of monthly water samples had Al-D higher than 0.087 mg/L, and 0.4% had Al-D higher than 0.750 mg/L. Since Florida has not adopted water quality criteria for aluminum, the above limit does not have any regulatory impact (USEPA 1988). Average DOC levels above 20 mg/L in EMCA and LHCA also suggest that background NOM in these sites may have reduced Al toxicity risks to organisms.

Liquid alum can be used very effectively to reduce restoration timelines. Without treatment, these sites may have taken years to be able to sustain macrophytes or be available for reconnection with adjacent water bodies and providing important wetland habitat. As shown by our treatment results, large amounts of phosphorus can be treated and stabilized safely and quickly in a cost-effective manner. Each site was unique, however, and presented a different set of challenges. The logistics of moving and correctly applying large amounts of chemicals under varying environmental conditions require organization, coordination, and communication.

Based on the results from the liquid alum applications in the UORB, we recommend the following:

- As previously stated by de Vicente et al (2008b), the complexity of the lake water chemistry does not allow the simple calculation of alum dose from the concentration of potentially competitive ions. Jar tests should be carried out for the receiving water prior to Al application.
- Do not conduct surface liquid alum applications in areas with dense emergent vegetation. Granular alum in such areas can provide an effective alternative to liquid alum. A successful granular alum application was conducted by the SJRWMD at Blue Cypress Marsh in 2012 at a cost of $857/ha (Hoge et al. 2013).
- If applying in shallow basins (1-2 m deep), obtain an accurate, high-resolution (<2 m) bathymetric map prior to treatment. The drafting depth of the barge is increased when loaded with chemical, therefore *a priori* site knowledge is important.
- Dosing rates based on both water column and sediment P should be considered in design plans to ensure proper floc formation and P removal efficiency. Under dosing can lead to microfloc formation, which can stay suspended in the water column for months, leading to increased particulate phosphorus and residual aluminum. Overdosing can lead to toxicity problems, so proper consideration of the water chemistry is vital.

- The pH and alkalinity should be continuously monitored during application to prevent potential toxicity problems.
- Recognizing the creation of microfloc at the time of application is difficult. The measurement of pH, SRP, and alkalinity is not sufficient. Particulate P and particulate Al must be measured to determine the extent of microfloc created.
- The dosing should be conducted as one event as opposed to multiple lesser applications. This will create a broad "sweep" flocculation and encourage enmeshment of suspended particles.
- Projecting anticipated water volumes for budgeting purposes is difficult. Flexibility in funding the projects according to the volume of water is needed. For most of the treatments, funds were not available for amending the contract scope of work. Several times, under-dosing occurred because of increased volumes of water that needed treatment. We suggest adding an appropriate contingency (up to 10%) to projected alum costs.
- The sudden increase in water clarity from the addition of alum may create favorable conditions for algal blooms, which may increase water column pH, and a release of Al-D can occur. If treating a shallow water body (<2m), then treatment should be performed when the potential for resuspension from high winds (or flows through structures) will be reduced. Approximately three months should be allowed for floc stabilization.

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APPENDIX A. Stage area curves and stages (NGVD29) during project timelines

Table A1. Area of inundation and water depths in Area 3 (LGFW, Q-cell) as a function of water stage, estimated from aerial photogrammetry

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac-ft	Ft
52	1									1	1	0.0
53	178	1								179	91	0.3
54	121	178	1							300	330	1.0
55	16	121	178	1						316	638	1.9
56	12	16	121	178	1					329	961	2.8
57	3	12	16	121	178	1				332	1,291	3.8
58	2	3	12	16	121	178	1			333	1,623	4.8
59	1	2	3	12	16	121	178	1		335	1,957	5.8
60	6	1	2	3	12	16	121	178	1	340	2,295	6.8

Table A2. Area of inundation and water depths in Area 3 (LGFW, T-cell) as a function of water stage, estimated from aerial photogrammetry

