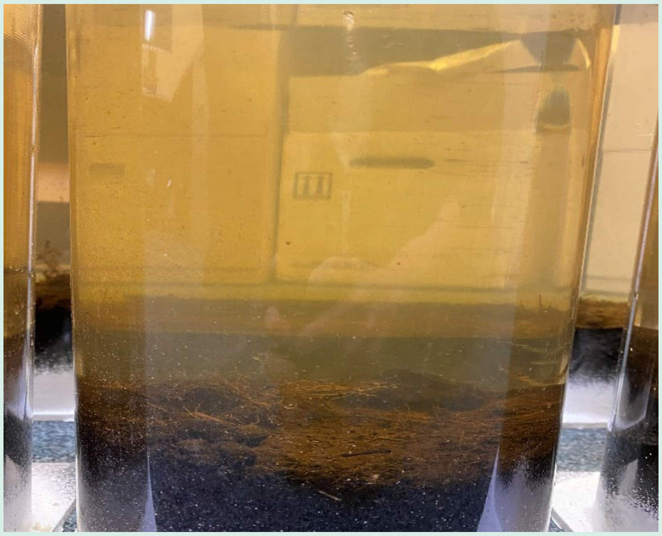
FINAL TECHNICAL REPORT ◦ JUNE 2021

Increasing Phosphorus Binding Capacity in Wetland Sediments: Phase I of a Laboratory Bench-scale Feasibility Study for Phoslock™



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Cover photos: Sample collection at Upper Klamath Lake (upper and bottom right) and reactor setup (upper and lower left).

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1 INTRODUCTION

Historically, Upper Klamath Lake (UKL), Oregon (Figure 1), has been characterized as eutrophic, or enriched with nutrients that support excessive levels of algal productivity (EPA 1974, Johnson 1985). Large-scale watershed development from the late-1800s through the 1900s has contributed to the lake's current hypereutrophic condition (USGS 1993), whereby extensive seasonal cyanobacteria blooms result in large diel fluctuations in dissolved oxygen (DO) concentrations and pH, elevated levels of un-ionized ammonia during bloom decomposition, and periodically high concentrations of the cyanotoxin microcystin (ODEQ 2002, Walker et al. 2012). Together, these conditions create a suboptimal environment for native aquatic biota and likely play a role in the decline of Endangered Species Act-listed shortnose and Lost River suckers (USGS 2000).

Phosphorus is currently understood to be the key driver of water quality issues in the Upper Klamath Basin (ODEQ 2002, Walker et al. 2012). Phosphorus occurs in relatively high levels in the local geology of the Upper Klamath Basin (ODEQ 2002, Walker et al. 2015), but has been, and continues to be, mobilized as a result of land use activities in the watershed (Walker et al. 2012, Walker et al. 2015). Average annual external phosphorus load to UKL is approximately 40 percent higher than the natural background (ODEQ 2002, Walker et al. 2012).

Numerous restoration and management actions have been recommended to reduce external phosphorus loads to UKL and improve water quality conditions within the lake. Two of these actions, restoration of lake-fringe wetlands and construction of diffuse source treatment wetlands (DSTWs), were identified by the Klamath Hydroelectric Settlement Agreement Interim Measures Implementation Committee as priority projects for water quality improvement in the Upper Klamath Basin. Wetlands, including DSTWs, sequester phosphorus through the following mechanisms:

- Settling of particulate phosphorus from the water column.
- Temporary uptake of inorganic dissolved phosphorus (soluble reactive phosphorus [SRP], the form most readily available to plants and algae) through redox-dependent sorption to metal hydroxide oxides (Mortimer 1941, 1942).
- Seasonal uptake of SRP in biomass (Kadlec 1997).
- More permanent uptake of SRP through accretion of plant litter into peat sediments, whereby a portion of wetland vegetation is not fully decomposed, and the associated phosphorus is sequestered in peat sediments (Kadlec 1997, Juston et al. 2013).

