environments

MDPI

Article

Slow-Release Lanthanum Effectively Reduces Phosphate in Eutrophic Ponds without Accumulating in Fish

Callie McCright, Jenna McCoy, Natalie Robbins and Steve Comfort *

School of Natural Resources, University of Nebraska, Lincoln, NE 68583, USA
* Correspondence: scomfort@unl.edu

Abstract: Nutrient runoff is a major water quality issue affecting water resources. Excess nutrients such as nitrate (NO_3^-) and phosphate (PO_4^{3-}) entering surface waters promote eutrophication. Recent research showed that floating treatment wetlands combined with slow-release lanthanum composites deployed through airlift pumps can reduce NO_3^- and PO_4^{3-} concentrations, minimize algae and weeds, and increase dissolved oxygen concentrations. While water quality improves following this biological and chemical approach, questions remain about the toxicity and potential accumulation of lanthanum in lentic organisms. We addressed this concern by analyzing flesh and liver of fish exposed to the slow-release lanthanum following two years of treatment and compared results to fish harvested from a control, untreated pond. We also conducted an aquarium fish study that used higher lanthanum concentrations than those observed in the field. The field study confirmed that under the concentrations of lanthanum released to treat eutrophic ponds (109 μg L^{-1}), no adverse effects were observed in harvested fish. We also observed no significant differences between lanthanum-exposed and -unexposed fish ($\alpha = 0.05$) in our controlled tank study. Given the laboratory tank lanthanum concentrations were approximately nine times higher (916 μg L^{-1}) than the observed field concentrations, we conclude the slow-release lanthanum composites used to treat eutrophic ponds are effective in improving water quality and do not lead to significant lanthanum accumulation in fish.

Keywords: environmental remediation; lanthanum; toxicity; slow-release lanthanum; airlift pump

check for updates

Citation: McCright, C.; McCoy, J.; Robbins, N.; Comfort, S. Slow-Release Lanthanum Effectively Reduces Phosphate in Eutrophic Ponds without Accumulating in Fish. *Environments* **2023**, *10*, 20. https://doi.org/10.3390/environments10020020

Academic Editor: Chin H. Wu

Received: 30 November 2022
Revised: 18 January 2023
Accepted: 24 January 2023
Published: 27 January 2023

1. Introduction

One of the most prevalent water quality issues in the U.S. and worldwide is the deterioration of surface waters caused by nutrient runoff [1]. Nonpoint sources of nutrients include surface runoff from residential, industrial, and agricultural lands [2,3]. Specific nutrient sources within urban watersheds include lawn fertilizers, pet waste, and grass clippings [4]. The two most problematic runoff nutrients are phosphorus and nitrogen, which include the anions nitrate (NO_3^-) and phosphate (PO_4^{3-}) [1,2,5]. Although human health concerns in connection to nitrate and phosphate consumption exist [6,7], greater attention should be paid to their environmental effects in surface water.

Nutrient runoff of excess nitrate and phosphorus threatens freshwater aquatic ecosystems [8]. Increased nutrient loads in surface water result in habitat alteration and harmful algal blooms [9]. Aside from reducing aesthetics and opportunities for recreation, algal blooms are detrimental to aquatic animals. Effects include clogged gills of fish and low dissolved oxygen concentrations (i.e., anoxia). These impacts alter the freshwater ecosystem and threaten biodiversity, water quality, and environmental health [10]. Decreasing nitrate and phosphorus in the water column must be performed simultaneously as algal blooms can increase if only nitrate is reduced [5].

To mitigate nitrate and phosphorus pollution, our previous research reported on a two-pronged, biological, and chemical strategy to treat eutrophic ponds [11]. The biological approach utilizes floating treatment wetlands (FTWs) to improve water quality. Wetland plants are deployed in floating frameworks, where their exposed roots are suspended in the water. General mechanisms for pollutant removal include plant uptake and denitrification [12]. McKercher et al. [11] initially suspended 13 wetland species in a floating framework to demonstrate this technique in a eutrophic pond (Figure 1). The submerged roots take up nitrogen and phosphorus from the water, while microbes on the plant roots convert nitrate to nitrogen gas (i.e., N_2O, N_2) when oxygen becomes limiting.

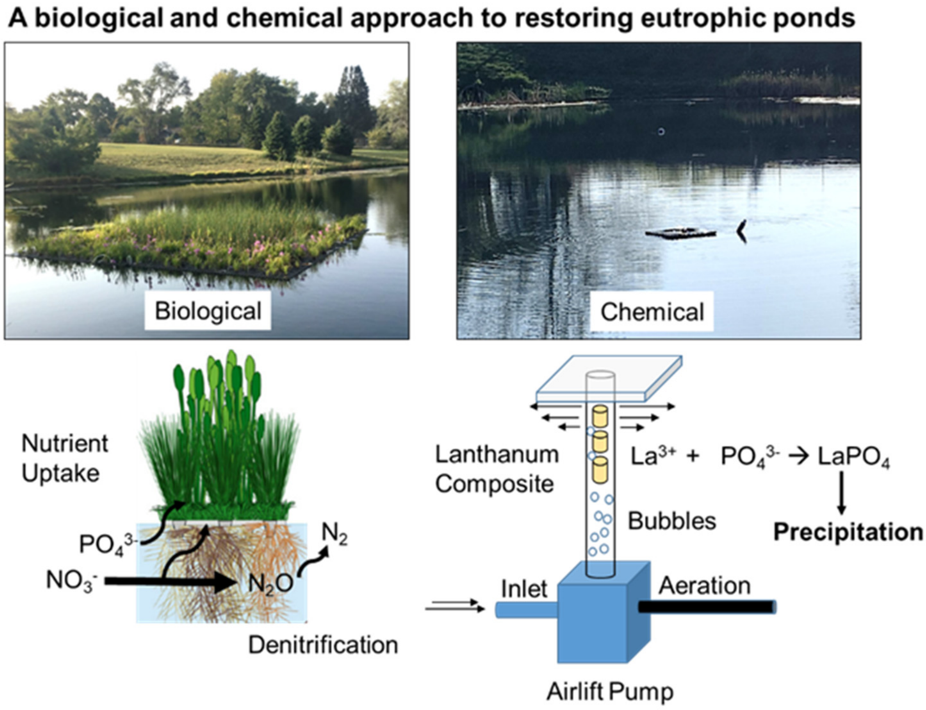

Figure 1. Biological and chemical approach to restoring eutrophic ponds.