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	10-11	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac-ft	Ft
52	19											19	0	0.0
53	134	19										153	86	0.2
54	47	134	19									199	262	0.6
55	16	47	134	19								215	469	1.1
56	31	16	47	134	19							246	699	1.6
57	32	31	16	47	134	19						278	961	2.2
58	37	32	31	16	47	134	19					316	1,258	2.9
59	81	37	32	31	16	47	134	19				396	1,614	3.7
60	36	81	37	32	31	16	47	134	19			432	2,028	4.6
61	11	36	81	37	32	31	16	47	134	19		442	2,465	5.6
62	2	11	36	81	37	32	31	16	47	134	19	445	2,908	6.6

Table A3. Area of inundation and water depths in Area 3 (LGFW, Z-cell) as a function of water stage, estimated from aerial photogrammetry

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac-ft	Ft
52	14										14	0	0.0
53	181	14									195	104	0.3
54	41	181	14								236	319	0.9
55	71	41	181	14							307	590	1.7
56	36	71	41	181	14						342	915	2.5
57	1	36	71	41	181	14					343	1,258	3.5
58	0	1	36	71	41	181	14				344	1,601	4.4
59	0	0	1	36	71	41	181	14			344	1,945	5.4
60	12	0	0	1	36	71	41	181	14		356	2,295	6.4
61	6	12	0	0	1	36	71	41	181	14	362	2,654	7.3

Table A4. Area of inundation and water depths in Area 4 (Lowrie Brown) as a function of water stage, estimated from aerial photogrammetry

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac-ft	Ft
52	5										5	3	0.0
53	31	5									36	23	0.04
54	62	31	5								98	90	0.15
55	190	62	31	5							288	283	0.46
56	125	190	62	31	5						413	634	1.03
57	77	125	190	62	31	5					490	1,085	1.77
58	23	77	125	190	62	31	5				513	1,587	2.58
59	13	23	77	125	190	62	31	5			526	2,106	3.43
60	65	13	23	77	125	190	62	31	5		591	2,665	4.34
61	23	65	13	23	77	125	190	62	31	5	614	3,267	5.32

Table A5. Area of inundation and water depths in Area 2 (Knight North) as a function of water stage, estimated from aerial photogrammetry

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	10-11	11-12	12-13	13-14	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac					Ac	Ac-ft	Ft
51	0														0	0	
52	4	0													4	2	0.0
53	13	4	0												17	13	0.03
54	64	13	4	0											81	62	0.14
55	87	64	13	4	0										168	186	0.44
56	50	87	64	13	4	0									218	379	0.89
57	27	50	87	64	13	4	0								245	611	1.43
58	33	27	50	87	64	13	4	0							278	872	2.05
59	32	33	27	50	87	64	13	4	0						310	1,166	2.74
60	106	32	33	27	50	87	64	13	4	0					416	1,529	3.59
61	10	106	32	33	27	50	87	64	13	4	0				426	1,950	4.58
62	2	10	106	32	33	27	50	87	64	13	4	0			428	2,377	5.58
63	1	2	10	106	32	33	27	50	87	64	13	4	0		429	2,806	6.59
64	1	1	2	10	106	32	33	27	50	87	64	13	4	0	430	3,235	7.59
65	1	1	1	2	10	106	32	33	27	50	87	64	13	4	431	3,666	8.90

Table A5. Area of inundation and water depths in Area 5 (Long Farm) as a function of water stage, estimated from aerial photogrammetry