However, restored wetlands, particularly when used previously for agricultural production and grazing, can also release SRP following re-inundation, and these wetlands may not function as phosphorus sinks for years to decades following completion of active restoration (Aldous et al. 2005, Graham et al. 2005). Similarly, DSTWs may have limited capacity to sequester SRP until robust emergent vegetation has been established. In Upper Klamath Basin areas exhibiting relatively high SRP (relative to particulate phosphorus) loads, such as the Wood River Valley, increasing wetland capacity to sequester SRP from the overlying water column would help to reduce the annual external phosphorus load to UKL.

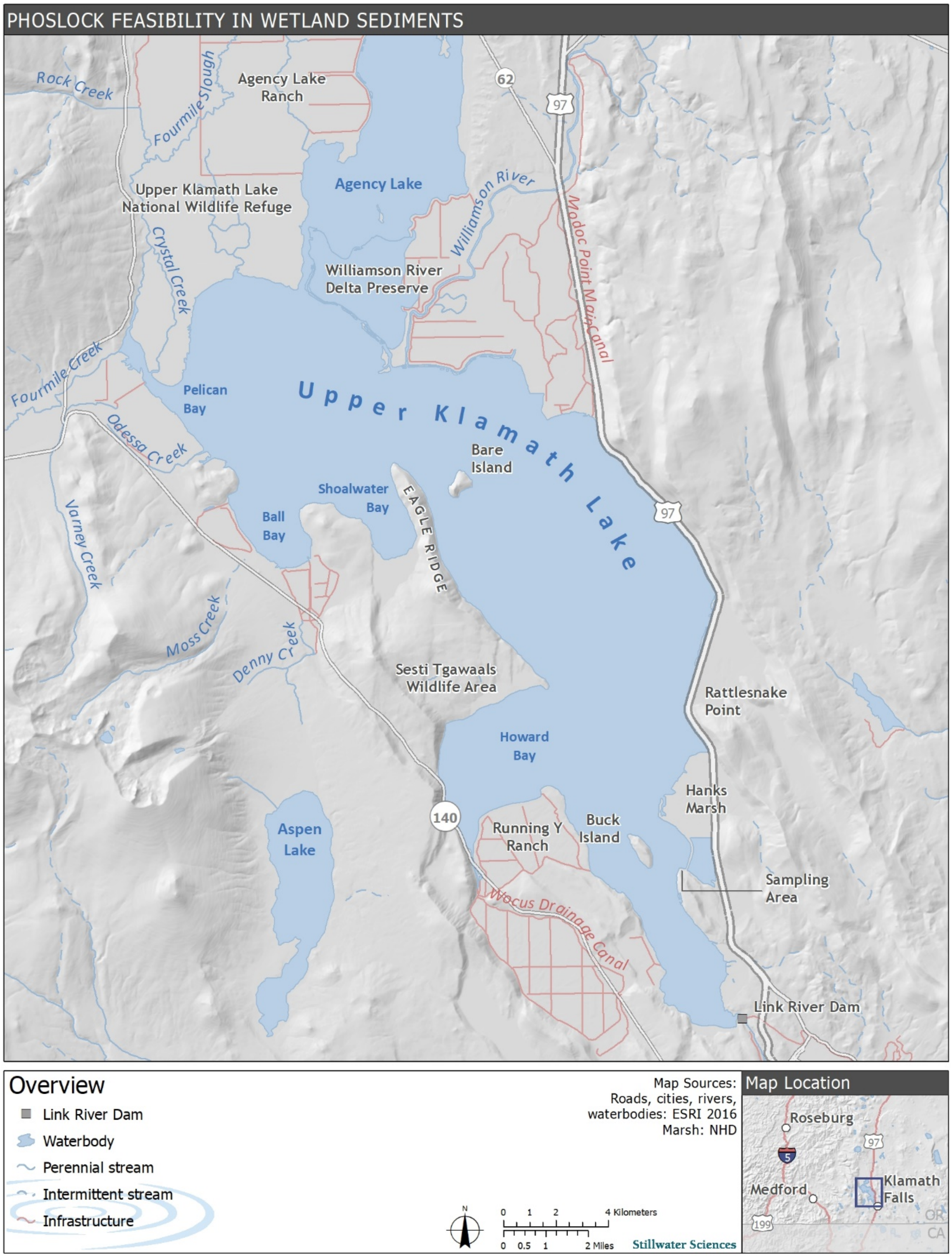


Figure 1. Overview of Upper Klamath Lake.