The chemical approach utilizes lanthanum, a soft metal lanthanide, to remove phosphorus from the water column. Lanthanum exhibits a high affinity to binding phosphate. The resulting compound, $LaPO_4$, is insoluble and unusable by algae and aquatic macrophytes. The key asset of lanthanum in phosphorus control is its ability to be used in diverse environmental conditions [13]. Historically, chemical amendments to remediate P-rich freshwater included aluminum (Al) or iron (Fe). However, their effectiveness was largely dependent on factors such as pH, redox, alkalinity, other ions, and dissolved organic carbon [13,14]. Furthermore, Al and Fe impact on lentic organisms has not been well documented [15].

With lanthanum's more robust affinity to binding with phosphate ($K_{sp} = 3.7 \times 10^{-23}$; [16]), its use in environmental remediation projects is growing. One of the most widespread commercial lanthanum products used for environmental treatment is Phoslock®. First manufactured in the 1990s by the Commonwealth Scientific and Industrial Research Organization, Phoslock® is a patented lanthanum-modified bentonite clay formula [15,17]. Application methods typically include one large dose delivered beneath a platform boat as it moves across the water surface. Phoslock® then removes phosphates from the water column as the phosphate–lanthanum–clay settles to the bottom [15]. The effect of high dose lanthanum treatments on aquatic organisms is not fully understood and toxicity concerns are present [15].

To avoid large, single lanthanum doses, McKercher et al. [11] added lanthanum using a slow-release composite that gradually released lanthanum into the water column. Lanthanum chloride ($LaCl_3$), paraffin wax, and sand are combined in a 3:2:1 ratio (*w*/*w*/*w*) to create a wax composite [11]. This composite is placed inside an airlift pump, which consists of a submerged PVC pipe where air is bubbled beneath the lanthanum to facilitate its release into the water column (Figures 1 and 2). Aeration aids in gradual lanthanum dispersal as well as oxygenation of the water; lanthanum composites are replaced monthly as needed. Using this approach, McKercher et al. [11] determined that lanthanum concentrations averaged 104 µg L^{-1}, with most concentration spikes well below 1000 µg L^{-1} [11].

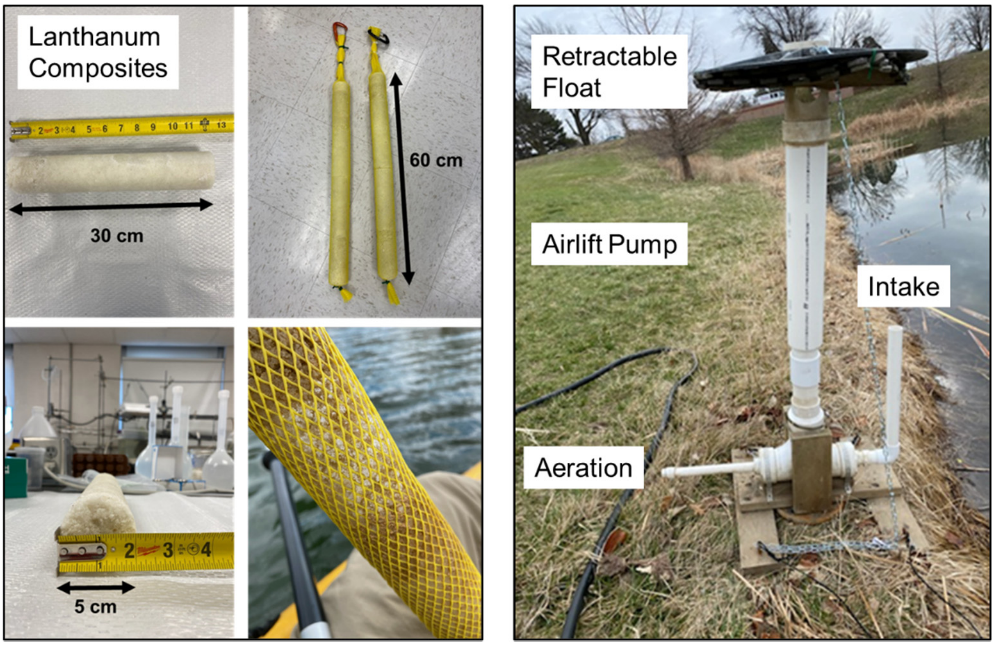

Figure 2. Photographs of slow-release lanthanum and airlift pump.

Our goal was to quantify the toxicological impacts of the slow-release lanthanum composites in treating eutrophic ponds. We accomplished this by harvesting fish from a pond exposed to the lanthanum treatment for two years and determining whether lanthanum had accumulated in the fish (liver or flesh/skeletal muscle). The field experiment also compared concentrations of lanthanum in the organs of bluegill and largemouth bass fish harvested from a lanthanum-treated and -non-treated pond. A supporting laboratory experiment was also performed that compared flesh and liver concentrations of bluegill fish raised in lanthanum-spiked tanks and control tanks following 5 weeks of exposure.

2. Materials and Methods

2.1. Field Site Description

The field site used for experimentation is the Densmore Pond, which is located in Densmore Park (Lincoln, NE, USA). Designed by Olsson Associates (Lincoln, NE, USA), Densmore Pond was initially constructed in 2002 to control urban runoff. The pond surface area is 0.5 hectares with an average depth of 1.3 m. The air temperatures of the site ranged from −35.0 °C to 39.4 °C in 2020 and 2021, and the site is within a humid continental climate zone [11].