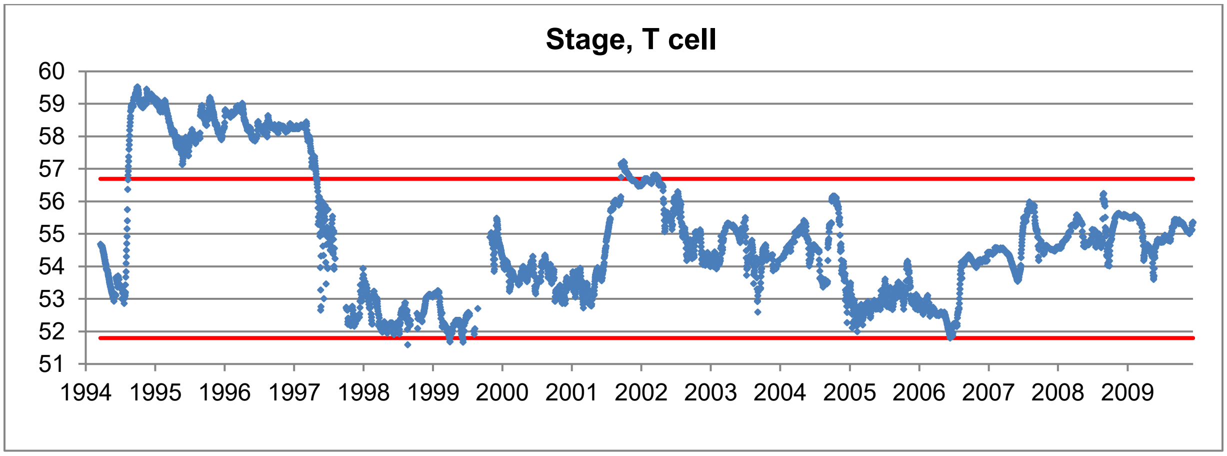
Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac-ft	Ft
51	10										10	5	0.00
52	120	10									130	75	0.06
53	291	120	10								421	351	0.27
54	175	291	120	10							596	859	0.67
55	100	175	291	120	10						696	1,505	1.18
56	83	100	175	291	120	10					779	2,243	1.76
57	116	83	100	175	291	120	10				895	3,080	2.42
58	115	116	83	100	175	291	120	10			1010	4,032	3.16
59	125	115	116	83	100	175	291	120	10		1135	5,105	4.00
60	90	125	115	116	83	100	175	291	120	10	1225	6,285	4.93
61	50	90	125	115	116	83	100	175	291	120	1275	7,535	5.91
62	6	50	90	125	115	116	83	100	175	291	1281	8,813	6.91

Table A6. Area of inundation and water depths in Area 7 (Eustis Muck Farm) as a function of water stage, estimated from aerial photogrammetry

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac-ft	Ft
51	25										25	13	0.02
52	215	25									240	145	0.26
53	130	215	25								370	450	0.81
54	80	130	215	25							450	860	1.54
55	40	80	130	215	25						490	1,330	2.38
56	10	40	80	130	215	25					500	1,825	3.27
57	0	10	40	80	130	215	25				500	2,325	4.17
58	20	0	10	40	80	130	215	25			520	2,835	5.08
59	10	20	0	10	40	80	130	215	25		530	3,360	6.02
60	20	10	20	0	10	40	80	130	215	25	550	3,900	6.99
61	5	20	10	20	0	10	40	80	130	215	555	4,453	7.98
62	2	5	20	10	20	0	10	40	80	130	227	5,566	8.98

Table A6. Area of inundation and water depths in LHCA as a function of water stage, estimated from aerial photogrammetry. Onsite plus offsite areas.

Depth	0-1’	1-2’	2-3’	3-4’	4-5’	5-6’	6-7’	7-8’	8-9’	9-10	10-11	11-12	12-13	13-14	Total	Volume	Mean Depth
Stage	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac					Ac	Ac-ft	Ft
54	0														0	0	0.00
55	220	0													222	111	0.13
56	108	222	0												330	387	0.47
57	65	108	222	0											395	750	0.91
58	89	65	108	222	0										484	1,189	1.44
59	66	89	65	108	222	0									550	1,706	2.07
60	73	66	89	65	108	222	0								623	2,293	2.78
61	34	73	66	89	65	108	222	0							657	2,933	3.56
62	95	34	73	66	89	65	108	222	0						752	3,637	4.41
63	40	95	34	73	66	89	65	108	222	0					792	4,409	5.35
64	32	40	95	34	73	66	89	65	108	222	0				824	5,217	6.33
65	0	32	40	95	34	73	66	89	65	108	222	0			824	6,041	7.33
66	0	0	32	40	95	34	73	66	89	65	108	222	0		824	6,865	8.33
67	0	0	0	32	40	95	34	73	66	89	65	108	222	0	824	7,689	9.33


