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A biological and chemical approach to restoring water quality: A case study in an urban eutrophic pond

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Abstract

Efforts to improve water quality of eutrophic ponds often involve implementing changes to watershed management practices to reduce external nutrient loads. While this is required for long-term recovery and prevention, eutrophic conditions are often sustained through the recycling of internal nutrients already present within the waterbody. In particular, internal phosphorus bound to organic material and adsorbed to sediment has the potential to delay lake recovery for decades. Thus, pond and watershed management techniques are needed that not only reduce external nutrient loading but also mitigate the effects of internal nutrients already present. Therefore, our objective was to demonstrate a biological and chemical approach to remove and

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sequester nutrients present and entering an urban retention pond. A novel biological and chemical management technique was designed by constructing a 37 m² (6.1 m × 6.1 m) floating treatment wetland coupled with a slow-release lanthanum composite inserted inside an airlift pump. The floating treatment wetland promoted microbial denitrification and plant uptake of nitrogen and phosphorus, while the airlift pump slowly released lanthanum to the water column over the growing season to reduce soluble reactive phosphorus. The design was tested at the microcosm and field scales, where nitrate-N and phosphate-P removal from the water column was significant ($\alpha = 0.05$) at the microcosm scale and observed at the field scale. Two seasons of field sampling showed both nitrate-N and phosphate-P concentrations were reduced from 50 $\mu\text{g L}^{-1}$ in 2020 to <10 $\mu\text{g L}^{-1}$ in 2021. Load calculations of incoming nitrate-N and phosphate-P entering the retention pond from the surrounding watershed indicate the presented biological-chemical treatment is sustainable and will minimize the effects of nutrient loading from nonpoint source pollution.

Keywords: Floating treatment wetland (FTW), Slow-release lanthanum, Eutrophication, Water quality, Nitrate-N, Phosphate-P

1. Introduction

Stormwater retention ponds are popular flood control features designed to receive runoff from urban watersheds. As population centers grow, increased urbanization converts natural land to impervious surfaces, increasing stormwater runoff and creating hydrological and water quality challenges (Kang et al., 1998). To meet state water quality requirements, retention ponds are implemented to reduce suspended sediments, fecal coliforms, nutrients, and heavy metals in stormwater (Mallin et al., 2002). These ponds operate by receiving and retaining incoming stormwater runoff long enough for pollutants and suspended sediments to settle out (~24 h) before discharging down gradient to receiving waterbodies within the watershed. As receptors of multiple stormwater events, it is not uncommon for retention ponds to accumulate excess nutrients, such as nitrogen (N) and phosphorus (P), which accelerate eutrophication (Smith and Schindler, 2009). While anoxic conditions eventually lead to nitrate-N ($\text{NO}_3\text{-N}$) loss via denitrification, a similar permanent biological transformation for phosphate-P ($\text{PO}_4\text{-P}$) does not exist. This leads to internal P loading and deterioration of water quality with the associated symptoms of excess vegetative growth, algal blooms, hypoxia, and occasional fish kills due to lowered dissolved oxygen (DO) concentrations and/or toxic algal blooms (Lewitus et al., 2008).

Homeowner associations often contact commercial vendors for assistance as ponds become eutrophic, which generally results in the addition of pond algacides, such as copper sulfate, to kill algal mats. While this offers temporary relief, it only treats the symptoms that excess nutrients in the water column create. Eutrophic conditions are often sustained by the internal re-cycling of nutrients within the waterbody. Internal loading of P in the form of $\text{PO}_4\text{-P}$ release, has been shown to delay lake recovery for years to decades (Cooke et al., 2005; Nürnberg, 2009; Sondergaard et al., 1999). Therefore, innovative biological and chemical management practices are needed to address both external and internal nutrient loadings for long-term water quality improvements. Two technologies known to reduce internal and incoming nutrient loads include floating treatment wetlands (FTWs) and chemical precipitation of $\text{PO}_4\text{-P}$ by the addition of metallic elements such as aluminum or lanthanum (Bishop and Richardson, 2018; Borne, 2014; Epe et al., 2017; Holz and Hoagland, 1999; Huser et al., 2011; White, 2021; Winston et al., 2013).

Floating treatment wetlands (FTWs) utilize native wetland plant species to remove nutrients and other water quality contaminants from impaired waters (Headley and Tanner, 2012). By suspending the plant roots into the water column, FTWs provide water quality treatment in-situ without requiring adjacent land, which is often either unavailable or expensive. Specifically, FTWs remove inorganic forms of nutrients from eutrophic water through various physical and biological processes including filtration, plant uptake, and denitrification (Pavlineri et al., 2017). FTWs may also be combined with activities that promote natural vegetation within and around the pond to facilitate nutrient uptake. FTW designs may vary, but the main design parameters include percent surface water coverage, supporting material to promote buoyancy, and native plant species selection. Determining appropriate FTW size is challenging and uncertain (Headley and Tanner, 2012); however, Borne et al. (2015) determined several smaller FTWs ($1\text{--}3\text{ m}^2$) were more suitable for creating aquatic habitat and one larger FTW ($>50\text{ m}^2$) was preferable for water quality improvement after retrofitting a 500 m^2 retention pond with several FTWs varying in size.

Another method proven to remove excess $\text{PO}_4\text{-P}$ from eutrophic water is lanthanum application (Van Oosterhout and Lürling, 2012; Yamada-Ferraz et al., 2015; Zamparas et al., 2015). Lanthanum is a rare-earth

element found mainly in monazite and bastnaesite, as well as sediments (Emsley, 2011). Lanthanum has a strong affinity to bind with PO_4^{3-} in aquatic environments due to the 1:1 M ratio between La^{3+} and PO_4^{3-} . The resultant compound is lanthanum phosphate (LaPO_4), a fine, white solid, which is very insoluble in water even under anoxic conditions ($K_{sp} = 3.7 \times 10^{-23}$; Dean, 1992). LaPO_4 is more insoluble than aluminum phosphate (AlPO_4 , $K_{sp} = 6.3 \times 10^{-19}$), which is the product of alum treatment. The insoluble LaPO_4 is not useable for plant or algae growth, which makes it suitable for removing PO_4^{3-} from eutrophic water. The most common lanthanum-containing material applied to P-rich waterbodies is lanthanum modified bentonite (LMB). LMB is commercially called Phoslock[®] and was created in the late 1990s by the Commonwealth Scientific and Industrial Research Organization (CSIRO) by replacing other cations in bentonite clay structure with lanthanum (Robb et al., 2003). Phoslock[®] is typically applied directly in a single dose to a waterbody as an aqueous slurry. Many studies have shown Phoslock[®] is an effective method to reduce soluble reactive P (Bishop and Richardson, 2018; Haghseresht et al., 2009; Robb et al., 2003).

Adding lanthanum to attenuate PO_4^{3-} within eutrophic waterbodies is an accepted practice; however, application must be controlled such that acute and chronic toxicity to aquatic organisms is minimized. Previous studies have shown lanthanum binding to PO_4^{3-} is dependent on pH, alkalinity, and the presence of other cations and competing agents (Herrmann et al., 2016). Zhi et al. (2021) observed reduced PO_4^{3-} sorption to lanthanum modified bentonite in water when pH was increased from 6 to 8.5 and natural organic matter content increased from 5.5 to 28.0 mg C L⁻¹.

In general, lanthanum toxicity to aquatic organisms is species specific. Lürling and Tolman (2010) found no detrimental growth effects on *Daphnia magna* in water spiked to a lanthanum concentration of 1000 $\mu\text{g L}^{-1}$. In contrast, Barry and Meehan (2000) observed 50% mortality in *Daphnia carinata* exposed to a lanthanum concentration of 1184 $\mu\text{g L}^{-1}$. Therefore, more research is required to fully assess lanthanum toxicity, both acute and chronic, to aquatic organisms. To avoid high lanthanum concentrations, a slow-release composite was developed for this study where lanthanum concentrations in the water column were routinely maintained below 1000 $\mu\text{g L}^{-1}$.

In this study, our goal was to use a combined biological and chemical

approach to restore the water quality of an urban eutrophic retention pond by removing N and P from the water column by plant uptake, denitrification and precipitation. This was accomplished by constructing a FTW paired with a slow-release lanthanum composite inserted inside an airlift pump. We acknowledge that of the three removal mechanisms, only denitrification removes nitrogen from the whole system (i.e., pond) whereas plant uptake temporarily removes N and P from the water column, and precipitation removes P from the water column by forming an insoluble salt (i.e., LaPO_4). Specific objectives included: (1) Provide proof-of-concept results for this specific biological-chemical approach by running a series of microcosm flow-through experiments that quantified $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ removal rates; (2) Determine the efficacy and longevity of the developed slow-release lanthanum composite to remove soluble reactive phosphorus (SRP) from eutrophic pond water in a pilot-scale mesocosm experiment; (3) Quantify water quality changes following the installation of a full-scale FTW and lanthanum composites during the first and second year of establishment.

2. Materials and methods

2.1. Slow-drip lanthanum chloride microcosm experiment

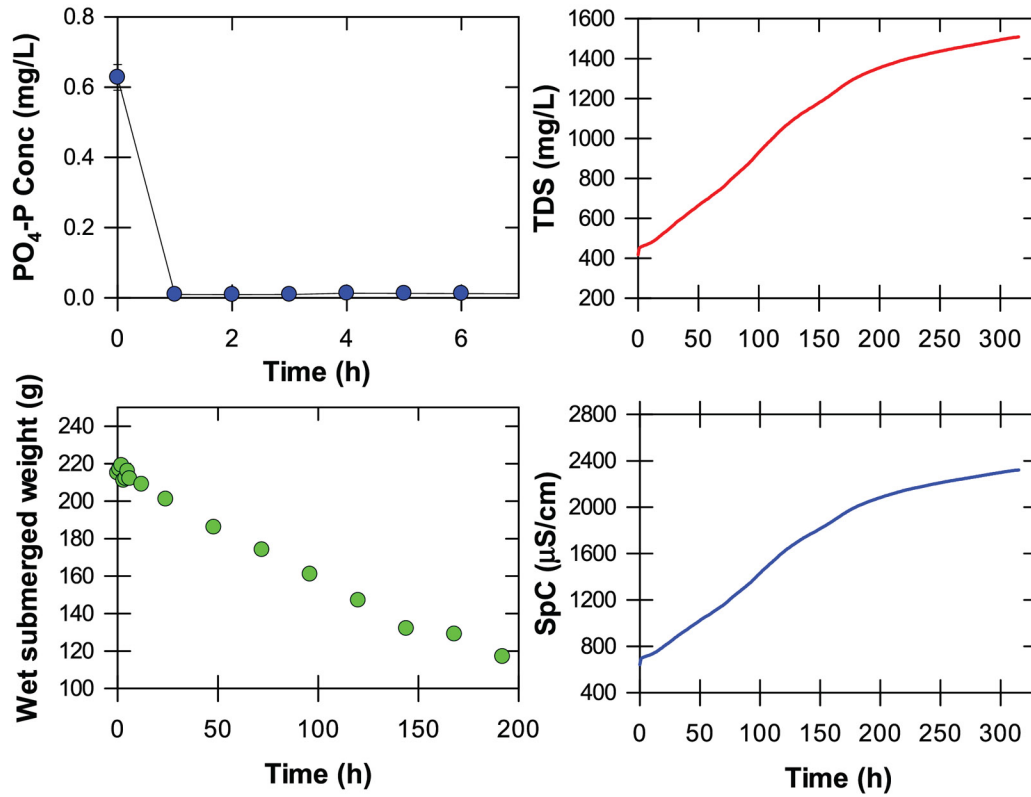
A set of microcosm-scale experiments were conducted to quantify the effectiveness of varying lanthanum chloride (LaCl_3) concentrations on SRP removal at the University of Nebraska-Lincoln (UNL; Lincoln, NE) in the Environmental Chemistry Laboratory. An 18-L microcosm tank was filled with 12 L of water and spiked to $1 \text{ mg PO}_4\text{-P L}^{-1}$ using 0.04 g of anhydrous sodium phosphate monobasic (Sigma-Aldrich, USA). The tank was first mixed via stirring, then aerated by a Sphere Two aquatic aeration pump (Deep Blue Professional, City of Industry, CA) connected via Thermo Scientific (Waltham, MA, USA) polyethylene airline tubing to the bottom of a 3.175 cm (OD) submerged PVC screen. Air was bubbled inside the PVC screen to create an airlift pump. The rising air bubbles created a buoyancy force within the microcosm tank that caused water to exit the top of the PVC screen and enter at the bottom. This circulation pattern was similar to what was observed at the field-scale with an airlift pump placed in the retention pond.

Three LaCl_3 solutions were prepared for the slow-drip experiment (0.47, 1.4, and 4.2 mg $\text{LaCl}_3 \text{ L}^{-1}$). The solutions were prepared using ultrapure water and LaCl_3 salt. The LaCl_3 solutions were dripped into the microcosm tank using a peristaltic pump (Thermo Fisher Scientific, Waltham, MA, USA) at 1 rpm, which resulted in a delivery rate of 8.3 mL h^{-1} . Samples were collected at 0, 2, 4, 6, 8, 10, 12, 24, and 30 h. SRP samples were filtered using a 0.45- μm filter paper and analyzed using an AQ300 discrete autoanalyzer (SEAL Analytical Inc., Mequon, WI, USA) using EPA method 145-D Rev. A.