Densmore pond is also highly accessible to the public. Located within 100 m from the Cooper YMCA (Lincoln, NE, USA), community members utilize the area for fishing. The local high school also teaches fishing skills at the Densmore Pond. Fish species within the pond are bluegill (*Lepomis macrochirus*) and largemouth bass (*Micropterus salmodies*) as well as Amur carp (*Cyprinus rubrofuscus*). Other wildlife includes red-winged blackbirds as well as migratory geese and ducks.

In 2020, the Densmore Pond displayed strong evidence of eutrophication (Figure S1 in Supplementary Materials). Approximately 80% of the pond surface was covered with a mat of algae and weeds. Dead fish were routinely observed in the water (Figure S1). In June 2020, UNL's biological and chemical treatment technology (Figure 1) was installed and consisted of one 400 ft^2 floating treatment wetland (FTW) and one airlift pump to deploy lanthanum

(Figures 1 and 2). In June 2021, a second FTW (400 ft^2) and airlift pump were installed. Details regarding maintenance of the biological–chemical treatment and weekly water quality sampling protocols performed in 2020 and 2021 are provided in McKercher et al. [11].

The control pond is Bowling Lake, also located in Lincoln, NE. This 11-hectare pond is owned by the Lincoln Airport Authority (LAA) and leased to the City of Lincoln Parks and Recreation Department. The Nebraska Game and Parks Commission (NGPC) manages the fishery of the lake, which includes large-mouth bass, crappie, small-mouth bass, and bluegill.

2.2. Fish Collection and Sampling from Densmore Pond

Following two seasons (spring–fall) of lanthanum treatment to the Densmore Pond, improvements in surface water appearance and clarity were evident and improvements in water quality indicators were recorded. Thus, in partnership with the Nebraska Game and Parks Commission (NGPC), bluegill and largemouth bass fish were collected from the Densmore pond on 14 September 2021, using a small electrofishing boat (Figure S2 in Supplementary Materials). Fish of varying sizes were collected (Figure S2) and euthanized following NGPC protocol. Each sample was immediately weighed and measured before being frozen at −18 °C until dissection and analysis. Similar procedures were used to harvest fish from the control pond, Bowling Lake, on 15 September 2021. Fish ages ranged from less than one year old to approximately four years old at all sites, based on fish length.

2.3. Lanthanum-Spiked Aquarium Experiment

To determine if lanthanum accumulates in bluegill fish raised in a controlled temperature and humidity environment, a tank study was performed in the University of Nebraska's Aquaculture Laboratory (Lincoln, NE, USA). The experimental units were four 37.85 L (10-gallon) aquariums filled to 30 L. Without accounting for sorption by filters, fish, or background phosphate concentrations in the water, we chose an initial target lanthanum (La^{3+}) concentration of 1.87 mg L^{-1}. This target concentration was achieved by making a 0.61 M lanthanum chloride spike solution (227.3 g L^{-1} $LaCl_3 \cdot 7H_2O$ dissolved in H_2O) and adding 0.660 mL to the 30 L. Lanthanum chloride was purchased from ALB Materials (Hendeson, NV, USA). Two tanks were spiked to a target concentration of 1.87 mg L^{-1} La; two tanks were not spiked and served as controls. The spiked tanks provided higher lanthanum concentrations than what was observed under field conditions.

The tanks circulated for 24 h before we added 10 bluegills to each tank. Bluegill fish had been previously harvested from a control pond and acclimated to the fish aquaculture laboratory for several weeks. Fish ages varied from less than one year old to approximately three years old. Each tank was equipped with a Marineland Bio-Wheel Penguin 100 Power Filter (Blacksburg, VA, USA). To adhere to the UNL's established fish rearing guidelines, each aquarium had to have 7 L of its 30 L removed and replaced every other day. To maintain an elevated lanthanum concentration for the duration of the experiment, 0.154 mL of the spike solution (0.61 M $LaCl_3$) was added to the lanthanum treatment tanks with each 7 L water replacement. This maintained the lanthanum concentration in the experimental tanks. After allowing the water to equilibrate following spiking, a water sample from each tank was collected to measure the lanthanum concentration.

Fish care included recording temperature and pH daily with an EcoSense ODO200 Dissolved Oxygen and Temperature instrument (YSI Inc, Yellow Springs, OH, USA). We monitored nitrate, nitrite, and ammonia levels weekly using API Freshwater Master Test Kit. Weekly water samples were collected using 125 mL high-density polyethylene (HDPE) sample bottles to measure lanthanum concentrations. Samples were preserved with three drops of concentrated nitric acid (HNO_3, J.T. Baker, Phillipsburg, NJ, USA), and refrigerated at 4 °C until analysis at the Water Science Laboratory using EPA method 6020. Following the 5-week experiment, each fish was euthanized using MS222 following FAU IACUC approved protocol [18]. Samples were weighed, measured, and frozen at −18 °C until dissection and analysis.

2.4. Dissection and Tissue Removal

Each fish was thawed in the refrigerator overnight to improve ease of dissection. Materials included scalpels, suture scissors, forceps, and trays. Tools and trays were cleaned using soap and water and sanitized with 80% antiseptic alcohol solution between consecutive samples.

A small incision was made at the anus up to the isthmus followed by an upward lateral cut to remove the liver. Using clean tools, a lateral line was cut directly upward from the point of primary incision to fillet the fish and remove a sample of the skeletal muscle or flesh (hereinafter referred to a "tissue" or "flesh" sample) from the left lateral side. Tissue and liver samples were then cut into approximately 2 mm pieces and placed in individual vials. Vials were frozen at −18 °C until analysis.

2.5. Liver, Tissue, and Statistical Analysis

All sample analyses were conducted at the University of Nebraska Water Science Laboratory. Liver and tissue samples were thawed overnight and then prepped for digestion with Microwave Accelerated Reaction System (MARS) Digestion Oven. Digested samples were run on the iCAP RQ ICPMS (Waltham, MA, USA). The EPA Standard Method 3052 for siliceous or organically based matrices was followed [19]. In following this method, 0.125 g of each sample was digested. The digestate was then diluted to a volume of 50 mL prior to analyzing for lanthanum content on the iCAP RQ ICPMS (Waltham, MA, USA). Due to the high organic content of the samples, we used 1 mL of hydrogen peroxide (H_2O_2) instead of the normal 0.125 mL, and 1 mL of trace metal grade nitric acid to aid in digestion.