Phoslock^{TM} application offers potential for increasing the capacity of wetland sediments to sequester phosphorus immediately following re-inundation, and in the months and years afterward. Phoslock^{TM} is a bentonite clay amended with lanthanum (La), where the latter is a rare earth metal. Phoslock^{TM} has been used in recent years for control of phosphorus in aquatic systems. In contrast to common water treatment coagulants (e.g., ferric chloride [$FeCl_3$], aluminum sulfate [$Al_2(SO_4)_3$]) that rely upon charge neutralization and flocculation of colloidal sized particulates, the La in Phoslock^{TM} binds with the phosphate anion (PO_4^{3-}) to form an insoluble and biologically inert mineral called rhabdophane ($La(PO_4)\cdot H_2O$). Although La and La compounds (e.g., lanthanum chloride [$LaCl_3$], lanthanum(III) oxide [La_2O_3]) have been shown to bioaccumulate and/or to result in toxicity at elevated concentrations (> 0.5 milligrams per liter [mg/L]) for aquatic species (Herrmann et al. 2016), there are currently no regulatory thresholds for La. Based on laboratory bioassays, Phoslock^{TM} appears to have low aquatic toxicity potential, particularly at lower application doses (Herrmann et al. 2016, Lürling and Tolman 2010, Afsar and Groves 2009). In recent jar tests of Upper Klamath Basin waters, Phoslock^{TM} applications were shown to reduce water column phosphorus concentrations without the changes in pH that are often associated with alum and ferric-based coagulants (CH2M Hill 2015). While several studies have focused on application of Phoslock^{TM} to lake or reservoir water columns, no studies appear to have examined the feasibility and/or effectiveness of applying this coagulant directly to wetland sediments or sediments prior to re-inundation as part of planned restoration activities.

The objective of this study was to serve as a feasibility test of the phosphorus binding capacity of Phoslock^{TM} and the potential for release of toxic levels of La when Phoslock^{TM} is applied at multiple dosing levels to re-inundated wetland sediments at a bench scale and in a laboratory setting. Funding for this study has been provided in two parts: Phase I focuses on the Phoslock^{TM} dosing levels, while Phase II expands the number of test variables and considers Phoslock^{TM} behavior under varying overlying water conditions (e.g., SRP concentration, water temperature, and pH). and is discussed in a separate report. If Phoslock^{TM} application to wetland sediments is determined to be an effective phosphorus binding agent at the laboratory bench scale in Phases I and II, next steps could include study of application across a range of wetland sediments and application at a larger scale.

2 HYPOTHESES

This feasibility study tested the following hypotheses at a bench scale in a laboratory setting:

> *Hypothesis 1: Direct application of Phoslock^{TM} to the wetland sediment surface prior to inundation will increase sediment binding capacity for SRP relative to non-amended sediments and will reduce the amount of SRP that fluxes out of the sediments as a response to inundation.*
>
> *Hypothesis 2: Application of Phoslock^{TM} to the wetland sediment surface prior to inundation will not result in a release of potentially toxic levels of lanthanum (La) as a response to inundation.*

3 METHODS

3.1 Experimental Design

The experimental design relied upon replicated bench-scale batch reactors containing sediments representative of historical wetlands that have been used for Upper Klamath Basin agricultural production over the past several decades, overlying water from Upper Klamath Lake, and varying doses of Phoslock^{TM}. A batch reactor is a closed system where the reaction of interest takes place in a controlled manner to minimize and/or quantify potentially confounding factors (e.g., pH, temperature, oxygen) and thus simplify observations to address the study hypotheses. There is no continuous flow of reactants entering the system or products leaving the system in a batch reactor. The experimental reactors were constructed from transparent acrylic tubes (approximately 50 centimeters [cm] tall, 14.5 cm in diameter [20 inches tall, 5.75 inches in diameter]) that were sealed on the bottom and initially open to the atmosphere at the top, then loosely covered after t_{24}.