2.2. Lanthanum composite mesocosm experiment

A second experiment was conducted to determine the efficacy and longevity of the developed slow-release lanthanum composite to remove SRP from eutrophic pond water and monitor changes in water quality parameters. A 208-L barrel was filled with 189 L (50 gallons) of tap water and spiked to an SRP concentration of 0.70 mg P L^{-1} using anhydrous sodium phosphate monobasic (Sigma-Aldrich, St. Louis, MO). The barrel was thoroughly mixed and then aerated using an airlift pump (height 0.70 m, diameter 7.6 cm) connected to an air compressor set at 4.0 L min^{-1} . The P solution in the barrel was mixed for 72 h before adding the lanthanum composite. A LaCl_3 wax composite was manufactured with a 3:2:1 (w/w) composition of 411 g LaCl_3 , 274 g paraffin wax, and 137 g fine sand. The composite was secured in plastic netting and hung into the screened PVC pipe, where air and water movement produced by the airlift pump facilitated lanthanum dispersal (**Fig. 1B**). Water samples were collected for SRP analysis at 0, 1, 2, 3, 4, 5, 6, 12, and 24 h. SRP samples were processed and analyzed as previously described. A YSI Sonde EXO2 (YSI Inc., Yellow Springs, Ohio, USA) was deployed at a depth of 0.30 m to measure specific conductivity (SpC; $\mu\text{S cm}^{-1}$), oxidation-reduction potential (ORP; mV), and total dissolved solids (TDS; mg L^{-1}) in 1 h intervals (**Fig. 1B**). A 500 g, mechanical hanging scale (OHAUS, Parsippany, NJ, USA) was utilized to monitor temporal mass loss from the composite into the water column (**Fig. 1B**).

A



B

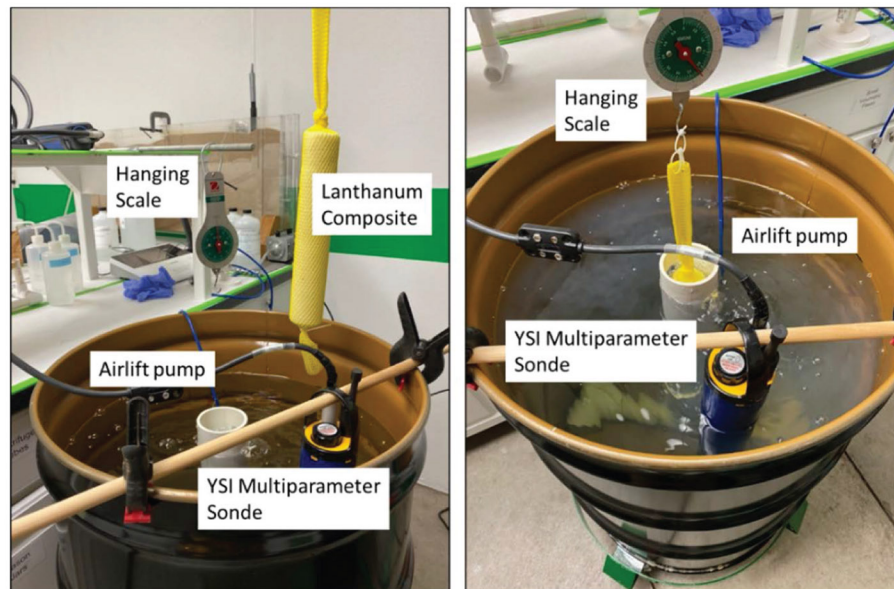


Fig. 1. (A) Temporal changes in soluble reactive phosphorus (SRP) concentrations, water quality parameters, and wet submerged weight during treatment of 189 L of phosphate solution (0.70 mg P L⁻¹) with slow-release lanthanum composite. (B) Photographs of mesocosm experiments.

2.3. Flow-through experiment

The experimental setup for the flow-through experiment (**Fig. 2A, 2B**) mimicked two treatments applied in the field-scale demonstration (i.e. FTW and the slow-release lanthanum composite), but allowed $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ removal rates to be isolated between each design component. Pond water was collected from the Densmore Pond in Lincoln, Nebraska in March 2021. Initial background nutrient concentrations of the pond water were quantified and found to be $0.1 \text{ mg NO}_3\text{-N L}^{-1}$ and 0.01 mg

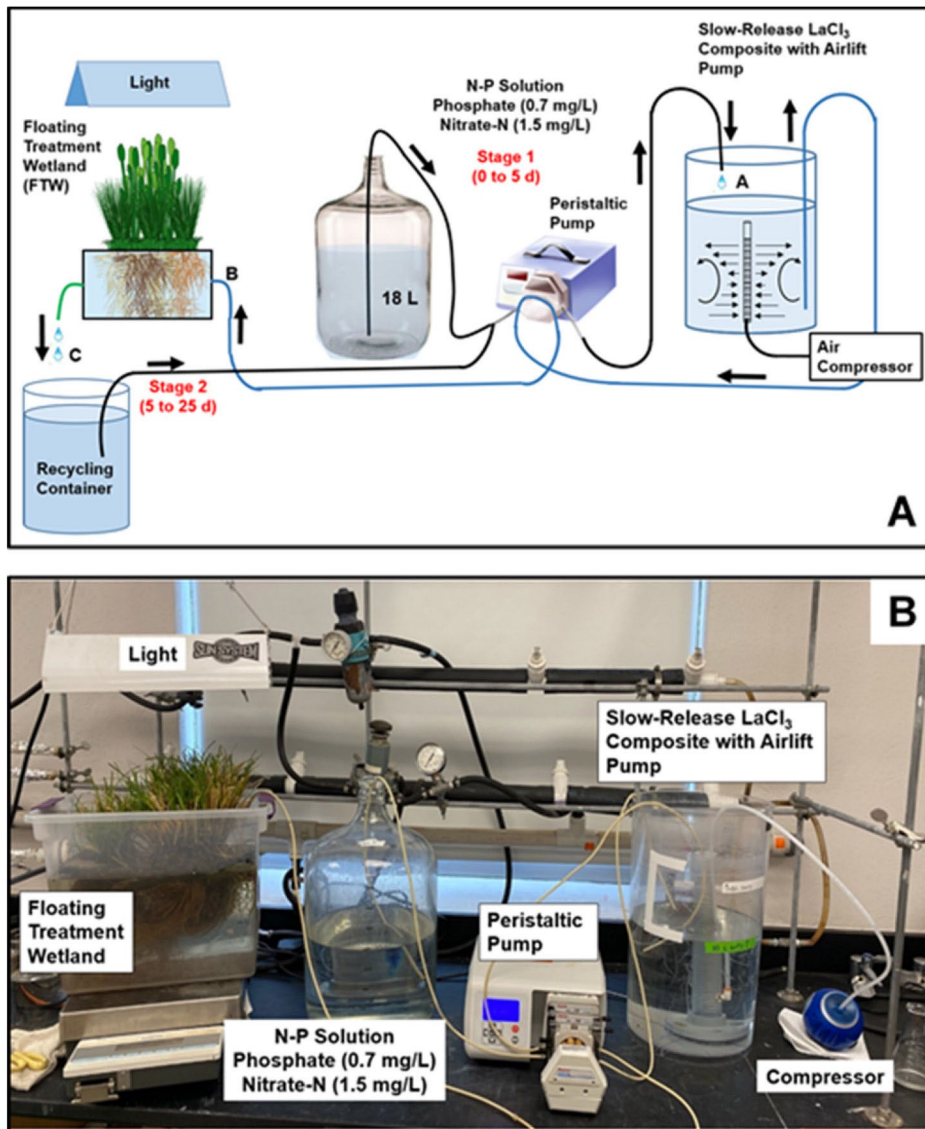


Fig. 2. (A) Schematic and (B) photograph of experimental setup of flow-through experiments.

$\text{PO}_4\text{-P L}^{-1}$. The experimental setup consisted of three 20-L tanks, each filled with 18 L of pond water. The pond water in each tank was spiked to a target $\text{NO}_3\text{-N}$ concentration of 1.5 mg L^{-1} , using potassium nitrate (KNO_3 ; LabChem, USA), and a target $\text{PO}_4\text{-P}$ concentration of 0.7 mg L^{-1} , using anhydrous sodium phosphate monobasic (NaH_2PO_4 ; Sigma-Aldrich, USA). Once the pond water was spiked, the tanks were connected with Thermo Fisher Scientific polyethylene tubing and allowed to mix with a peristaltic pump (Fig. 2A, 2B) for 24 h prior to experimentation.

To remove the $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ nutrients from the water column, a chemical-biological treatment system was imposed as follows: solution from the nutrient tank containing the spiked pond water flowed through a peristaltic pump into a second tank containing an aerated slow-release lanthanum composite. The lanthanum composite consisted of LaCl_3 , sand and paraffin wax in a 3:2:1 (w/w) ratio. The initial mass of the lanthanum composite was 12.06 g. The composite was inside a submerged PVC screen (height 0.30 m, diameter 3.6 cm) that was aerated at the base with a Sphere Two aquatic aeration pump (Deep Blue Professional, City of Industry, CA, USA), creating continuous circulation within the tank. Solution from the lanthanum tank was then pumped to a FTW tank, which contained a 2 year old, fully matured fox sedge (*Carex vulpinoidea*) monoculture suspended on a foam buoyant mat (Beemats LLC; New Smyrna Beach, FL, USA). The FTW covered approximately 25% of the water tank surface area.

The three tanks were connected in series by a multichannel cartridge pump (Thermo Fisher Scientific; Waltham, MA, USA), which recirculated water at a rate of 150 mL h^{-1} (Fig. 2A, 2B). The recirculation time of each tank was 5 d (120 h). The experiment was completed in two stages. During Stage 1, water was pumped from the nutrient tank and samples were collected once per day for 5 d after exiting each tank (sampling locations are labeled A, B, C, Fig. 2A). At each sampling point, 15 mL samples were collected in triplicates from the outlet (i.e., sampling points A, B, C) for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ analysis. Solution exiting the FTW was collected in an empty container, which, after 5 d, Stage 2 began where the collected water was circulated back into the lanthanum tank. Samples were then collected each day at collection points A, B, and C for an additional 20 d until nutrient concentrations were below detection. All nutrient samples were analyzed using an AQ300 (SEAL Analytical Inc., Mequon, WI, USA) using methods previously described.

2.4. Field site

2.4.1. Field site description

The field-scale FTW and lanthanum treatment system was constructed and installed in June 2020, and expanded in 2021 (two FTWs, two airlift pumps). The field study was located at the Densmore Pond within Densmore Park (Lincoln, NE). The 0.5 ha (1.25 acre) pond was designed in 1998 by Olsson Associates (Lincoln, NE, USA) and constructed in 2002 to attenuate runoff coming from a 55.4 ha (137 ac) urban watershed. The average depth of the Densmore Pond was 1.3 m. Majority of the contributing watershed area resided within the Lincoln Memorial Cemetery located east of Densmore Pond (Fig. SM1). Densmore Pond was designed to handle 100-year storms (i.e., 1% annual probability of occurring) and drains to a 0.9-m diameter, 48-m length culvert located in the northwest corner. Located in a humid continental climate zone, air temperatures at Densmore Pond ranged from $-35.0\text{ }^{\circ}\text{C}$ to $39.4\text{ }^{\circ}\text{C}$ in 2020 and 2021.

In addition to stormwater storage and treatment, Densmore Pond is a popular recreational destination for locals. Lincoln Southwest High School, located <1 km from Densmore Pond, offers an introduction to fishing course taught on-site at Densmore Pond. Known fish species within the pond include Amur carp (*Cyprinus rubrofuscus*), bluegill (*Lepomis macrochirus*), and largemouth bass (*Micropterus salmoides*). Densmore Pond is adjacent to the Rock Island Bike Trail, a popular bike path. Migratory waterfowl species (i.e., geese and ducks) are commonly found in the water or on the banks of the Densmore Pond.