All standards were prepared using SPEX Certiprep™ 1000 μg mL^{-1} standard solutions and trace metal grade nitric acid. The detection limit for digested samples was 0.003 μg g^{-1}. A surrogate spike of indium was added to each sample to ensure adequate recovery of 90 to 110%. Additional quality control procedures included running a duplicate sample first against itself and fortified blanks of known concentration, which similarly required recovery of 90 to 110%.

Unpaired standardized t-tests were used to compare lanthanum accumulation between groups using GraphPad Software (San Diego, CA, USA). Outliers were excluded.

3. Results and Discussion

3.1. Field Site Results: Improvements in Water Quality

Following two seasons of treating the Densmore Pond with the floating treatment wetlands (FTWs) and lanthanum composites via an airlift pump, we observed noticeable changes in water quality parameters, such as temporal changes in phosphorus and nitrate concentrations and dissolved oxygen (Figure 3). Specifically, both phosphorus and nitrate concentrations decreased with treatment, while dissolved oxygen concentrations increased (Figure 3). These changes corresponded with noticeable decreases in algae and weed growth in the second year (Figure 4) and significantly greater water clarity (Figure 5).

3.2. Field Site Results: Fish Analysis

While improvements to water quality were clearly visible and quantifiable (Figures 3–5), it was important to determine whether the lanthanum released from the lanthanum–wax composites were negatively impacting lentic organisms. Results from our fish analysis following two years of treatment showed higher lanthanum concentrations in the liver (1.02 μg g^{-1}) than the tissue (0.50 μg g^{-1}) for all fish harvested from the Densmore Pond (Table 1). While higher lanthanum concentrations in the liver was expected, significant differences between the liver and tissue were not observed (Table 1). Landman et al. [20] similarly determined that trout (*Oncorhynchus mykiss*) and koura (*Paranephrops planifrons*) in Lake Okareka (New Zealand) accumulated lanthanum in the liver and hepatopancrease tissues following two years of Phoslock® application, but minimal lanthanum was detected in the flesh.

Table 1. Lanthanum accumulation in organs (flesh vs. liver) of all lanthanum-treated fish harvested from field study (Densmore Pond).

Organ	Average (μg g^{-1})	Number of Samples	Standard Deviation	*p*-Value	Significance (α = 0.05)
Flesh	0.50	11	0.46	0.30	Not significant
Liver	1.02	10	1.56		

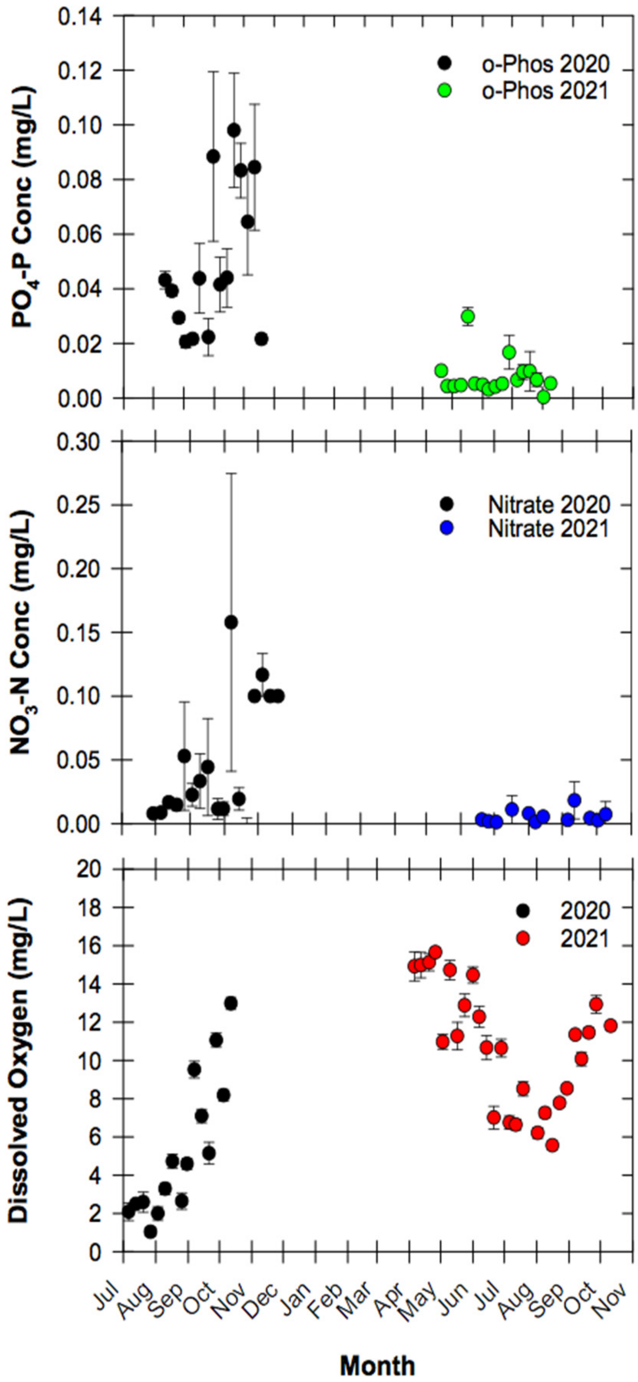

Figure 3. Temporal changes in phosphate, nitrate, and dissolved oxygen concentrations between 2020 and 2021.