Stage, T cell
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1994
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2004
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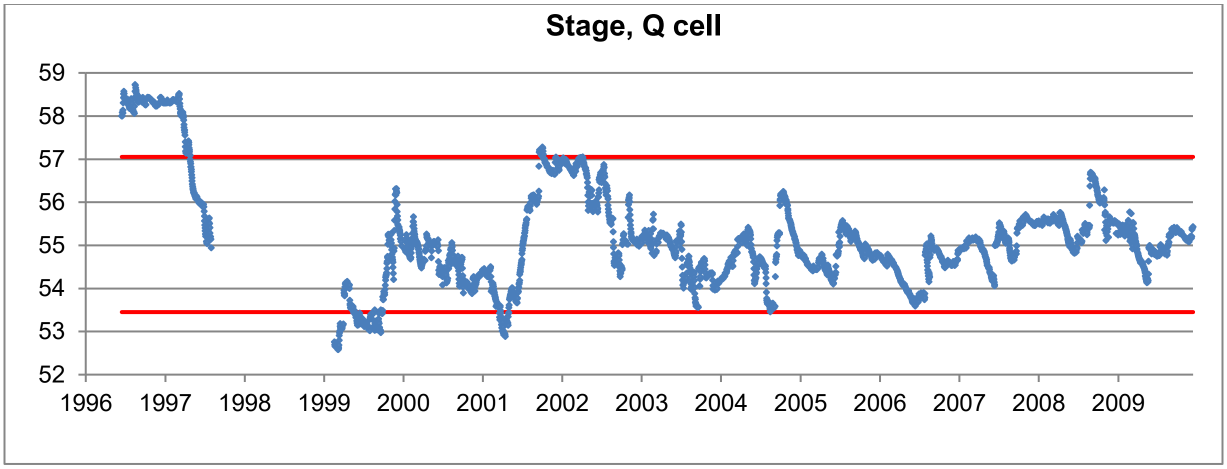
2007
2008
2009


Stage, Q cell
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1996
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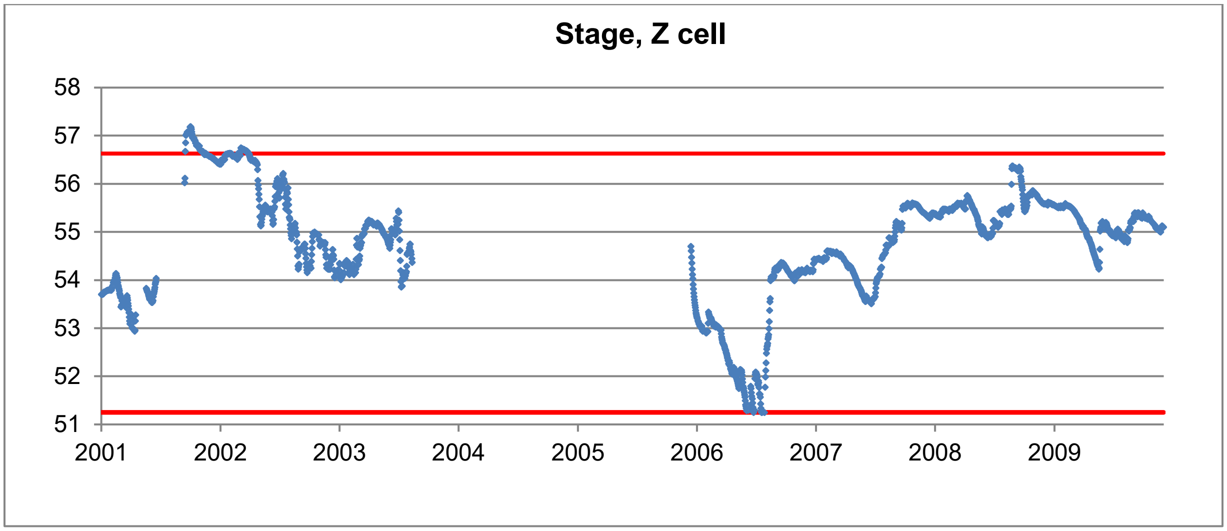
2008
2009