2.4.2. Airlift pump construction and installation

One of the main components of the treatment design was deploying an airlift pump at the Densmore Pond. Airlift pumps are historical devices (circa 1800) proven to be a reliable and low maintenance method for recirculating liquids (Hanafizadeh and Ghorbani, 2012; Yoshinaga and Sato, 1996). In its simplest form, a compressor is used to inject air into the bottom of a submerged pipe and because air has a lower density than liquid water, it rises and creates a circulation pattern around the submerged pipe with water exiting the top and entering at the bottom. The airlift pump was designed by AirLift Environmental LLC (Lincoln, NE),

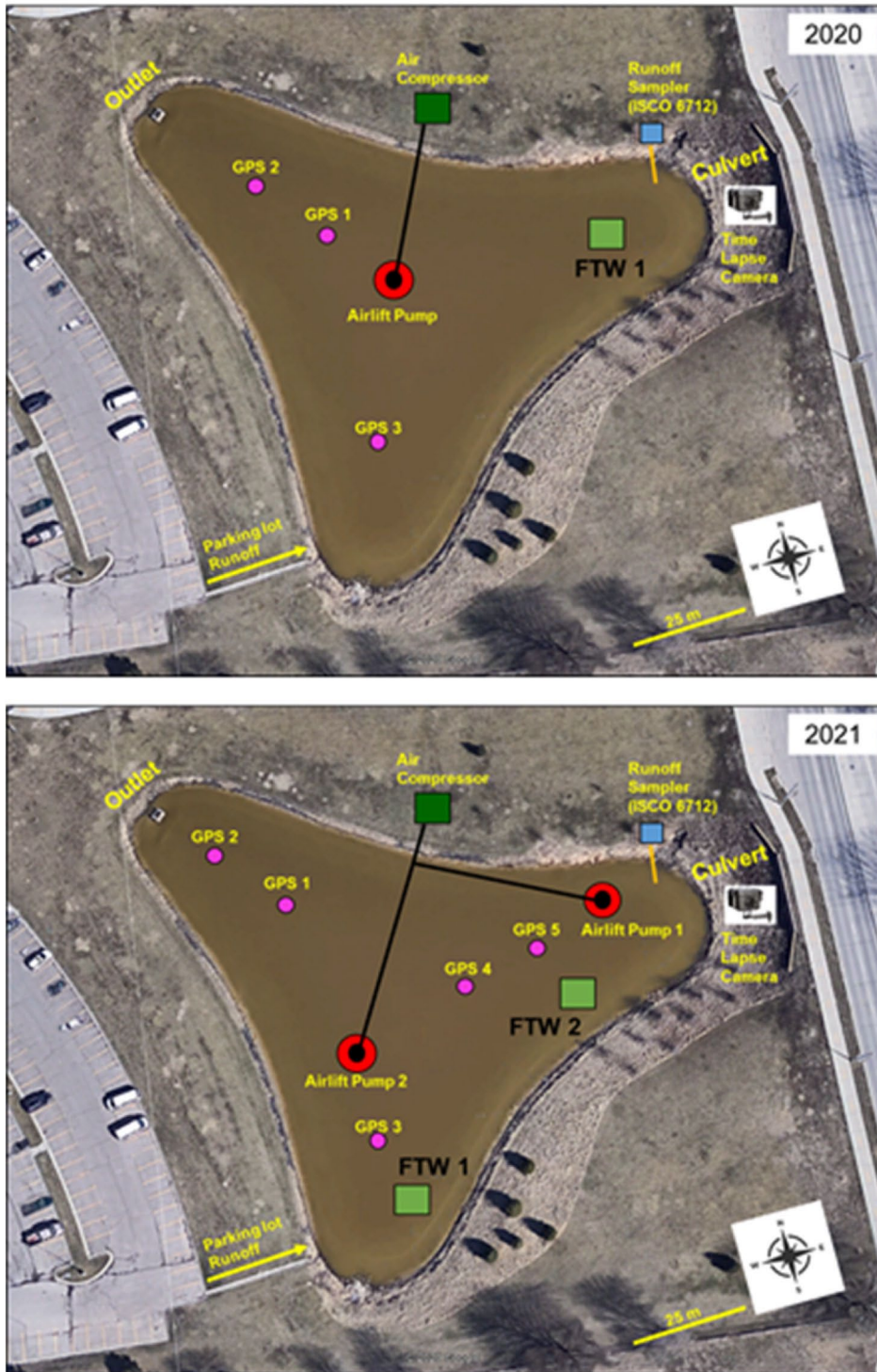


Fig. 3. Denmore Pond infrastructure in 2020 and 2021, including sampling locations. FTW – floating treatment wetlands; GPS – water sampling locations.

and donated to UNL for experimental use. Air supply was provided by a ½ HP, 115v air compressor which was connected to the airlift pump by 15 m of weighted 1.9 cm (ID) airline tubing (Pentair Aquatic Eco-Systems, Inc., Apopka, FL, USA). Lanthanum salts (2020) and lanthanum composites (2021, Fig. SM2) were inserted inside the top of the airlift and replaced on a weekly (2020) and monthly (2021) basis. The rising air bubbles around the lanthanum composite created a continuous circulation flow pattern that facilitated the spreading of the lanthanum and oxygenated water throughout the pond.

2.4.3. Lanthanum addition

Lanthanum was added to the Densmore Pond in 2020 from June through October in varying compositions and amounts using both LaCl_3 and lanthanum sulfate ($\text{La}_2(\text{SO}_4)_3$) (Fig. SM3). Variations in compositions included the type of binding agent (wax, starch, or oil), mass of sand and ratios used. Increased water and air movement created by the airlift pump facilitated lanthanum dispersion throughout the pond but in 2020 the initial lanthanum compositions fabricated did not last long and required new lanthanum compositions be added on a weekly to biweekly basis (Fig. SM3). In total, 10.23 kg of $\text{La}_2(\text{SO}_4)_3$ and 2.52 kg of LaCl_3 was added to the Densmore Pond in 2020, which resulted in 6.45 kg of elemental lanthanum addition. In 2021, improvements to the lanthanum composite were made using a 3:2:1 (w/w) ratio of LaCl_3 , wax and sand. This composition was molded into 5.08 cm diameter cylinders (30 cm length) that were easy to deploy inside the airlift pump (Fig. SM2, SM4). The total mass of each lanthanum composite was approximately 822 g, of which 411 g was LaCl_3 . Lanthanum release was found to be more sustained from the 2021 lanthanum composition, with lanthanum being released for several weeks (details provided in Sec. 3.2).

2.4.4. FTW construction and installation

The field-scale FTW was constructed and installed on June 23, 2020. All FTW plants were purchased from the Nebraska Statewide Arboretum (Lincoln, NE) as seedlings and were native to the region. Each of the plants were added to aerator pots with additional potting soil. Taller plants (i.e. softstem bulrush) were placed in the center of the FTW, while

sedges and flowering species were placed near the edges to maximize the visual aesthetic of the FTW and not shade shorter vegetation. The FTW was anchored using two 9.1 kg boat anchors. In 2021, a second FTW of identical dimensions was planted on May 21, 2021.

In 2020, a variety of native plant species were used to determine which plant species would have the greatest survival rate following winters in the upper Midwest region of the United States (U.S.). The 13 species used in the FTW included Helen's flower (*Helenium autumnale*), Culver's root (*Veronicastrum virginicum*), tussock sedge (*Carex stricta*), spotted joe-pye weed (*Eupatorium maculatum*), fringed sedge (*Carex crinita*), obedient plant (*Physostegia virginiana*), New England aster (*Aster novae-angliae*), longhair sedge (*Carex comosa*), swamp milkweed (*Asclepias incarnata*), Frank's sedge (*Carex frankii*), soft-stem bulrush (*Schoenoplectus tabernaemontani*), monkey flower (*Mimulus ringens*), and blue flag iris (*Iris shrevei*). In 2021, only species that survived over the 2020 winter were used in replanting, which included tussock sedge, fringed sedge, longhair sedge, Frank's sedge, and soft-stem bulrush.

2.4.5. Water-quality sampling at field site

Water quality samples were collected in 2020 from June 29 to October 19. Five locations were distinctly positioned throughout the pond and marked using anchored buoys to create representative sampling points for weekly sampling, which were accessed by kayak (**Fig. 3**). These sampling points were labeled Airlift Pump, FTW, GPS 1, GPS 2, and GPS 3. The three GPS (Global Positioning System) points were spaced throughout the treatment pond, with GPS 1 closest in proximity to the airlift pump, and GPS 2 and GPS 3 further away from the airlift pump in opposing directions.

Water-quality grab samples were collected from the designated sample points by using 125-mL high-density polyethylene (HDPE) sample bottles at a depth of 0.3 m. Each sample bottle was rinsed three times prior to sampling. In order to collect water samples from underneath the FTW, an Arnold siphon pump kit was utilized to pump 100 mL of water through each portion of the polyethylene (PE) tubing into 125 mL HDPE sampling bottles. The PE tubing was rinsed for 5 s via the siphon pump kit prior to sample collection. All water quality grab samples were

transported to the laboratory refrigerator until sample analysis could be performed. Water quality samples were assessed for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ using procedures previously described.

An additional set of grab water quality samples were collected weekly from the Airlift Pump, GPS 1, and GPS 2 sampling points throughout the field season to be analyzed for lanthanum concentration. Lanthanum water quality grab sampling began on June 23, June 29, and August 3 for the Airlift Pump, GPS 1, and GPS 2, respectively. One hundred mL samples were collected using 125-mL HDPE sample bottles at a depth of 0.3 m. The samples were then returned to the laboratory, preserved with concentrated nitric acid (HNO_3 , J.T. Baker, USA), and refrigerated at 4 °C until sample analysis was performed. All lanthanum water sample analysis was performed by the Water Sciences Laboratory at UNL using an iCAP RQ ICP-MS (Thermo Scientific, Waltham, MA, USA) using EPA method 6020.

During each sampling event from July 6 to October 19, 2020, water temperature (°C), pH, DO concentration (mg L^{-1}), SpC ($\mu\text{S/cm}$), and ORP (mV) were measured at field sample locations using a YSI quatro ProDSS Multiparameter water quality meter (YSI Inc.; Yellow Springs, Ohio). The water quality meter was consistently deployed at a depth of 0.3 m. A Secchi disk was also used weekly from July 27 to October 19, 2020 to measure water turbidity.

Weekly water quality sampling was reinitiated after the pond thawed in 2021 from April 5 to June 28. Two additional sampling locations labeled GPS 4 and GPS 5 were added to quantify lanthanum concentrations in water following lanthanum composite addition and to measure nutrient concentrations in response to the treatment (Fig. 3). Water-quality parameter measurements and Secchi disk depth measurements were continued as well.

2.4.6. FTW plant sampling and analysis

Plant tissue analysis was conducted at the end of the growing season in October 2020 to determine nutrient uptake (mass in g) of both nitrogen and phosphorus for the various FTW plant species. A destructive harvest was performed for eight plant species, where biomass was oven dried then separated into aboveground (i.e. above Beemat) biomass (shoots and flowers [if applicable]) and belowground biomass (roots). The plant

tissue samples were sent to Ward Laboratories (Kearney, NE, USA) for total nitrogen (TN) analysis using the Dumas Combustion Method (Sweeney, 1989) and total phosphorus (TP) content using inductively coupled plasma optical emission spectrometry (ICP-OES). The %N and %P values obtained via plant tissue analysis were multiplied by the dry biomass weight for the above- and below-ground biomass samples for each plant species and the number of planted species in the FTW to determine total nitrogen and total phosphorus mass uptake in the FTW.

2.4.7. Runoff sampling

To determine the mass load of nutrients entering the Densmore Pond via runoff, an ISCO 6712 auto sampler (Teledyne, Inc., Lincoln, NE, USA) was installed near the inlet of the pond in June 2020. The auto sampler was used in conjunction with an ISCO 674 rain gauge (0.01-Inch Tip) which triggered the auto sampler to begin collecting samples during rain events. The ISCO 6712 was programmed to collect 12–500 mL water samples sequentially in 12 min increments immediately after being triggered by 0.254 cm of rainfall within 1 h. Details of runoff collection procedures and curve number methods used to estimate nutrient mass inputs from runoff are provided in supplementary materials (SM).

2.5. Statistics

A one-way analysis of variance (ANOVA) using Minitab® 20.2 was used to determine differences in $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ removal rates as affected by FTW, lanthanum addition, and combined treatment strategies within flow-through experiments ($\alpha = 0.05$). A Tukey's range test was also conducted to differentiate $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentration means by sampling location (Nutrient tank, FTW tank, Lanthanum tank).

3. Results and discussion

3.1. SRP removal via slow-drip lanthanum chloride solutions

To mimic the release of lanthanum from the lanthanum composite inside the airlift pump, lanthanum chloride was slowly dripped into a

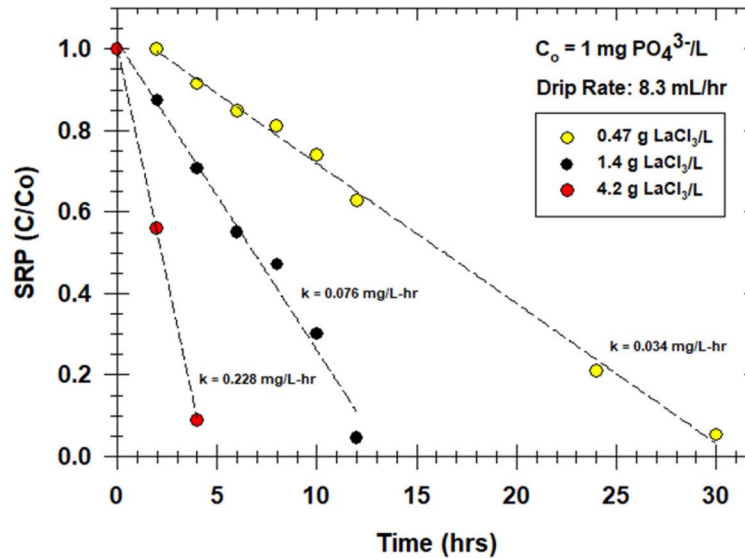


Fig. 4. Temporal changes in soluble reactive phosphate (SRP) following slow drip additions of LaCl_3 .

circulating airlift pump under laboratory conditions. SRP removal followed zero-order kinetics for each of the three lanthanum chloride solutions (**Fig. 4**). The observed rate constants for three different LaCl_3 concentrations were: $0.034 \text{ mg L}^{-1} \text{ h}^{-1}$ ($0.47 \text{ mg LaCl}_3 \text{ L}^{-1}$), $0.076 \text{ mg L}^{-1} \text{ h}^{-1}$ ($1.4 \text{ mg LaCl}_3 \text{ L}^{-1}$), and $0.228 \text{ mg L}^{-1} \text{ h}^{-1}$ ($4.2 \text{ mg LaCl}_3 \text{ L}^{-1}$). As expected, the use of higher lanthanum concentrations resulted in faster SRP removal from the water column. Lanthanum concentrations in the microcosm tank at the completion of the three experiments ranged from 500 to $6880 \mu\text{g L}^{-1}$, demonstrating slowly released lanthanum additions could remove SRP within a few days from P-rich water.