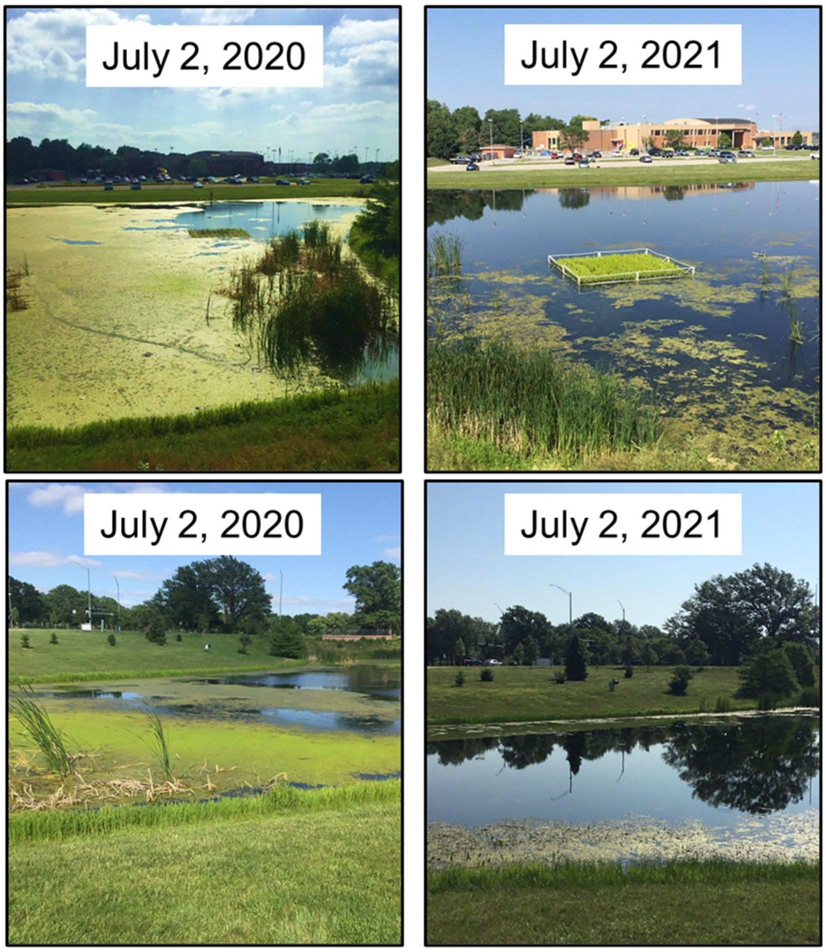

Figure 4. Changes in surface water appearance of Densmore Pond following two years of biological–chemical treatment (2020 vs. 2021).

Figure 5. Visible improvements in water clarity after lanthanum composite addition.

We also compared lanthanum accumulation between experimental (La^{3+}-treated) and control ponds using fish from similar ages and sizes. Statistical analyses were performed on all bluegill and largemouth bass collected. The tissue samples of fish collected from the experimental site resulted in an average of 0.50 μg/g lanthanum in fish of all ages (Table 2). The control group exhibited an average lanthanum concentration of 0.27 μg/g (Table 2). The overall p-value was 0.18. While this analysis does not demonstrate a significant difference ($\alpha = 0.05$), results indicate a trend toward higher lanthanum accumulation in the tissue (flesh) of fish at the Densmore pond versus the control site. Likewise, higher liver lanthanum concentrations were also observed in fish from the Densmore pond than the control pond, but again values were not significantly different (α = 0.05, Table 2).

Table 2. Lanthanum accumulation in organs of all fish harvested from field study ponds (lanthanum treated vs. control).

Treatment/Organs	Average ($\mu g\ g^{-1}$)	Number of Samples	Standard Deviation	*p*-Value	Significance (α = 0.05)
Lanthanum—Flesh	0.50	11	0.46	0.18	Not significant
Control—Flesh	0.27	9	0.20		
Lanthanum—Liver	1.02	10	1.55	0.31	Not significant
Control—Liver	0.33	6	0.32		

Past studies offer mixed reviews on the effects of lanthanum on various study species. Lanthanum accumulation is highest in the internal organs and hepatopancreas of fish [21–24]. Localized accumulation in internal organs, which are less frequently consumed by humans, as opposed to fish flesh, indicates human health concerns are limited. One study determined lanthanum concentrations in fish liver reverted to baseline concentrations several months after Phoslock® application [20]. Given Phoslock® is typically applied in one large dose, it is expected that lanthanum concentrations in the water column would be initially high after application and gradually decline as the lanthanum–clay suspensions settled out. A decrease in lanthanum liver concentrations months after Phoslock® applications indicate internal organs are capable of lanthanum detoxification, excretion, or both [20,22]. It is perhaps noteworthy that in the upper Midwest (USA), a similar decline in lanthanum concentrations could also be observed in treated ponds. Using the lanthanum composite-airlift pump approach (Figure 1), the slow-release lanthanum composites would only be deployed during spring through fall (i.e., March to October); this would leave several fall and winter months where the lanthanum composites would not be present and overall lanthanum concentrations in the water column would decrease. Given the fish harvested in this field study occurred during the end of active treatment (i.e., mid-September), detoxification or removal of lanthanum from the fish may occur during the winter months when lanthanum composites are not deployed. This could result in even lower lanthanum concentrations in the fish tissue than reported (Tables 1 and 2).

Regarding human consumption, the safety threshold for lanthanum toxicity in humans is high [25]. Lanthanum is used to lower high blood phosphate concentrations in people who are on dialysis due to severe kidney disease. Specifically, lanthanum carbonate is used in the prescription medication, Fosrenol®, which acts as a phosphate-binding agent to treat hyperphosphatemia [26]. The U.S. Food and Drug Administration has approved Fosrenol® dosages of 750 to 3000 mg per day. Further, Harrison and Scott [27] reported that up to 3 g per day of elemental lanthanum was tolerated per person without any toxic effects following four years of study. Given the concentrations of lanthanum we observed in the fish tissue (0.27–1.02 $\mu g\ g^{-1}$; Tables 1 and 2), exceeding this daily lanthanum dose from over consumption of fish would not be possible. Despite this, ensuring the lanthanum treatment is within the consumable fish species' biological depuration capacity is essential to confirm human and environmental safety. Given the low lanthanum concentrations in the water column during treatment and the four or five months of non-treatment during the calendar year in the upper Midwest (USA), we believe the environmental safety of fish and humans (from fish consumption) is being preserved.