Stage, Z cell
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2001
2002
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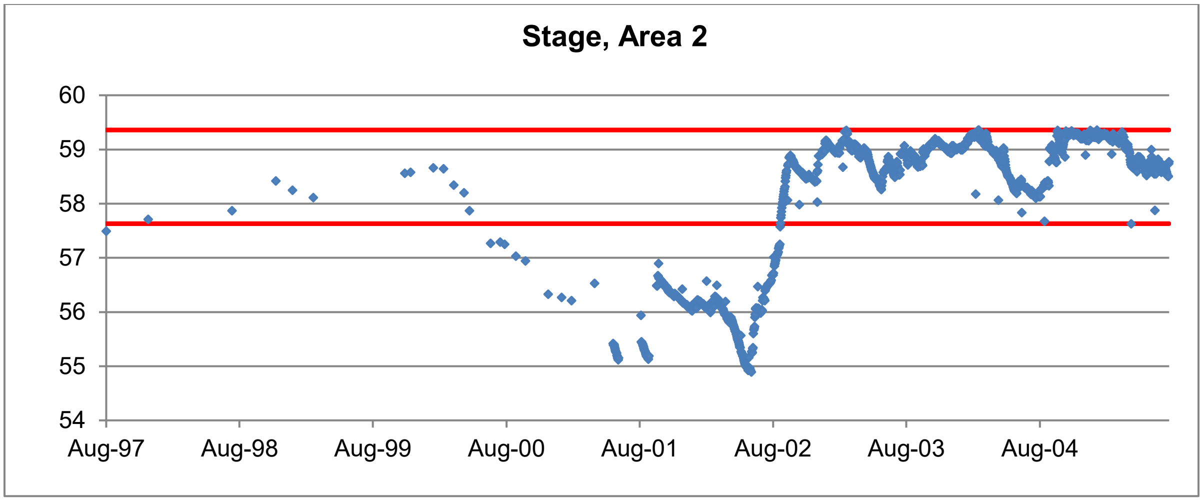
2005
2006
2007
2008
2009


Stage, Area 2
60
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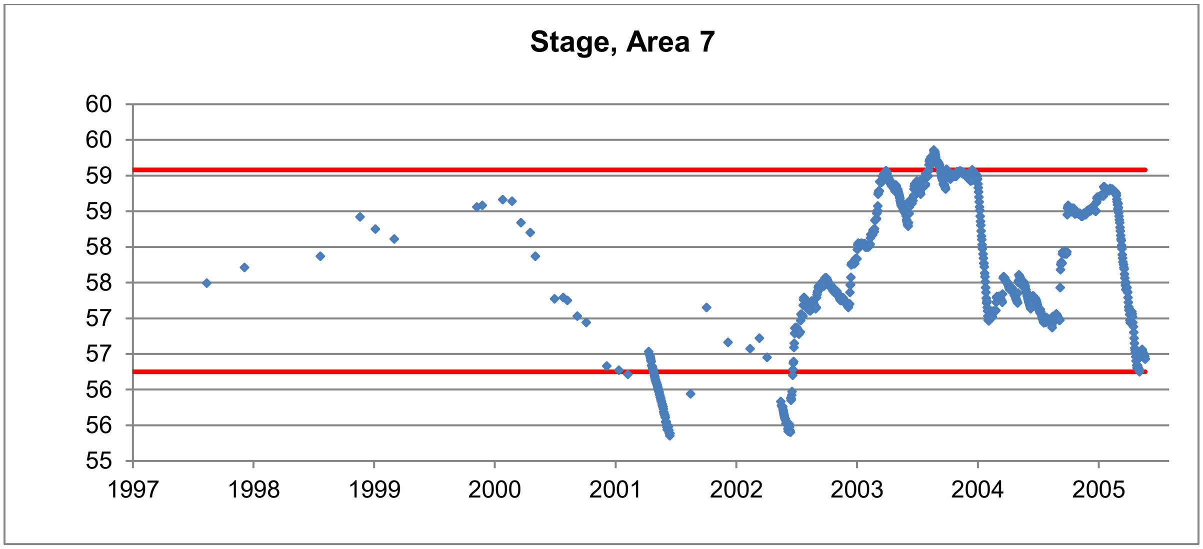
54
Aug-97
Aug-98
Aug-99
Aug-00
Aug-01
Aug-02
Aug-03
Aug-04