3.2. Lanthanum composite mesocosm experiment

Lanthanum chloride is extremely soluble (957 g L^{-1} at 20°C) and hygroscopic. Thus, controlling LaCl_3 release in water is challenging. By coating LaCl_3 with paraffin wax and including sand for strength, a workable solid lanthanum composite was developed that could be easily inserted into the airlift pump (Figs. SM2, SM4). Lanthanum release was quantified from a 30.5-cm length, 5-cm diameter cylinder in a 208-L barrel.

Lanthanum addition via the slow-release LaCl_3 composite reduced $\text{PO}_4\text{-P}$ concentrations in the barrel from 0.63 to 0.01 mg L^{-1} (98% removal) in 1 h (Fig. 1A). Lanthanum chloride was consistently released from the slow-release composite over the first 200 h (8.3 d) as indicated by a zero-order decrease in wet mass measured by the hanging scale (Fig. 1A). Wet submerged weight of the lanthanum chloride composite decreased from 215 g to 117 g by day 8 of the experiment, equivalent to 12.25 g d^{-1} . This mass loss rate is similar to what we observed from the lanthanum composites placed in the airlift pump in the pond, where individual 30-cm length, 5 cm-diameter lanthanum composites containing 411 g of LaCl_3 consistently released approximately 75% of their initial weight in 28 d. Assuming the majority of the weight loss was due to LaCl_3 dissolution (~ 308 g in 28 d), this rate was approximately 11 g d^{-1} . YSI Sonde EXO2 measurements of TDS and SpC increased over time as lanthanum was released (Fig. 1A). As observed with the wet weight measurement (i.e., zero-order rate), both water quality parameters increased linearly for the first 200 h then eventually slowed (Fig. 1A). Changes in TDS and SpC rates after 200 h were likely indicative of less LaCl_3 mass being released due to increased porosity paths created as the dissolving front of the LaCl_3 receded into the core of the composite.

Combining a lanthanum composite with an airlift pump offers an alternative to the widely used lanthanum modified bentonite (LMB), which is generally applied as a single dose. Many researchers have studied LMB with positive results, which has increased public acceptance of this chemical approach (Copetti et al., 2016; Dithmer et al., 2016; Kuroki et al., 2014; Robb et al., 2003; Spears et al., 2013, 2016). An advantage of the slow-release composite was that it provided steady, low concentrations of lanthanum to the water column, which allowed lanthanum to bind with reactive phosphates during both runoff events or through the seasonal mineralization of organic P (i.e. decaying plants, organic matter, weeds or algae; Holz and Hoagland, 1999). Likewise, in the event lanthanum concentrations increased beyond desired thresholds, the lanthanum composites can be easily removed from the airlift pump to stop further distribution.

3.3. Flow-through experiment

To quantify $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ removal rates from the combined biological and chemical treatments, a flow-through experiment was designed

to monitor nutrient concentrations entering and exiting the FTW and lanthanum tanks (Fig. 2A, 2B). Stage 1 of the flow-through experiment steadily pumped a constant N and P source ($0.7 \text{ mg PO}_4\text{-P L}^{-1}$ and $1.5 \text{ mg NO}_3\text{-N L}^{-1}$) for 5 d. $\text{PO}_4\text{-P}$ concentrations in the lanthanum tank decreased from 0.62 mg P L^{-1} to 0.01 mg P L^{-1} within 24 h (98% removal, **Fig. 5**). $\text{PO}_4\text{-P}$ concentrations before and after the FTW tank (Sampling points B, C, Fig. 2A) decreased from 0.64 mg P L^{-1} to 0.14 mg P L^{-1} (78% removal, Fig. 5) over 5 d. This decrease was attributed to mostly dilution coming from the lanthanum tank and minimal plant uptake. Control flow-through experiments isolated the individual contributions of

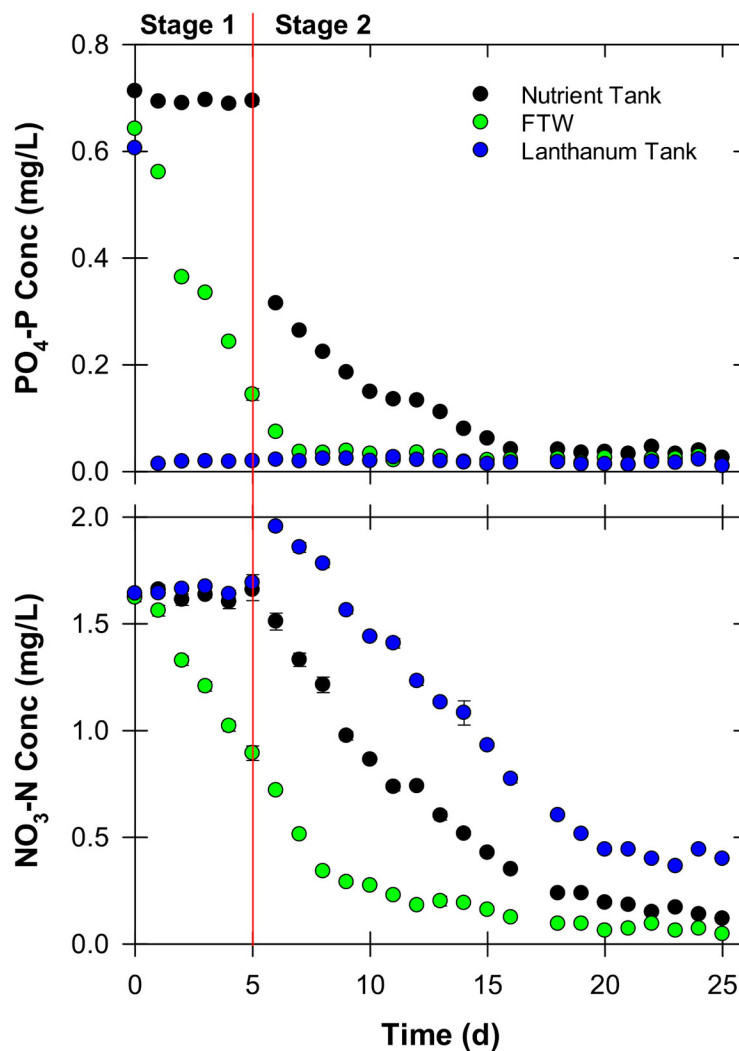


Fig. 5. $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ removal for combined FTW/Lanthanum addition flow-through experiment.

the FTW and lanthanum additions also support that the lanthanum was largely responsible for SRP removal while the FTW plants showed minor, yet significant ($p < 0.001$) decreases in P (Fig. SM5).

Changes in $\text{NO}_3\text{-N}$ concentrations during Stage 1 of the flow-through experiment were also significant ($p < 0.001$). $\text{NO}_3\text{-N}$ in the FTW tank significantly decreased from 1.62 mg L^{-1} to 0.89 mg L^{-1} (45% removal, Fig. 5) after 5 d. The $\text{NO}_3\text{-N}$ removal mechanisms included both plant uptake and denitrification. $\text{NO}_3\text{-N}$ was not significantly removed from the lanthanum tank during Stage 1 in the control treatments ($p = 0.878$) (Fig. 5; Fig. SM5). Moreover, both $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ concentrations in the nutrient tank remained constant when no treatment strategy was employed.

Messer et al. (2017) reported microbial denitrification was likely a key removal process in FTWs, accounting for approximately 60% of $\text{NO}_3\text{-N}$ removal after 10 d in a mesocosm-scale investigation. Conditions facilitating denitrification include a near-neutral pH (6–8), warmer water temperature, the presence of $\text{NO}_3\text{-N}$, readily available organic matter for a carbon source, and anaerobic conditions to allow facultative anaerobes to thrive (Burchell et al., 2007; Hefting et al., 2005; Rust et al., 2000). Despite the general belief that denitrification is the main driver for nitrate removal, there are few studies that have compared $\text{NO}_3\text{-N}$ removal in FTWs via plant uptake versus microbial denitrification. Gao et al. (2018) used a mass balance approach to report majority of observed TN removal ($C_{\text{in}} = 14.5 \pm 1.2 \text{ mg N L}^{-1}$) using an FTW was a result of thiosulfate-driven denitrification, whereas Keizer-Vlek et al. (2014) used a similar mass balance approach and found plant uptake (*Iris pseudacorus*) played a major role in TN (74%) and TP (60%) removal. However, Keizer-Vlek et al. (2014) also noted that reduced oxygen concentrations under the FTW likely played a key role in facilitating denitrification.

Lynch et al. (2015) evaluated removal of N and P from stormwater by two commercial floating wetland systems and reported between 25 and 40% TN removal and 4–48% TP removal. Differences in TN removal between these three studies may have been result of plant species selection, influent nutrient concentrations, FTW water surface coverage, or thiosulfate addition (Gao et al., 2018).

In Stage 2 of the flow-through experiment, water collected from the FTW was recycled through the system several times from 5 to 25 d (Fig. 2A). At the end of Stage 1, $\text{PO}_4\text{-P}$ concentrations were already reduced in the lanthanum tank (0.03 mg P L^{-1}) and FTW (0.14 mg P L^{-1}). However,

the recycled water had higher $\text{PO}_4\text{-P}$ concentrations, which decreased from 0.69 mg P L^{-1} to 0.03 mg P L^{-1} (96% removal; Fig. 5) once recycled back through the system (5–25 d). $\text{PO}_4\text{-P}$ concentration reduction was attributed to both dilution and sorption to lanthanum from the lanthanum and FTW tanks, which were connected in series. $\text{NO}_3\text{-N}$ removal was observed in all three tanks during Stage 2. $\text{NO}_3\text{-N}$ removal in the FTW tank from 0 to 25 d was fit to a first order rate expression ($R^2 = 0.98$) where the first order rate constant, k , was 0.165 d^{-1} . Similarly, Keilhauer et al. (2019) reported a first order rate constant, k , of $0.12 \pm 0.08 \text{ d}^{-1}$ for $\text{NO}_3\text{-N}$ removal within a mesocosm study using a FTW planted in common rush (*Juncus effusus*) and Torrey's rush (*Juncus torreyi*). Wang and Sample (2013) developed a unique, first-order kinetics model to assess FTW nutrient removal performance. The model was calibrated using 71 nutrient concentration time series data sets across ten studies and observed an R^2 value of 0.78 ± 0.42 for TN removal. The authors ultimately determined that first-order kinetics was satisfactory for predicting FTW nutrient removal performance. $\text{NO}_3\text{-N}$ removal from the lanthanum and nutrient tanks followed a similar first order rate expression during Stage 2 as spiked pond water continued to flow through the FTW tank and recycle back through the system.

The $\text{NO}_3\text{-N}$ concentration of the water collected in the recycling contained had an initially higher concentration ($0.3\text{--}0.4 \text{ mg N L}^{-1}$) than the original source water of the nutrient tank. We attribute this to the mineralization of organic N originating from the floating plants, roots, and microbial community. Nitrification would also be rapid in the aerated lanthanum tank, as shown in other studies monitoring nitrogen transformation processes under oxic and anoxic conditions (i.e. Tallec et al., 2008).

Results from the flow-through experiment exhibited significant removal of $\text{NO}_3\text{-N}$ ($p < 0.001$) and $\text{PO}_4\text{-P}$ ($p < 0.001$) from eutrophic water using a FTW paired with lanthanum treatment design. To initiate this combined biological and chemical approach, we constructed a 37 m^2 ($6.1 \text{ m} \times 6.1 \text{ m}$) FTW and paired this with a slow-release lanthanum composite inserted inside an airlift pump (Fig. SM2, SM4).

3.4. Densmore Pond

After nearly two decades of stormwater retention (2002–2021), the Densmore Pond exhibited several signs of eutrophication. Densmore

Pond sediment was observed at depths greater than 0.6 m in some regions of the pond with extractable nutrient contents of $1.67 \text{ mg NO}_3\text{-N kg}^{-1}$ and $11 \text{ mg PO}_4\text{-P kg}^{-1}$ (Table SM1). A thick mat of *Cladophora*, a lime green filamentous algae species, often covered the pond surface throughout the growing season pre-treatment. DO concentrations were observed as low as 0.89 mg L^{-1} on July 6, 2020. Dead Amur carp (*Cyprinus rubrofuscus*) were commonly found floating on the water surface prior to and at the start of the treatment period, likely caused by low DO concentrations within the pond. The aesthetic value provided by the Densmore Pond pre-treatment was minimal. For these reasons, the Densmore Pond provided an exemplary test site to implement our biological and chemical treatment.

3.4.1. Nutrients, Lanthanum, water quality parameters

Once the FTW and airlift pump were installed in June 2020, soluble reactive phosphorus (SRP) was measured weekly at designed sampling points (Fig. 3). SRP results are displayed with precipitation and lanthanum concentrations superimposed (**Fig. 6A, 6B**). Temporal sampling showed SRP concentrations were initially around $40 \text{ } \mu\text{g PO}_4\text{-P L}^{-1}$ and decreased to $20 \text{ } \mu\text{g PO}_4\text{-P L}^{-1}$ during the first month of treatment (**Fig. 7**). Higher air and pond water temperatures (Fig. 7), along with runoff in August and September corresponded with an increase in SRP to $>100 \text{ } \mu\text{g PO}_4\text{-P L}^{-1}$ (Fig. 6A). In 2020, the mass, salt (i.e., LaCl_3 or $\text{La}_2(\text{SO}_4)_3$) and composition of the lanthanum added was adjusted throughout the season (Fig. SM3). The higher SRP concentrations observed in August and September 2020 also corresponded with very low lanthanum concentrations at our sampling locations (Fig. 6B). Possible reasons for this correlation include: (i) the lower masses of lanthanum added in August 2020 (SM2); (ii) increased mineralization of organic P during the warmer months occurred (Gudasz et al., 2010), resulting in a more rapid consumption of the added lanthanum, and (iii) the lanthanum composition used in 2020 released lanthanum too quickly, which prevented the lanthanum from getting widely distributed in the pond from the single airlift pump. Following an increase of lanthanum addition in September and October (Fig. SM3), the spike in SRP observed in August eventually declined to concentrations below $20 \text{ } \mu\text{g PO}_4\text{-P L}^{-1}$ (Fig. 7).