Phoslock^{TM} was added at three dosing levels to six treatment reactors (n=2 each) and was absent from three control reactors, for a total of nine reactors (Table 1). To simulate a potentially low-cost application method for Phoslock^{TM} in wetland restoration projects in the Upper Klamath Basin, Phoslock^{TM} was added as a water-based slurry on top of 10 cm of "field-condition" sediments (i.e., no purposeful drying or wetting of sediments was conducted prior to their use) in the treatment reactors at the beginning of the experiment, after which Upper Klamath Lake water amended with SRP was added to all reactors to simulate "flood up" of the wetland. The SRP amendment was undertaken to align with Phase II experiments that included overlying water SRP as a variable. All Phase I reactors (including the controls) were amended with 290 mg of 1,000 mg/L PO_4^{3-} standard solution to achieve 0.05 mg/L SRP for each reactor.

No additional water was added to the reactors for the remainder of the experiment. Immediately following slurry application, approximately 5.4 liters (L) (32 cm water depth) of anoxic native water was added to each reactor to represent wetland "flood up." Low oxygen conditions (< 2 mg/L) in the flood-up water were achieved by pre-sparging the water with nitrogen (N_2) gas, then sparging with carbon dioxide (CO_2), to provide low redox conditions at the sediment-water interface and within sediment pore waters and to support SRP release from wetland sediments at "flood up" or shortly thereafter, while maintaining circumneutral pH. Reactors were stored in an artificially cooled space to maintain water temperatures at or near 15 degrees Celsius (°C), and they were held at ambient pH (7.0 to 7.5 standard units [s.u.]) and in the dark for the duration of the experiment.

Table 1. Phase 1 Phoslock^{TM} experimental design, including dosing level assumptions for coagulant testing batch reactors.

Sediment amendment	Number of batch reactors	Phoslock^{TM} areal dosing level		Assumptions for calculating areal Phoslock^{TM} dosing level La:P
Phoslock^{TM}	2	Low [1,2,3]	114 g m^{-2}	1:1 La:P (molar basis)
	2	Medium [4]	250 g m^{-2}	Sediment capping dose (Ross et al. 2008)
	2	High [1,2,3]	389 g m^{-2}	100:1 Phoslock^{TM}: bioavailable P (mass basis) = 3.4 La:P (molar basis)

Sediment amendment	Number of batch reactors	Phoslock^{TM} areal dosing level		Assumptions for calculating areal Phoslock^{TM} dosing level
				La:P
None (Control)	3	–	–	–

[1] Based on Aldous et al. (2005), 6% of sediment TP for Upper Klamath Lake restoration wetlands = 12.7 µg P/cm^3.
[2] The source of native water used to make the Phoslock^{TM} slurry was the southern end of Upper Klamath Lake adjacent to the sediment collection site.
[3] Phoslock^{TM} is 5% La by mass.
[4] Rule of thumb for Phoslock^{TM} use as a sediment cap (Ross et al. 2008).

Nine sets of total phosphorus (TP), SRP, dissolved La concentrations, and *in situ* water quality parameters (water temperature, dissolved oxygen, pH, turbidity) in the overlying water in each of the treatment and control reactors were measured at specified time intervals to test study Hypotheses 1 and 2 (see Section 2). The samples and measurements were collected from each reactor at the following intervals during the experiment: immediately before water was added to each reactor (t_0), 2, 6, 12, and 24 hours after inundation (t_2, t_6, t_{12}, t_{24}), and 2, 4, 8, and 16 days (48, 96, 192, and 384 hours) after inundation (t_{48}, t_{96}, t_{192}, t_{384}). These time increments were selected based on preliminary tests indicating that more than 10 days would be required to reach equilibrium (Table 2). Total suspended solids (TSS) were measured in the overlying water column of a subset of reactors at four sampling intervals only (t_2, t_6, t_{12}, t_{24}) because the TSS sample volume required approximately 10% of the initial total reactor water volume.