3.3. Controlled Tank Results: Lanthanum Treated versus Control

Analysis of fish from the Densmore Pond revealed that the concentration of lanthanum used to combat eutrophication was detectable in the fish liver and flesh but not significantly different from fish harvested from the control pond. Lanthanum concentrations in the water column at the Densmore pond averaged 104 μg L^{-1} and generally ranged between 50 and 200 μg L^{-1} [11].

To supplement the field results and determine whether higher lanthanum concentrations would result in significant differences in fish tissues between lanthanum-treated and -non-treated tanks, we initiated a five-week controlled tank experiment (Figure 6) that used a nine-fold higher concentration of lanthanum. The average concentration in the experimental tanks was 916 μg L^{-1} (Figure 7). Statistical analysis was performed on all bluegills raised under experimental (lanthanum) and control conditions. No statistical difference was observed between these two treatments (Table 3).

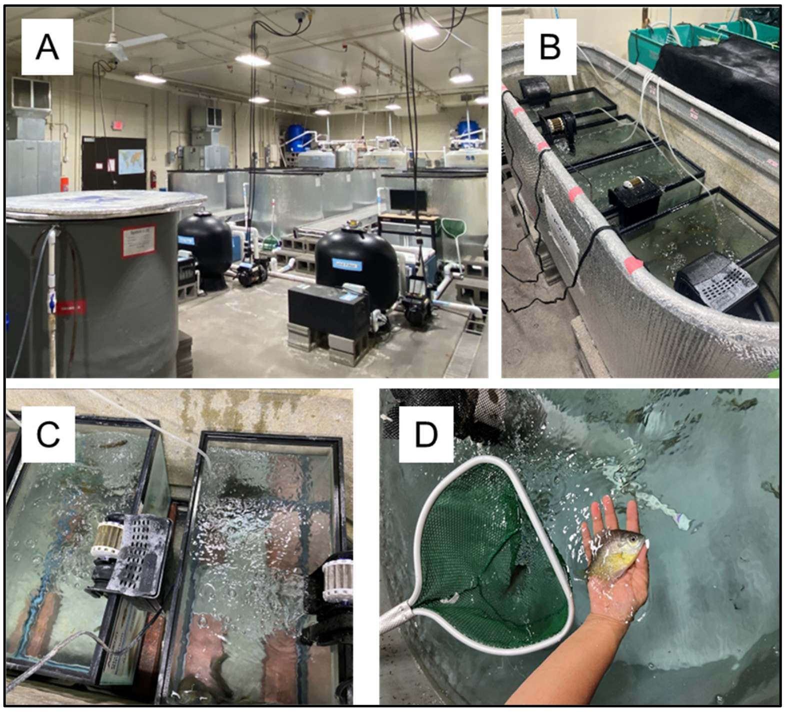

Figure 6. (**A**) UNL Aquaculture Laboratory; (**B**) Fish aquarium tank enclosure; (**C**) Individual aquariums; (**D**) Bluegill fish during acclimation period before start of five-week laboratory experiment.

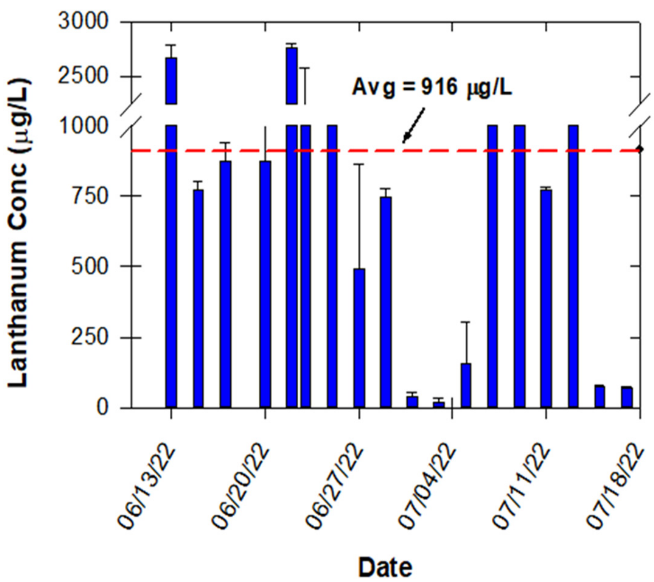

Figure 7. Measured lanthanum concentrations in lanthanum-treated aquariums over five weeks.

Table 3. Lanthanum accumulation in organs of bluegill fish grown in aquarium tanks for five weeks (lanthanum treated vs. control).

Treatment/Organs	Average (μg g^{-1})	Number of Samples	Standard Deviation	*p*-Value	Significance (α = 0.05)
Lanthanum—Flesh	3.54	6	1.80	0.27	Not significant
Control—Flesh	2.63	7	0.98		
Lanthanum—Liver	1.92	7	2.05	0.31	Not significant
Control—Liver	2.71	7	0.32		

A second analysis was performed on experimental fish based on their date of mortality. We compared lanthanum concentrations in bluegill fish that experienced premature death (PD) versus those that survived the full five-week experiment (FE). Unfortunately, some bluegill fish developed symptoms characteristic of red sore disease, which is a common disease in freshwater game fish and typically caused by two organisms: *Aeromonas hydrophila*, a bacterium, and *Heteropolaria* sp., a protozoan [28]. The analysis of these two groups (PD vs. FE) did not reach the $\alpha \leq 0.05$ threshold (Table 4); however, we observed a trend toward significance. The PD treatment group displayed a higher liver concentration of lanthanum (average = 4.91 μg L^{-1}) than the FE treatment group (average = 2.71 μg L^{-1}) with a *p*-value of 0.14 (Table 4). Whether the lanthanum treatment predisposed the bluegills to red sore disease is unknown. While previous research has shown increased mortality of fish following lanthanum exposure [29], usually at higher concentrations, the lanthanum concentrations observed in our tank study (Figure 7) were not high enough to produce significant differences in observed results (Tables 3 and 4).