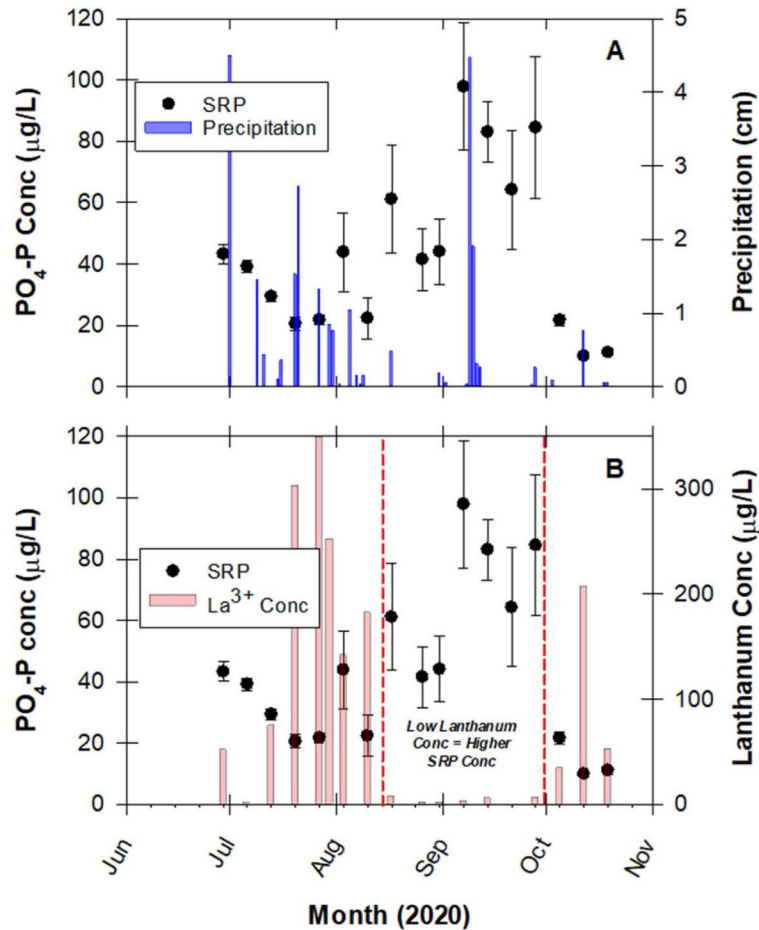


Fig. 6. Temporal changes in SRP in Densmore Pond in 2020 superimposed with (A) precipitation and (B) lanthanum concentrations observed at GPS sampling points.

In 2021, the lanthanum composites were added every 4 weeks (Fig. SM3) to the airlift pumps and lanthanum concentrations at the designated points were measured weekly. The individual 30-cm length, 5 cm-diameter lanthanum composites containing 411 g of LaCl₃ consistently released approximately 75% of their initial weight in 28 d. Assuming majority of the weight loss was due to LaCl₃ dissolution (~308 g in 28 d), this release rate was approximately 11 g d⁻¹, which was similar to the release rate (12.25 g d⁻¹) of the LaCl₃ composite used in the lanthanum composite mesocosm experiment (Section 3.2.). Weekly lanthanum concentrations remained in the microgram per liter range, indicating the two airlift pumps adequately distributed the lanthanum throughout the pond. While concentrations varied between locations on individual

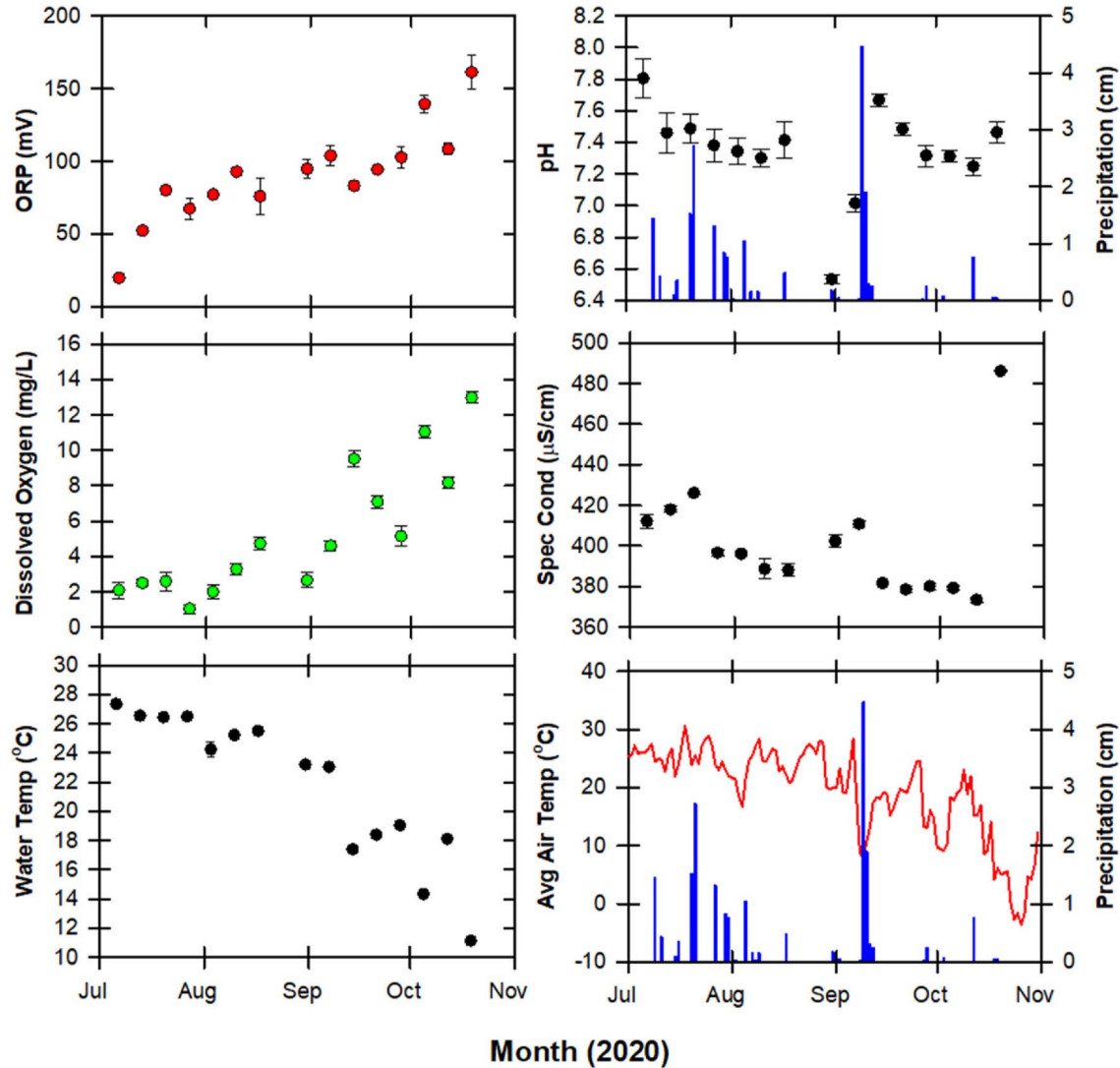


Fig. 7. Temporal changes in water quality parameters in Densmore Pond, along with air temperature and precipitation in 2020.

dates, averages across locations indicated lanthanum concentrations were sustained (**Table 1**), which negated large spikes in SRP concentrations such as those observed in 2020 (**Fig. 8**).

ORP and DO concentrations increased throughout the growing season (Fig. 7). Moreover, DO in 2021 remained high while SRP concentrations remained low ($<20 \mu\text{g L}^{-1}$). $\text{NO}_3\text{-N}$ concentrations remained generally low throughout the study; however, $\text{NO}_3\text{-N}$ concentrations were lower in 2021 compared to 2020 (Fig. 8).

Table 1 Lanthanum concentrations spatially and temporally observed at sampling locations (GPS) in Densmore Pond in 2021.

Sampling Point	Month (day)								
	April 5*	April 12	April 20	April 26	May 3*	May 10	May 17	May 24	June 1*
	<i>Lanthanum Concentration ($\mu\text{g L}^{-1}$)</i>								
GPS 1	1.09	44.2	179.97	10.49	212.67	2.13	6.14	259.24	11.14
GPS 2	14.11	131.13	117.3	561.94	166.85	1.62	25.17	24.95	27.2
GPS 3	10.28	19.9	109.81	34.82	3.63	2.03	17.23	320.37	41.51
GPS 4	-	42.34	319.97	21.83	48.0	1.59	66.7	12.42	174.44
GPS 5	-	36.59	72.76	166.47	40.88	7.33	1.71	5.82	1139.45
AVG	8.49	54.83	159.96	159.11	94.41	2.94	23.39	124.56	278.75
STDEV	6.69	43.71	91.39	233.83	90.13	2.47	25.91	152.54	485.50

* Lanthanum composites were added to Airlift pumps (Fig. SM2) on April 5, May 3, and June 1 after sampling the GPS locations. Two composites were added per airlift pump on April 5 and May 3 and four composites per pump on June 1.

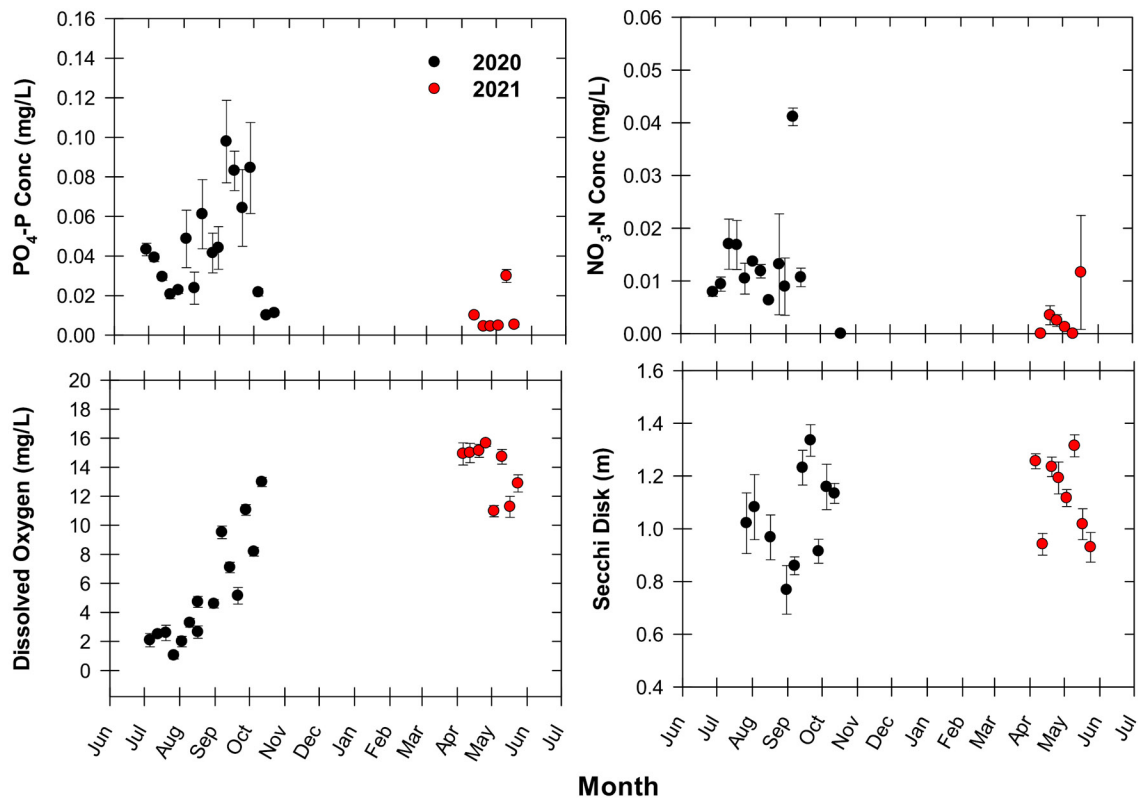


Fig. 8. Temporal changes in soluble reactive phosphate (SRP) following slow drip additions of LaCl_3 .

In our study, the dissolved oxygen concentrations were taken at several discrete locations in the pond (Fig. 3), just below the surface. We did not routinely sample under the FTW mats but did document and photograph the large root systems that became established (Fig. 9). We believe this pervasive root system would provide a large surface area for microbial populations to colonize. It is likely that heterotrophic



Fig. 9. Photographs of plant and root growth in FTW in Densmore pond, 2020

consumption of plant root exudates and dead roots contributed to considerable oxygen consumption. Reddy and DeLaune (2008) reported anoxic and anaerobic micro zones are likely to occur beneath floating mats, in the soil media, and in biofilms, with the potential to induce microbial denitrification. This may even increase at nighttime, when photosynthesis is not operative, and respiration could lead to decreased oxygen concentrations.