While the original experimental design called for TP to be measured within the Phoslock^{TM} slurry at the beginning and end of the experiment, preliminary tests suggested that organic debris at the sediment water interface would interfere with formation of a distinct slurry layer and would not allow discrete sampling of this layer. Instead, TP was measured in the top 1 cm of sediment and the 1-cm layer of near-bottom water at the end of the experiment to assess how much phosphorus may have been captured by Phoslock^{TM} near the sediment-water interface (Table 2).

Phoslock^{TM} additions to the treatment reactors were designed to achieve three dosing levels expressed on an areal basis (Table 1). While the original experimental design called for Phoslock^{TM} doses of 37, 127, and 250 grams per square meter (g m^{-2}) based on the measured amount of TP in the sediments, preliminary tests indicated that this range would likely be too low to result in measurable reductions in SRP and TP fluxes across the sediment-water interface and thus the range was shifted upwards (Table 2) and the TP amount in the sediments was recorded for later comparison to TP in sediments at the end of the experiment. The rationale for the three Phoslock^{TM} dosing levels used in the experiment is detailed below.

The low and high Phoslock^{TM} dosing levels were based on the estimated amount of sediment-associated forms of phosphorus that could diffuse through sediment pore waters and across the sediment-water interface during the experimental time period (i.e., hours to days), and would be likely to bind to Phoslock^{TM}. These forms of phosphorus were considered to be "potentially releasable bioavailable phosphorus" and included soluble inorganic phosphorus (i.e., SRP), and other colloidal materials containing inorganic phosphorus (e.g., orthophosphorus bound to iron hydroxides, manganese compounds, and metal oxides) (Bishop et al. 2014). For wetland sediments collected in a prior study from six locations around Upper Klamath Lake (i.e., Hank's Marsh, Sesti Tgawaals Wildlife Area, Upper Klamath Lake National Wildlife Refuge, Agency Lake Ranch, Running Y Ranch, Williamson River Delta; see Figure 1), this potentially releasable bioavailable phosphorus represented approximately 6% (SE_{pooled} ±1.2%) of TP in sediments or

12.7 micrograms phosphorus per cubic centimeter (µg P/cm^3) (Aldous et al. 2005), which was assumed to also represent the bioavailable phosphorus content in sediments collected for experimental reactors.

Using the 12.7 µg P/cm^3 as an estimate of potentially releasable bioavailable phosphorus from the reactor sediments, the low dosing level was based on the assumption that La in Phoslock^{TM} will adsorb SRP at a 1:1 molar ratio, with sufficient Phoslock^{TM} added to bind 100% of the estimated potentially releasable bioavailable phosphorus in reactor sediments (Phoslock^{TM} contains 5% La by weight) (Table 1). Also assuming 12.7 µg P/cm^3 of potentially releasable bioavailable phosphorus, the high dosing level was based on a "rule of thumb" for lake applications that 100 grams (g) Phoslock^{TM} are required to bind 1 g of bioavailable phosphorus, with sufficient Phoslock^{TM} added to bind 100% of the estimated potentially releasable bioavailable phosphorus in reactor sediments (Table 1).

The medium Phoslock^{TM} dosing level was based on a different "rule of thumb" for Phoslock^{TM} required to "cap" potentially releasable bioavailable phosphorus in lake sediments at 250 g m^{-2} (Ross et al. 2008) and was not estimated using an assumed amount of potentially releasable bioavailable phosphorus (Table 1).

Although some bioavailable phosphorus was present in the native water used to make the Phoslock^{TM} slurry, concentrations of SRP in collected Upper Klamath Lake water were measured following collection and found to be relatively low (< 0.05 mg/L), and thus were not expected to substantially interfere with Phoslock^{TM} uptake of sediment bioavailable phosphorus in any of the treatment reactors.

Table 2. Changes to original experimental design.