Table 4. Lanthanum accumulation in bluegill organs grown in lanthanum-treated aquarium tanks. Comparison between fish that survived the full experiment (FE) versus fish that had premature deaths (PD).

Treatment/Organs	Average (μg g^{-1})	Number of Samples	Standard Deviation	*p*-Value	Significance (α = 0.05)
FE—Flesh	3.54	6	1.80	0.86	Not significant
PD—Flesh	3.86	5	4.07		
FE—Liver	1.92	7	2.05	0.14	Not significant
PD—Liver	4.91	5	4.44		

Lanthanum is a rare earth element (REE) and as such, there has been considerable research on lanthanum due to the increased use of REEs in high technology applications. Arienzo et al. [29] recently provided an excellent review of REE, which included a review of the mechanisms involved in lanthanum bioavailability and toxicity. What is clear from the literature is that the toxicology of REEs resembles non-essential metals and low toxicity can be expected at low concentrations. In addition, the concentration of the free La ion is what has been shown to be a good indicator of toxicity. When phosphate is available, it readily binds with lanthanum and fewer toxic effects are observed in aquatic organisms [29]. It is noteworthy that the water used in the tank study did not have elevated phosphate concentrations, as was present in the Densmore pond (Figure 5). This means less speciation (i.e., complexation) of the added lanthanum in the tank study occurred and more free La may have been present. This would not be the case in the field where slow-release lanthanum composites are used to remove phosphate from eutrophic ponds.

4. Conclusions

The United Nations 2030 agenda for sustainable development includes 17 goals that lay the blueprint for peace and prosperity for people and the planet [30]. One of the United Nations' sustainable development goals is to ensure clean water and sanitation [30]. This goal will require efforts on many fronts to combat the effects of nutrient loads on freshwater ecosystems. While reducing the mass of nutrients entering freshwater systems is the key to prevention, having a chemical and biological approach to restoring deteriorated inland waters could also be useful to some communities.

The University of Nebraska's (UNL) biological and chemical approach to treating eutrophic ponds is a novel technology for removing nitrogen and phosphorus from the water column, reducing algae and weeds, and increasing dissolved oxygen and water clarity. While improvements in water quality are clearly visible following one or two years of treatment (see Figures 4 and 5), questions remain about the toxicity of the lanthanum used with the chemical approach and the possible accumulation of lanthanum in fish tissue.

We analyzed the tissue of fish exposed to the field treatment after two years and a controlled tank study that used higher lanthanum concentrations than those observed in the field. The field site confirmed that under the concentrations of lanthanum being released to treat eutrophic ponds, no adverse effects were observed in fish harvested from the field site. Likewise, no significant differences were observed in our controlled tank study between lanthanum exposed and unexposed fish. We observed increased mortality and higher lanthanum concentrations in the liver of fish exposed to lanthanum in the tank study, but treatments were not significantly different ($\alpha = 0.05$). Given that the laboratory tank lanthanum concentrations were nine times higher (916 μg L^{-1}) than what we observed under field conditions (104 μg L^{-1}), we conclude that the lanthanum composite treatment of eutrophic ponds exhibits no significant accumulation in fish tissue. Future work should continue to monitor fish exposed to slow-release lanthanum over more years than those of the present study and use a larger sample size with additional fish species.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/environments10020020/s1, Figure S1. A. and B. Photographs of eutrophic pond (Densmore Pond, Lincoln, NE, USA) in 2020. C. Dead koi fish at Densmore Pond, July 2020. Figure S2. A. Nebraska Game and Parks electrofishing at Densmore Pond. B. Largemouth bass and bluegills harvested from electrofishing.

Author Contributions: Conceptualization, C.M., J.M. and S.C.; methodology, C.M., J.M. and N.R.; validation, C.M. and J.M.; formal analysis, C.M. and S.C.; resources, S.C.; writing—original draft preparation, C.M. and S.C.; writing—review and editing, C.M., J.M., N.R. and S.C.; funding acquisition, C.M. and S.C. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support was provided by the Nebraska Environmental Trust (PIE Grant 21-06-3P) and the International Agriculture and Natural Resources Institute Undergraduate Research Award. Data analysis was supported by the UNL Water Science Laboratory and School of Natural Resources. This paper is a contribution of Agric. Res. Div. Hatch Project NEB-38-111.

Data Availability Statement: Not applicable.

Acknowledgments: We thank Mark Pegg and Becky Young for technical assistance and editorial suggestions, and Israt Jahan for assistance with the tank experiments performed in UNL's aquacultural laboratory. We also thank Levi McKercher for establishing project infrastructure and initial guidance, and Jeff Jackson and Matthew Perrion of the Nebraska Game and Parks commission for assistance with electrofishing the field sites. Chemical analyses were supported by the UNL Water Science Laboratory and School of Natural Resources.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Smith, V.H.; Schindler, D.W. Eutrophication science: Where do we go from here? *Trends Ecol. Evol.* **2009**, *24*, 201–207. [CrossRef]
2. Khan, M.N.; Mohammad, F. Eutrophication: Challenges and Solutions. *Eutrophication Causes Conseq. Control* **2013**, 1–15. [CrossRef]
3. Pieterse, N.M.; Bleuten, W.; Jørgensen, S.E. Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. *J. Hydrol.* **2003**, *271*, 213–225. [CrossRef]
4. Malmqvist, P.-A. *Urban Stormwater Pollutant Sources: An Analysis of Inflows and Outflows of Nitrogen, Phosphorus, Lead, Zinc, and Copper in Urban Areas*; Chalmers Tekniska Hogskola: Göteborg, Sweden, 1983.
5. Carpenter, S.R. Phosphorus control is critical to mitigating eutrophication. *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 11039–11040. [CrossRef]
6. Majumdar, D. The Blue Baby Syndrome. *Resonance* **2003**, *8*, 20–30. [CrossRef]