Further evidence that denitrifying conditions can form under FTW was reported by Borne et al. (2015) who showed that the size of the FTW can influence DO concentrations. A 23 m² FTW in North Carolina (NC) maintained DO concentration below 0.5 mg L⁻¹ for 5–7% of the time while a 50 m² FTW in New Zealand induced denitrification conditions (DO < 0.5 mg/L) during most of the summer months. In both sites, DO was always much more elevated (i.e., aerobic) in open water. By comparison, our FTW was 37 m². Given other researchers have documented that denitrifying conditions can form under similar sized FTW, we believe denitrification was responsible for some N loss. Given that our biological-chemical treatment increased DO throughout the pond (Fig. 8), using larger FTW that favor denitrifying conditions is recommended. It is also noteworthy that in 2021, the above mat plant growth in the FTW began to exhibit nitrogen deficiency symptoms (light green leafy tissue). The fact that the plants became nitrogen deficient also supports that plant uptake was not the sole loss mechanism.

3.4.2. Field-scale FTW plant growth and over-winter survival

One of the major FTW nutrient removal pathways is via plant uptake. In 2020, plant growth (shoot and root) was significant, with a good development of the root systems observed (Fig. 9). TN and TP uptake for both above- and below-mat biomass was quantified for seven plant species included in the field-scale FTW design (**Fig. 10**). In total, the 1000 plants in the field-scale FTW removed approximately 185 g of TN and 10 g of TP via plant uptake after a 4-month deployment from June to October 2020.

Sustainability is a key component when considering FTW design and cost; therefore, FTW plant species survival was evaluated after 4- and 10-months following installation. Three plant species out of the 13 utilized in the FTW design did not survive past 4 months of deployment. These included *Iris shrevi*, *Eupatorium maculatum*, and *Asclepias*

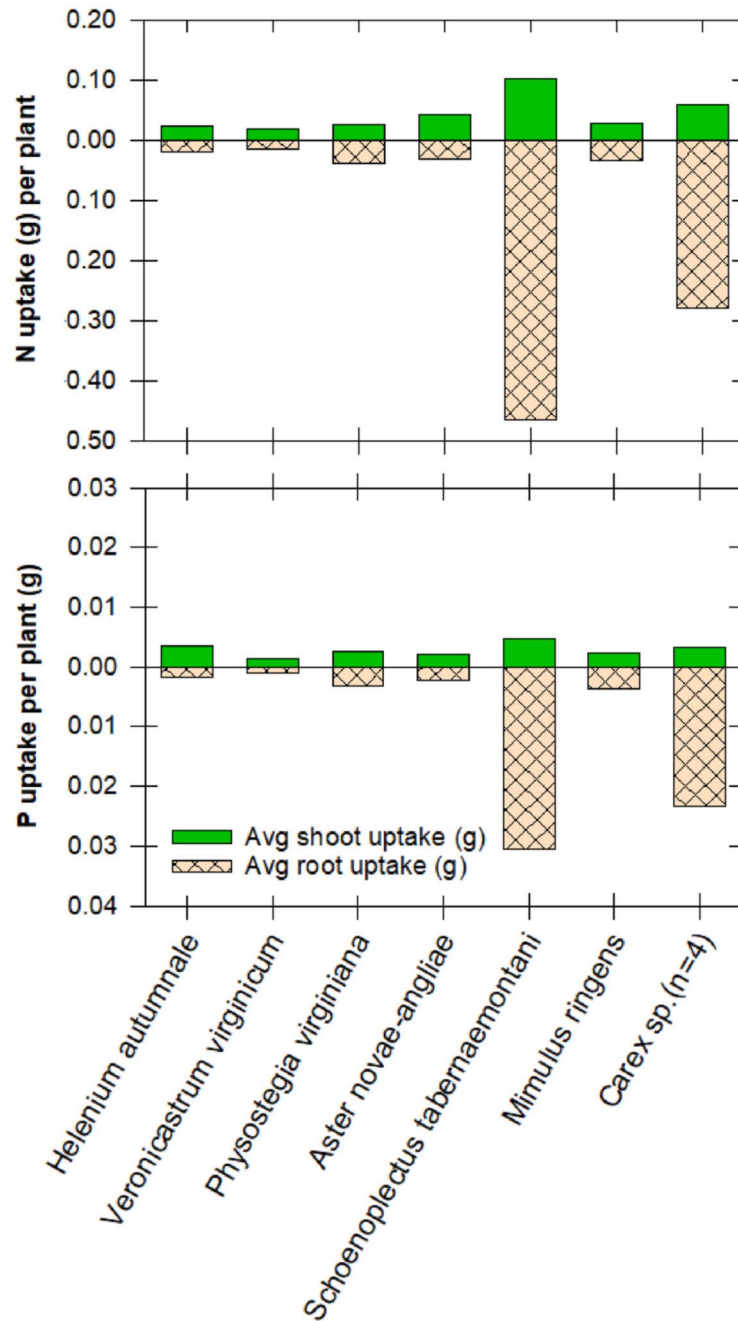


Fig. 10. Field-scale N and P uptake after four months of deployment (Densmore Pond, 2020)

incarnata. Potential causes of death include interspecies competition, lanthanum toxicity, or other. The FTW over-winter survival rate was assessed after 10 months of installation in May 2021. The average daily temperature observed during this winter season was 32.8 °C, the

minimum daily temperature was -35°C , and the maximum daily snowfall depth was 28 cm. Five plant species out of 13 utilized in the FTW design survived. These were *Carex stricta*, *Carex crinita*, *Carex comosa*, *Carex frankii*, and *Schoenoplectus tabernaemontani*. In total, 387 of the 1000 FTW plants survived the winter (38.7% survival rate) based on a visual assessment in the field paired with aerial images collected via drone imagery in May 2021 (Fig. SM6). Tharp et al. (2019) performed a similar assessment of FTW plant survival following the first growing season and after the first winter in South Burlington, Vermont, USA. The authors observed all of the softstem bulrush (*Schoenoplectus tabernaemontani*) and approximately 85% of longhair sedge (*Carex comosa*) included in the FTW survived the first winter season, which was consistent with observations in this study. In 2021, the original FTW was refurbished by replanting the empty plant holes in the Beemats with *Carex* and *Schoenoplectus* species.

3.4.3. Nutrient runoff and mass balance considerations

For the proposed biological-chemical treatment to be effective and sustainable, sequestration and attenuation of nutrients entering the pond on an annual basis is critical. Based on the individual components of the watershed surrounding the Densmore Pond (Fig. SM1), as well as the concentrations of the runoff samples, SCS Curve Number calculations (see SM), changes in surface water levels, and numerous site visits during rainfall events, we believe the predominant nutrient fluxes into the Densmore pond were from the adjacent street, parking lot, immediate green space, and south residential area (Fig. SM1). Using these four contributing areas, annual $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ inputs were estimated to be 0.829 kg of $\text{NO}_3\text{-N}$ and 0.134 kg of $\text{PO}_4\text{-P}$ (**Table 2**). By using the mass of lanthanum added during 2020 (5.6 kg lanthanum) and assuming a 1:1 stoichiometric removal of phosphate, enough lanthanum was added over the 2020 season to remove 1.26 kg of $\text{PO}_4\text{-P}$ (**Table 3**). Thus, the mass of lanthanum added was more than what was needed to neutralize runoff phosphorus. Lanthanum added in excess of annual P inputs can then be used to treat internal P sources.

To account for the mass of $\text{PO}_4\text{-P}$ initially present in the water column, we estimated the volume of the Densmore Pond to be 4046.85 m^3 . Using a mean $\text{PO}_4\text{-P}$ concentration of $50\text{ }\mu\text{g L}^{-1}$, the mass of P in the water

Table 2 Nutrient input estimates of watershed components for Densmore Pond (Lincoln, NE) during 2020.

<i>Watershed component</i>	<i>Contributing area</i>	<i>Total runoff contribution</i>	<i>PO₄-P Load</i>	<i>NO₃-N Load</i>
<i>Units</i>	<i>Ha</i>	<i>m³</i>	<i>kg</i>	<i>kg</i>
Street	0.73	769	0.046	0.285
YMCA Parking lot	0.45	470	0.028	0.174
Pond green space	1.13	363	0.022	0.134
Residential area	1.98	637	0.038	0.236
TOTAL	4.29	2239	0.134	0.829

Table 3 Hypothetical PO₄-P removal based on lanthanum additions to Densmore Pond in 2020 and 2021.

<i>Year</i>	<i>LaCl₃ addition</i>	<i>La₂(SO₄)₃ addition</i>	<i>Lanthanum addition</i>	<i>Hypothetical PO₄-P mass removed</i>
	<i>kg</i>	<i>kg</i>	<i>kg</i>	<i>kg</i>
2020	2.52	8.63	5.66	1.26
2021y	39.46	0	22.35	4.98
TOTAL	41.98	8.63	28.01	6.24

column was 0.202 kg of PO₄-P. Sediment-bound P was also estimated by performing an adsorption isotherm with the Densmore Pond sediment, where sediment had a high capacity to adsorb phosphate (Langmuir adsorption maximum ~194 mg/kg, Fig. SM7). By contrast, the extractable P of the sediment (11 mg kg⁻¹, Table SM1) was at the lower end of this adsorption potential. Therefore, the sediment was not likely a significant source of PO₄-P into the water column even during low DO conditions.

Based on the mass of lanthanum added in 2020 and 2021 (Table 3), enough lanthanum was added to sequester the readily available PO₄-P in the water column, which resulted in observed increases in water clarity, greater light penetration, higher DO concentrations and less organic matter on the benthic layer as evidenced by less rooted aquatic vegetation and more bare spots clearly visible. Moreover, a time-lapse camera on site captured hourly images during 2020 and 2021 and a comparison of the two years clearly shows less algae mats present in 2021 than in 2020 (Fig. SM8).

4. Conclusions

Stormwater retention ponds are important infrastructures for many urban neighborhoods. Retention ponds minimize flooding from storms and provide aesthetic and recreational value. Over time, however, retention ponds accumulate nutrients. Herein, a biological and chemical approach was effectively tested at the microcosm and mesocosm scales and fully implemented at the field scale. The slow-release lanthanum composite and airlift pump was effective in removing phosphorus from the water column. Results from the Densmore Pond show that N and P decreased in the water column while DO increased. Increased DO likely facilitated microbial mineralization of organic material (e.g., TN, TP). Plant uptake can temporarily remove nutrients from the water column, but permanent N removal requires creating anaerobic zones beneath the FTW that induce denitrification. Using FTW large enough to facilitate denitrification is recommended. Future work should evaluate the percentage of N removal via plant uptake versus the percentage of N removal via microbial denitrification facilitated by FTWs at the field scale.

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Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data to this article can be found following the References.

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Further reading

Hansen, S., Messer, T., Mittelstet, A., Berry, E.D., Bartelt-Hunt, S., Abimbola, O., 2020. *Escherichia coli* concentrations in waters of a reservoir system impacted by cattle and migratory waterfowl. *Sci. Total Environ.* 705, 135607 <https://doi.org/10.1016/j.scitotenv.2019.135607>

Satiroff, J.A., Messer, T.L., Mittelstet, A.R., Snow, D.D., 2021. Pesticide occurrence and persistence entering recreational lakes in watersheds of varying land uses. *Environ. Pollut.* 273, 116399 <https://doi.org/10.1016/j.envpol.2020.116399>

Appendix A. Supplementary data *follows.*



A biological and chemical approach to restoring water quality: A case study in an urban eutrophic pond

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Supplementary Materials (SM)

1 Table

9 Figures

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2.4.5. *Water-quality sampling at field site*

Water-quality grab samples were collected from the designated sample points by using 125-mL HDPE sample bottles at a depth of 0.3 m. Each sample bottle was rinsed three times prior to sampling. In order to collect water samples from underneath the FTW, an Arnold siphon pump kit was utilized to pump 100 mL of water through each portion of the polyethylene (PE) tubing into 125 mL HDPE sampling bottles. The PE tubing was rinsed for 5 seconds via the siphon pump kit prior to sample collection. All water quality grab samples were transported to the laboratory refrigerator until sample analysis could be performed. Water quality samples were assessed for NO₃-N and PO₄-P using procedures previously described.

An additional set of grab water quality samples were collected weekly from the Airlift Pump, GPS 1, and GPS 2 sampling points throughout the field season to be analyzed for lanthanum concentration. Lanthanum water quality grab sampling began on June 23, June 29, and August 3 for the Airlift Pump, GPS 1, and GPS 2, respectively. One hundred mL samples were collected using 125-mL HDPE sample bottles at a depth of 0.3 m. The samples were then returned to the laboratory, preserved with concentrated nitric acid (HNO₃, J.T. Baker, USA), and refrigerated at 4°C until sample analysis was performed. All lanthanum water sample analysis was performed by the Water Sciences Laboratory at UNL using an iCAP RQ ICP-MS (Thermo Scientific, Waltham, MA, USA) using EPA method 6020.

During each sampling event from July 6 to October 19, 2020, water temperature (°C), pH, DO concentration (mg L⁻¹), specific conductivity, SpC (µS/cm), and ORP (mV) were measured at field sample locations using a YSI quatro ProDSS Multiparameter water quality meter (YSI Inc.; Yellow Springs, Ohio). The water quality meter was consistently deployed at a depth of 0.3 m. A Secchi disk was also used weekly from July 27 to October 19, 2020 to measure water turbidity.

Weekly water quality sampling was reinitiated after the pond thawed in 2021, starting on April 5. Two additional sampling locations labelled GPS 4 and GPS 5 were added to quantify lanthanum concentrations in water following lanthanum composite addition and to measure

nutrient concentrations in response to the treatment (Fig. 3). Water-quality parameter measurements and Secchi disk depth measurements were continued as well.