Original	Change	Reason	Report section
TP to be measured in Phoslock^{TM} slurry at beginning and end of experiment	TP measured in sediments and 1-cm layer of overlying water at end of experiment	Phoslock^{TM} slurry not feasible to collect as a discrete sample	3.1
Phoslock^{TM} dosing levels 37, 127, and 250 g m^{-2}	Dosing at 114, 250, and 389 g m^{-2}	Preliminary tests indicated treatment doses were too low	3.1
Reactors to be left undisturbed except for sampling	Reactors were sparged a second time, after 8 days	Dissolved oxygen (DO) increased rapidly during the experiment	3.2
Reactor water sampling interval: every 6 hours for first 24 hours, then 2, 4, 6, 10 days	Sampling interval: 2, 6, 12, 24 hours, then 2, 4, 8, 16 days	Preliminary tests indicated it would be necessary to extend experiment duration to reach SRP/TP equilibrium concentrations in water	3.3
TP samples to be acidified by analytical lab	TP samples acidified in-house	Change of analytical lab necessary due to COVID-19 capacity restrictions	3.3
TP method detection limit (MDL) = 0.002 mg/L for SM4500-P E in water	No MDL reported	Change of analytical lab necessary due to COVID-19 capacity restrictions and new lab did not support MDL = 0.002 mg/L	3.3

Original	Change	Reason	Report section
SRP MDL = 0.002 mg/L for SM4500-P E in water	No MDL reported	Change of analytical lab necessary due to COVID-19 capacity restrictions and new lab did not support MDL = 0.002 mg/L	3.3

3.2 Sediment and Water Collection and Handling

Approximately 0.19 cubic meters (m^3) (6.6 cubic feet [ft^3]) of sediments were collected from a roughly 13 square meter area, 6 inches deep on December 11, 2020, from Cove Point Lakeside Farms (see sample area label in Figure 1). Sediments were homogenized, then placed in covered plastic containers and further chilled for transport and storage. Following transport from the field collection site, three sediment samples were composited into a glass jar and stored at 4°C until shipment to the laboratory for analysis of TP.

Approximately 85 L (22.5 gallons) of Upper Klamath Lake surface water were collected from the eastern Upper Klamath Lake shoreline on December 11, 2020. The lake surface was partially frozen at the time of collection (Figure 2). No algal biomass was observed in the lake water when collected. The surface water was homogenized and then placed in covered 5-gallon buckets and further chilled for transport and storage until it was added to the experimental reactors. Three samples were composited into a single sample that was submitted to the analytical laboratory for SRP analysis following transport. Prior to adding the lake water to the reactors, the water was sparged with nitrogen (N_2) gas and carbon dioxide (CO_2) (see Section 3.1). Due to rising dissolved oxygen concentrations during the first several days of the experiment, reactor water was sparged a second time with N_2 immediately before sampling at t_{196} (see also Table 2 and Section 4.1.1).

Figure 2. Water collection site from Upper Klamath Lake, with ice visible in the foreground (Dec 11, 2020).

3.3 Methods for Reactor Sediment, Phoslock^{TM}, and Water Sampling and Laboratory Analysis

For sediment TP determination in the top 1 cm of the reactor sediments, a portion of the top 1 cm of the sediment in each reactor was collected by scraping the surface of the sediments into a glass jar at the completion of the experiment (t_{384}). Each TP sample was stored in a glass jar at 4°C until shipment for TP analysis. Following transport from the field collection site and prior to adding sediments to the reactors, three sediment subsamples were composited into a glass jar and stored at 4°C until shipment to the laboratory for analysis of TP at t_0. For sediment La determination, reactor sediment samples were collected two times for each reactor: prior to inundation (t_0), and at the completion of each reactor experiment (t_{384}). Sediment cores (1 cm diameter, 10 cm depth) were collected in triplicate for each t_0 and t_{384} sampling event and combined into composite samples, then stored in a glass jar at 4°C until shipment for La analysis. Analytical methods for sediment analyses of lanthanum and TP are shown in Table 3.