7. Kumar, M.; Puri, A. A review of permissible limits of drinking water. *Indian J. Occup. Environ. Med.* **2012**, *16*, 40–44. [CrossRef] [PubMed]
8. Wurtsbaugh, W.A.; Paerl, H.W.; Dodds, W.K. Nutrients, eutrophication and harmful algal blooms along the freshwater to marine continuum. *Wiley Interdiscip. Rev. Water* **2019**, *6*, e1373. [CrossRef]
9. Glibert, P.; Seitzinger, S.; Heil, C.; Burkholder, J.A.; Parrow, M.; Codispoti, L.; Kelly, V. The role of eutrophication in the global proliferation of harmful algal blooms. *Oceanography* **2005**, *18*, 198–209. [CrossRef]
10. Durham, M.M. Effects of Eutrophication. In *Eutrophication: Causes, Consequences and Control*; Springer: Dordrecht, The Netherlands, 2013; pp. 29–44.
11. McKercher, L.J.; Messer, T.L.; Mittelstet, A.R.; Comfort, S.D. A biological and chemical approach to restoring water quality: A case study in an urban eutrophic pond. *J. Environ. Manag.* **2022**, *318*, 115463. [CrossRef]
12. Pavlineri, N.; Skoulikidis, N.T.; Tsihrintzis, V.A. Constructed floating wetlands: A review of research, design, operation and management aspects, and data meta-analysis. *Chem. Eng. J.* **2017**, *308*, 1120–1132. [CrossRef]
13. Zhi, Y.; Zhang, C.; Hjorth, R.; Baun, A.; Duckworth, O.W.; Call, D.F.; Knappe, D.R.U.; Jones, J.L.; Grieger, K. Emerging lanthanum (III)-containing materials for phosphate removal from water: A review towards future developments. *Environ. Int.* **2020**, *145*, 106115. [CrossRef] [PubMed]
14. Yamada-Ferraz, T.M.; Sueitt, A.P.; Oliveira, A.F.; Botta, C.M.R.; Fadini, P.S.; Nascimento, M.R.L.; Faria, B.M.; Mozeto, A.A. Assessment of Phoslock® application in a tropical eutrophic reservoir: An integrated evaluation from laboratory to field experiments. *Environ. Technol. Innov.* **2015**, *4*, 194–205. [CrossRef]
15. Spears, B.M.; Lürling, M.; Yasseri, S.; Castro-Castellon, A.T.; Gibbs, M.; Meis, S.; McDonald, C.; McIntosh, J.; Sleep, D.; Van Oosterhout, F. Lake responses following lanthanum-modified Bentonite clay (Phoslock®) application: An analysis of water column lanthanum data from 16 case study lakes. *Water Res.* **2013**, *47*, 5930–5942. [CrossRef] [PubMed]
16. Yamada-Ferraz, J.A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw Hill: New York, NY, USA, 1992.
17. Bishop, W.M.; Richardson, R.J. Influence of Phoslock® on legacy phosphorus, nutrient ratios, and algal assemblage composition in hypereutrophic water resources. *Environ. Sci. Pollut. Res.* **2018**, *25*, 4544–4557. [CrossRef] [PubMed]
18. FAU IACUC. Guidelines for the Preparation and Use of MS222 (TMS, Tricaine Methanesulfonate) for Animal Procedures. 2014. Available online: https://www.fau.edu/research-admin/comparative-medicine/files/guidelines-for-the-preparation-and-use-of-ms222-final.pdf (accessed on 1 September 2022).
19. United States Environmental Protection Agency. Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. Method 3052. Available online: https://www.epa.gov/sites/default/files/2015-12/documents/3052.pdf (accessed on 1 September 2022).
20. Landman, M.; Brijs, J.; Glover, C.; Ling, N. *Lake Okareka and Tikitapu Fish Health Monitoring*; Scion Report; SCION: Rotorua, New Zealand, 2007.
21. Herrmann, H.; Nolde, J.; Berger, S.; Heise, S. Aquatic ecotoxicity of lanthanum—A review and an attempt to derive water and sediment quality criteria. *Ecotoxicol. Environ. Saf.* **2016**, *124*, 213–238. [CrossRef] [PubMed]
22. Hao, S.; Xiaorong, W.; Zhaozhe, H.; Chonghua, W.; Liansheng, W.; Lemei, D.; Zhong, L.; Yijun, C. Bioconcentration and elimination of five light rare earth elements in carp (Cyprinus carpio L.). *Chemosphere* **1996**, *33*, 1475–1483. [CrossRef]
23. Behets, G.J.; Mubiana, K.V.; Lamberts, L.; Finsterle, K.; Traill, N.; Blust, R.; D'Haese, P.C. Use of lanthanum for water treatment a matter of concern? *Chemosphere* **2020**, *239*, 124780. [CrossRef]
24. Mayfield, D.B.; Fairbrother, A. Examination of rare earth element concentration patterns in freshwater fish tissues. *Chemosphere* **2015**, *120*, 68–74. [CrossRef]
25. SePRO Corporation. *An Overview of Phoslock and Use in Aquatic Environments*; SePRO Corporation: Carmel, IN, USA, 2012.
26. Albaaj, F.; Hutchison, A.J. Lanthanum carbonate (Fosrenol®): A novel agent for the treatment of hyperphosphataemia in renal failure and dialysis patients. *Int. J. Clin. Pract.* **2005**, *59*, 1091–1096. [CrossRef]
27. Harrison, T.S.; Scott, L.J. Lanthanum carbonate. *Drugs* **2004**, *64*, 985–996. [CrossRef] [PubMed]
28. Reed, P.; Francis-Floyd, R. Red Sore Disease in Game Fish. Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida. 2011. Available online: https://wbefc.org/wp-content/uploads/2017/05/Sores-on-Fish.pdf (accessed on 1 September 2022).
29. Arienzo, M.; Ferrara, L.; Trifuoggi, M.; Toscanesi, M. Advances in the Fate of Rare Earth Elements, REE, in Transitional Environments: Coasts and Estuaries. *Water* **2022**, *14*, 401. [CrossRef]
30. United Nations Department of Economic and Social Affairs. Sustainable Development. Available online: https://sdgs.un.org (accessed on 13 January 2023).