2.4.7. SCS Curve Number method to estimate runoff

The runoff collection dates during the 2020 field season are as follows: June 19, June 22, July 8, July 19, July 20, July 25, July 29, August 5, and August 17. The average rainfall amount for these nine events was 1.6 cm (0.63 in). The runoff samples were collected from the ISCO auto sampler within 24 h of the rain event, transported to the laboratory, and refrigerated at 4 degrees C until nutrient analysis was performed. Samples were filtered using Whatman 0.45 Micron GF/F filter papers and analyzed for both nitrate-N and phosphate-P on an AQ300 discrete autoanalyzer (Seal Analytical; Mequon, Wisconsin) using EPA methods EPA-127-D Rev. 2A and EPA-145-D Rev. A for nitrate-N and phosphate-P, respectively.

The SCS Curve Number method was used to estimate the volume of runoff that entered the treatment pond for the 2020 field season. The governing equation for this method is as follows:

$$Q = \frac{(P - 0.2S)^2}{(P + 0.8S)} \quad [\text{Eqn. 1}]$$

Where Q is the depth of runoff in inches, P is the rainfall depth in inches, and S is the potential maximum retention after runoff begins. The S term in this equation is calculated using the equation below:

$$S = \frac{1000}{CN} - 10 \quad [\text{Eqn. 2}]$$

Where the CN value, termed CNII, is the average CN based on the land use classification and hydrologic soil group (A, B, C, or D) for each type of land use classification within the contributing watershed. This value (84) was obtained from the drainage and grading plan developed in 1998 for the YMCA Densmore Park. In order to account for antecedent moisture conditions in soil which determine the amount of runoff coming from a storm event, two more equations were incorporated:

$$CN (I) = \frac{CNII}{2.334 - 0.01334 * CNII} \quad [\text{Eqn. 3}]$$

$$CN (III) = \frac{CNII}{0.4036 + 0.0059 * CNII} \quad [\text{Eqn. 4}]$$

Curve Number I (69) represents the minimum curve number value for dry antecedent conditions. This value was used to calculate S for all rain events where a previous rainfall event did not occur within 5 d. Curve Number III (93) represents the maximum curve number value for wet saturated conditions. This value was used to calculate S for all rain events where a rainfall event occurred within 5 d. Impervious areas within the drainage area such as parking lots and streets are represented by a curve number of 98 which does not change under varying moisture conditions. The method used in this study was adapted from Satiroff et al. (2021).

For this study, daily rainfall data was obtained from the High Plains Regional Climate Center ACIS-CLIMOD database using gauging station Lincoln 4.6 S. The hydrologic soil group for the contributing watershed was determined by creating an AOI of the watershed using the NRCS Web Soil Survey. The entire contributing watershed area was determined to be hydrologic soil group D.

To calculate nutrient loads entering the Densmore Pond, exceedance probabilities were determined for both PO₄-P and NO₃-N (Fig. SM9) in runoff water coming from the culvert which drains the contributing watershed (Hansen et al., 2020; Winston et al., 2013). The incoming runoff volume for each storm event as determined by the SCS CN method was multiplied by the phosphate-P (0.06 mg P/L) and nitrate-N (0.37 mg N/L) values that represented 50% exceedance values to obtain a nutrient mass load for each rainfall event.

Table SM1
Soil Characteristics of Densmore Pond Sediment

Parameter¹	Units	Average Results (Standard Deviation)
		7.9
Soil pH (1:1)		(0.00)
		0.427
Soluble salts	mmho/cm	(0.025)
		1.07
Organic Matter LOI (%)	%	(0.047)
		1.67
Nitrate-N KCl (mg N/kg)	mg/kg	(0.125)
		11.0
Phosphorus M3 (mg P/kg)	mg/kg	(0.00)
		303.67
Potassium NH₄OAc (mg K/kg)	mg/kg	(6.128)
		65.83
Sulfate M3 (mg S/kg)	mg/kg	(4.170)
		5473
Calcium NH₄OAc (mg Ca/kg)	mg/kg	(77.99)
		339.67
Magnesium NH₄OAc (mg Mg/kg)	mg/kg	(3.86)
		66
Sodium NH₄OAc (mg Na/kg)	mg/kg	(0.816)
		0.708
Total Carbon (% C)	%	(0.007)

1 – LOI, loss on ignition; M3- Mehlich-3 extraction; NH₄OAc – ammonium acetate extraction

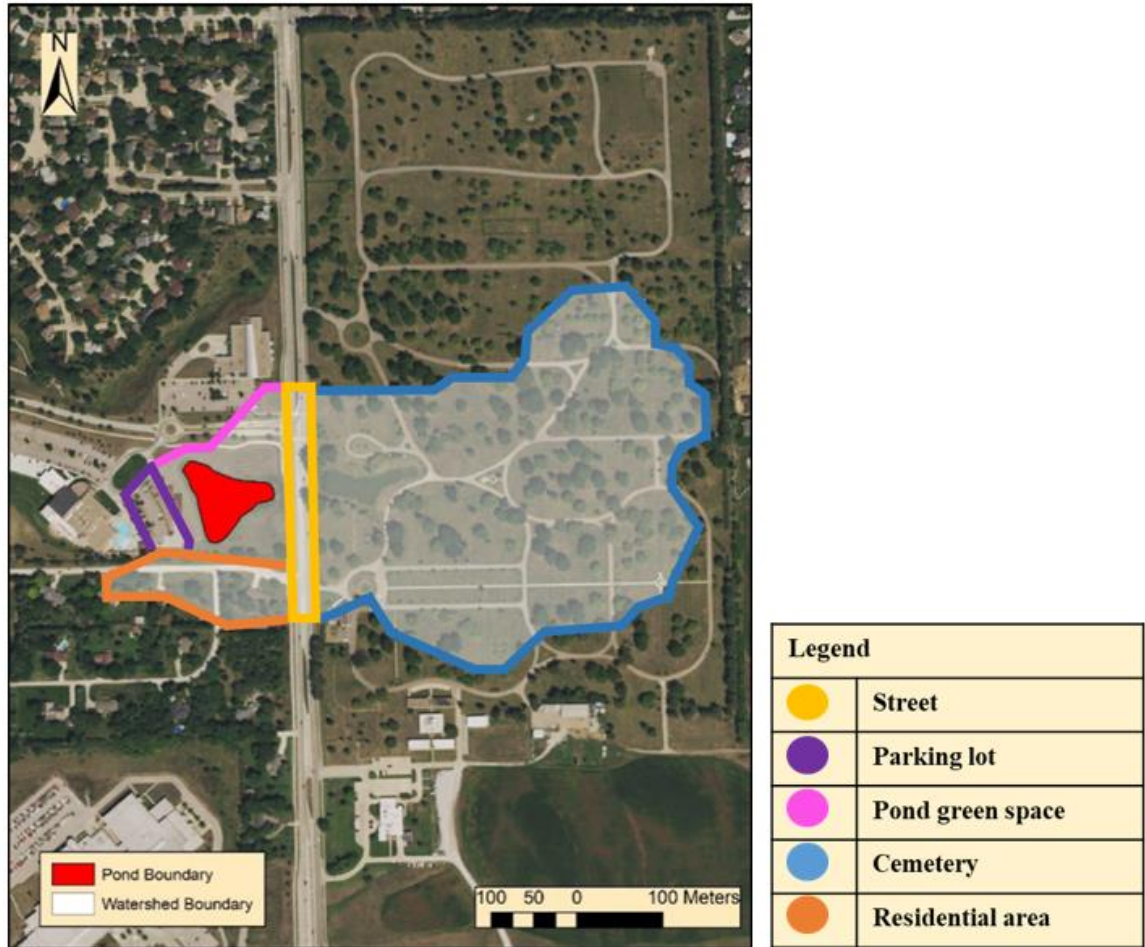


Figure SM1. Overhead view of Densmore Pond and its contributing watershed, subdivided by land use components



Figure SM2. Airlift pump v1 used in 2020, 2021 (left); Airlift pump v2 added in 2021 (right)

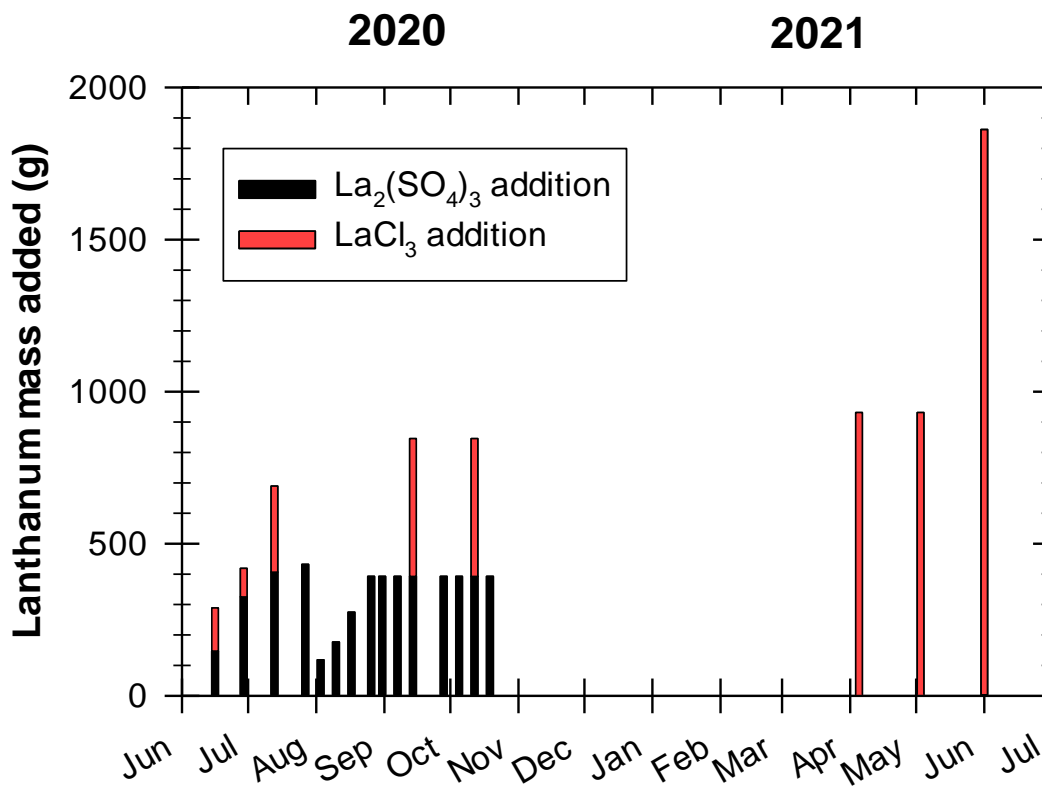


Figure SM3. Mass of lanthanum added (La^{3+}) to Densmore Pond either in the form of $\text{La}_2(\text{SO}_4)_3$ or LaCl_3 in 2020 or 2021.

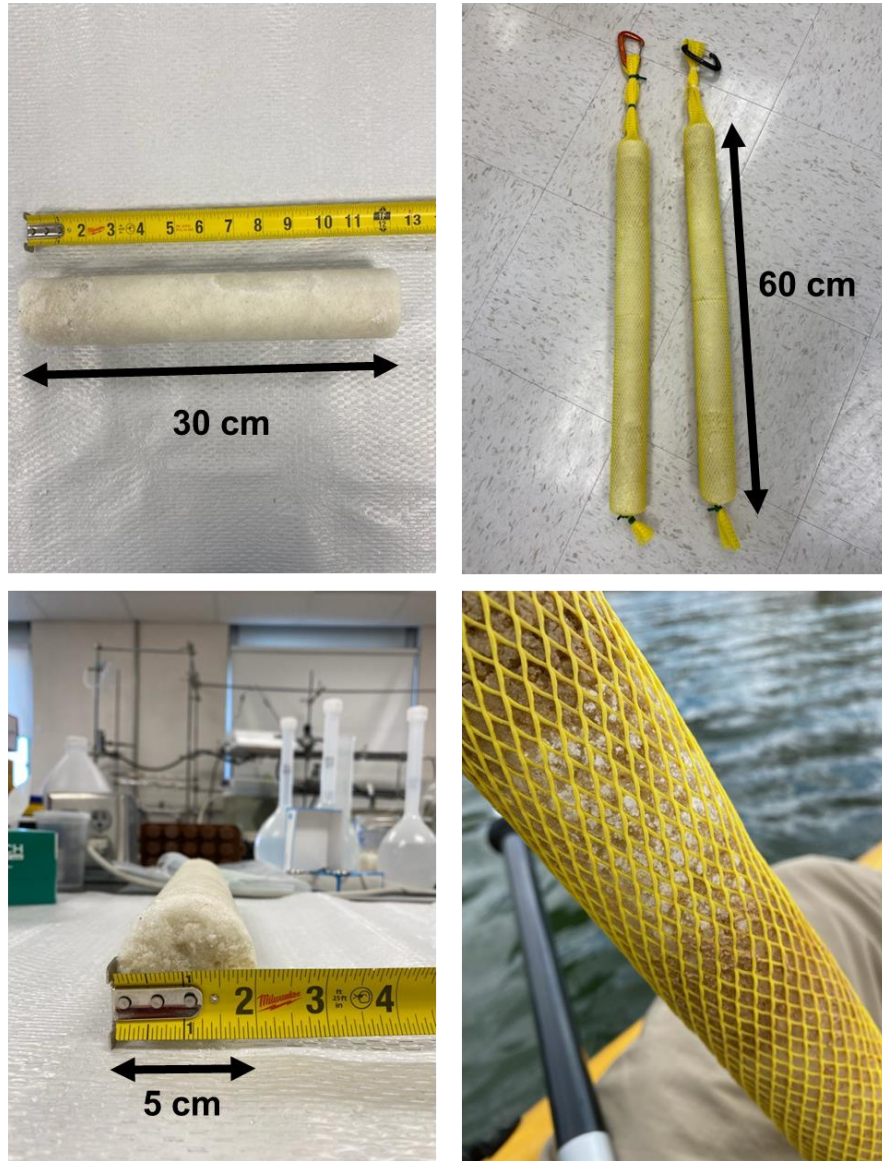


Figure SM4. Photographs of lanthanum composite used in mesocosm (barrel) experiment and Densmore Pond in 2021.