Stage, Area 7
60
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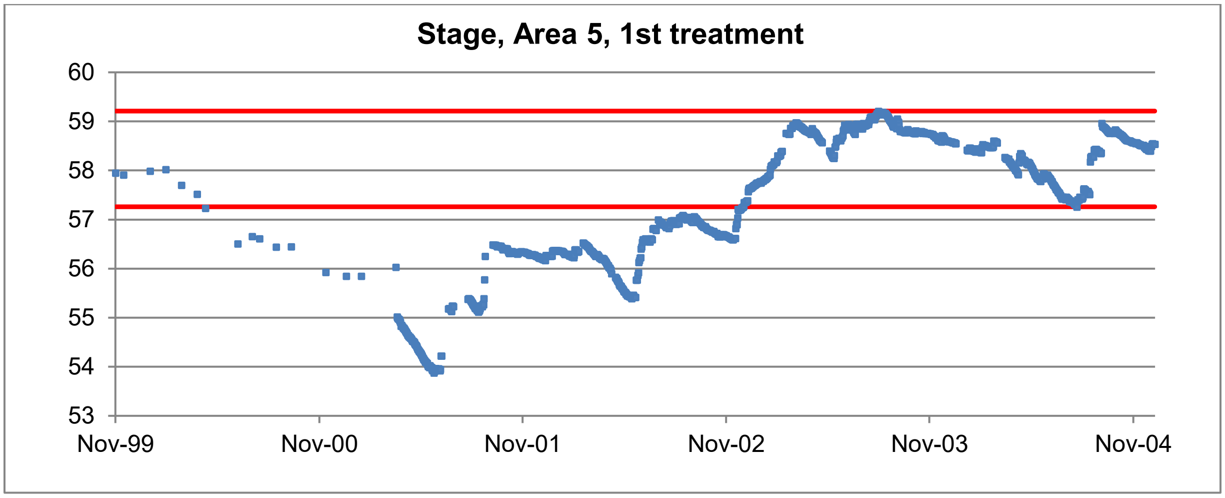
1997
1998
1999
2000
2001
2002
2003
2004
2005


Stage, Area 5, 1st treatment
60
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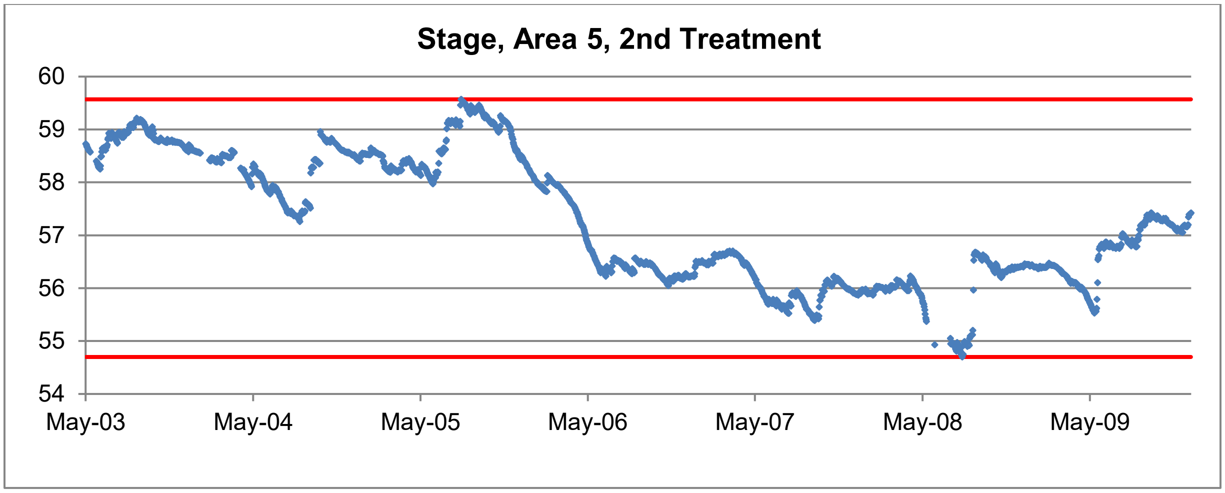
Nov-99
Nov-00
Nov-01
Nov-02
Nov-03
Nov-04


Stage, Area 5, 2nd Treatment
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May-03
May-04
May-05
May-06
May-07
May-08
May-09