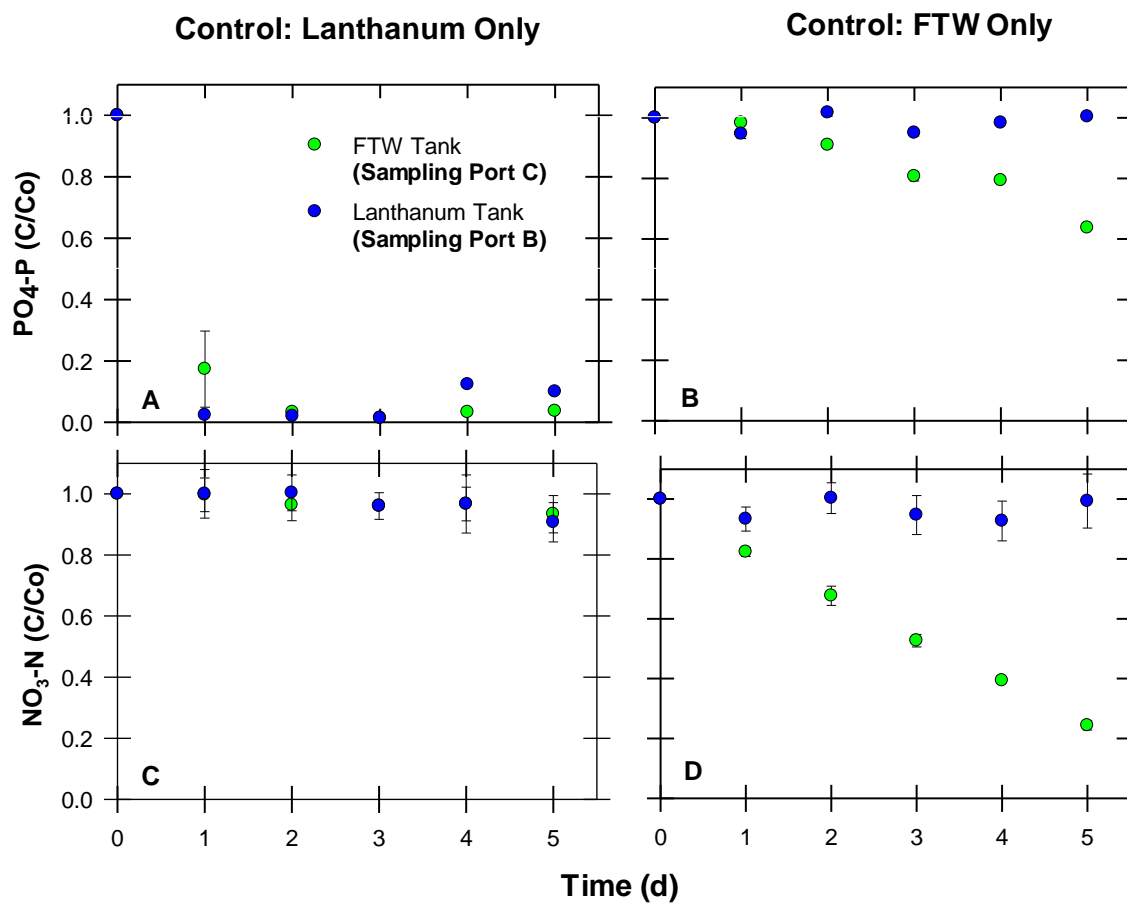


Figure SM5. Temporal NO₃-N and PO₄-P concentrations (as C/Co) for FTW-only and Lanthanum-only supporting flow-through experiments.

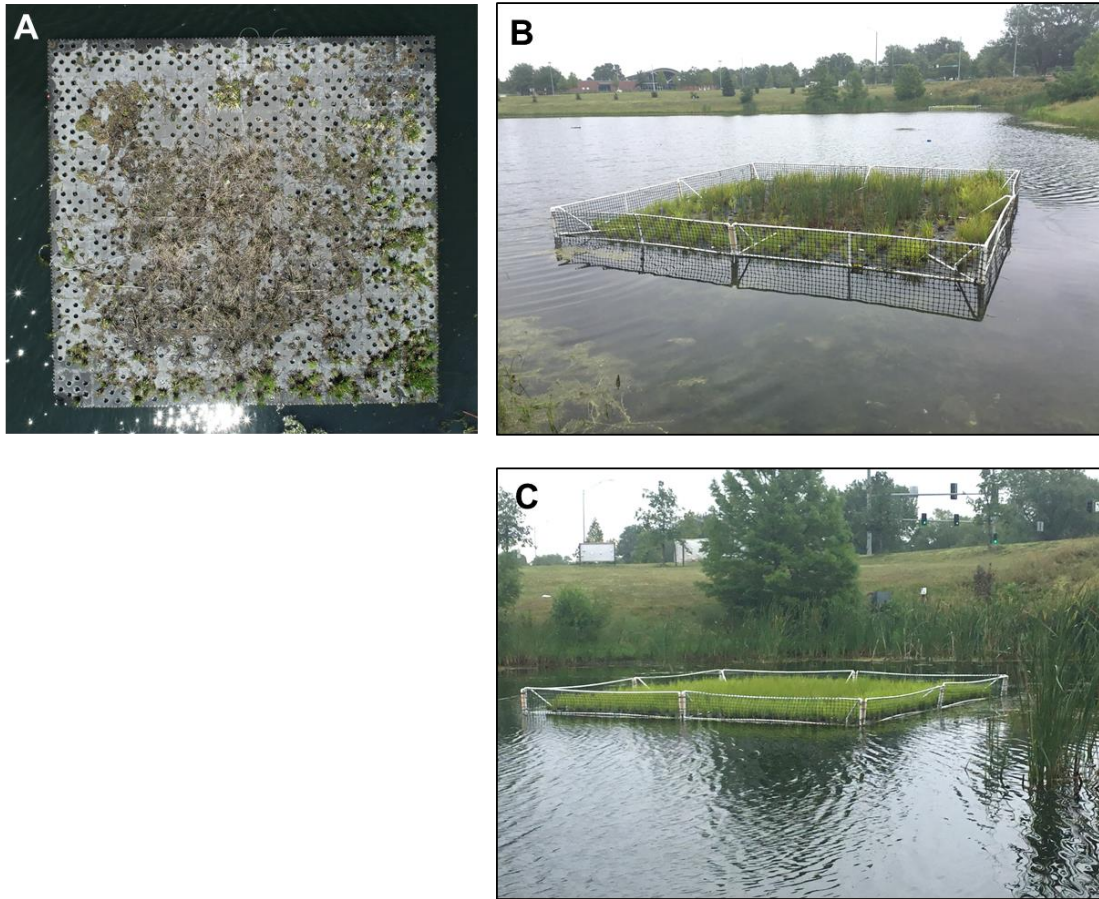


Figure SM6. A. FTW1 aerial image captured via drone, May 2021; B. FTW1 following replanting, July 7, 2021; C. FTW2 planted with only bulrush and sedges, July 7, 2021.

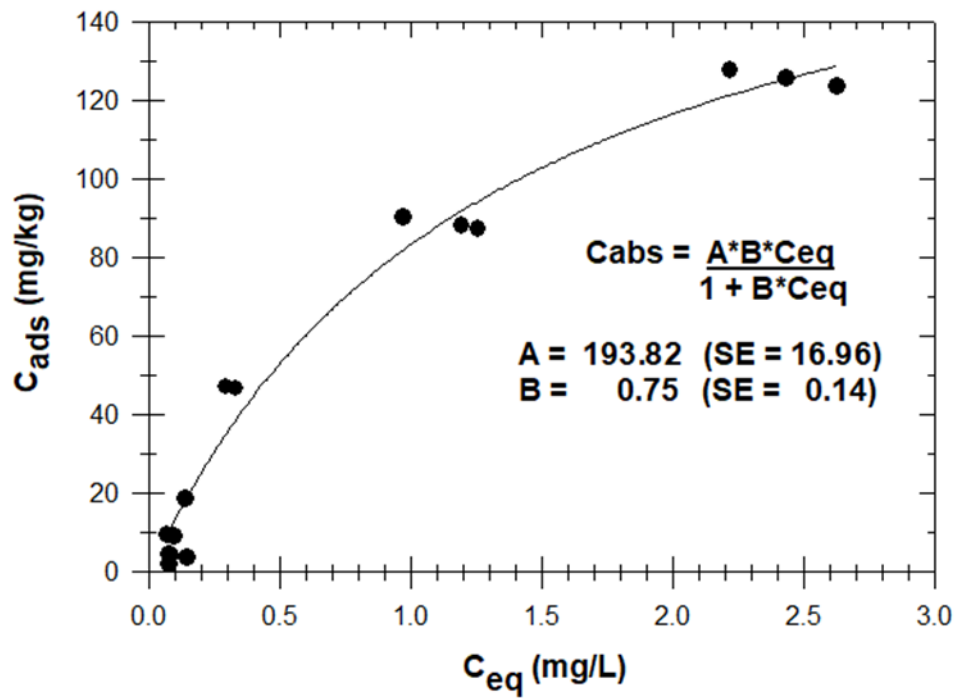


Figure SM7. Adsorption isotherm conducted in 2020 using Densmore Pond sediment



Figure SM8. Photographs of Densmore Pond in 2020 and 2021.

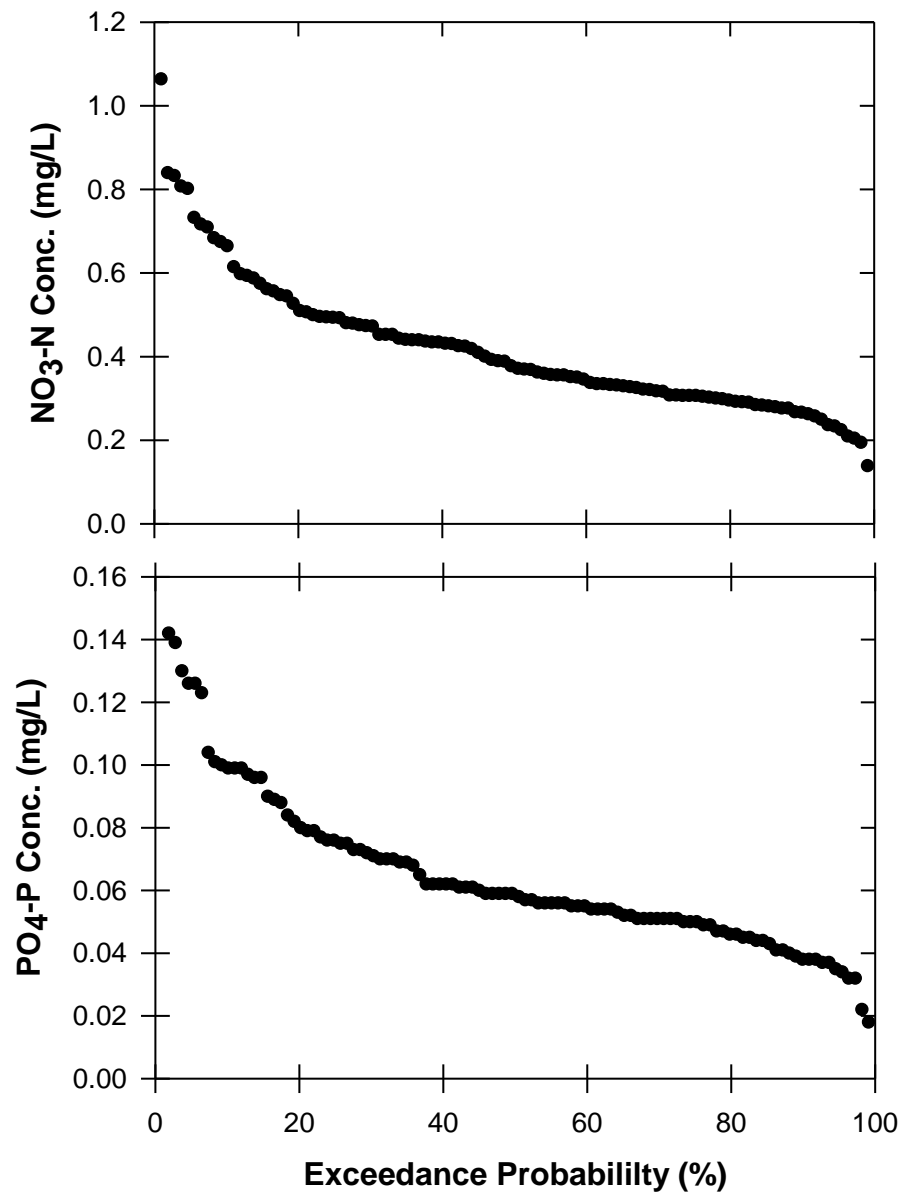


Figure SM9. Exceedance probabilities for NO₃-N and PO₄-P in runoff entering the Densmore Pond in 2020