In situ water temperature, dissolved oxygen, pH, and turbidity were measured from the overlying water in the reactors using a YSI ProPlus water quality sonde and a Hach 2100Q portable turbidity meter (Table 3). TP, SRP, and dissolved La water samples were collected from reactors at the same time intervals as *in situ* parameters using a polypropylene syringe, taking care not to disturb the sediments. The near-bottom TP water samples collected 1 cm above the sediments at the end of the experiment were also collected with a polypropylene syringe, after carefully decanting the overlying water in the reactors. All TP samples were acidified to a pH of 2 with trace metal-grade sulfuric acid then stored at 4°C in the dark, and SRP samples were filtered using 0.45-micrometer (µm) cellulose acetate filters then frozen until shipment to the analytical laboratory. Dissolved La samples were filtered immediately following collection using 0.45-micron polyethersulfone filters and stored at 4°C in the dark until shipment to the analytical laboratory within the 14-day hold time. Total suspended solids were measured in a subset of reactors at four sampling intervals only. Laboratory analytical methods for determining concentrations of TP, SRP, dissolved La, and TSS in reactor water are listed in Table 4.

Table 3. Instruments used for *in situ* water quality parameter measurement and corresponding instrument parameter precision and accuracy.

Instrument	Parameter	Instrument resolution	Instrument accuracy
YSI ProPlus	Temperature	0.1 °C	±0.35 °C
	Dissolved Oxygen	0.01 mg/L	±0.2 mg/L
	pH	0.01 s.u.	±0.2 s.u.
Hach 2100Q	Turbidity	0.01 NTU	±2% NTU

Table 4. Water and sediment phosphorus analysis methods.

Analyte	Matrix	Method	MDL	MRL	Units
Total lanthanum	Sediment	EPA 6020, mod. with EPA 3050B digestion	0.02 – 0.03	0.2 – 0.3	mg/kg
Total phosphorus (TP)	Sediment	SM4500-P E in sediment	2.5	5.0	mg/kg
	Water	SM4500-P E in water	0.01[a]	0.05[b]	mg/L
Soluble reactive phosphorus (SRP)	Water	SM4500-P E in water	0.01[a]	0.05[b]	mg/L
Total Suspended Solids (TSS)	Water	SM2540D in water	2	5	mg/L
Dissolved lanthanum	Water	EPA 1638, mod. with closed-vessel digestion	0.004	0.041	µg/L

[a] *Standard Methods for the Examination of Water and Wastewater*. DOI: 10.2105/SMWW.2882.093

[b] The analytical laboratory did not quantify values between the MRL and the MDL.

3.4 Quality Assurance/Quality Control

For *in situ* water quality parameters (i.e., water temperature, dissolved oxygen, pH, turbidity), the sonde was calibrated at the start of the experiment (Appendix A, Table A-2) and checked at the beginning of each sampling day (Appendix A, Table A-3). Calibration checks were recorded on a calibration log that includes measurement quality objective criteria for real-time comparison (Table 5). All parameters were within the acceptable objective criteria at each check (Appendix A, Table A-3). All analytical samples (sediment TP, sediment La, SRP, dissolved La, TSS) were collected, handled, and shipped to the analytical laboratory consistent with standard methods (Table 2). Appropriate quality assurance (QA) methods and documentation were followed, including accurate and thoroughly completed sample labels, data sheets, and chain of custody and sample log forms. Sample labels included sample identification code, date, time, collector's name, and sample type. The laboratory prepared all sample bottles. Data were subjected to supplemental quality control (QC) checks (audits) while in the laboratory at the completion of each sampling event to ensure that any erroneous data were addressed and clearly noted on data sheets.

Table 5. Measurement quality objectives criteria for *in situ* parameter comparisons between pre-sampling calibration and post-sampling calibration checks.

Parameter	Units	Accept	Qualify	Reject
Dissolved oxygen	% Saturation	≤ 5%	> 5% and ≤10%	> 10%
pH	s.u.	≤ 0.2	> 0.2 and ≤0.5	> 0.5
Turbidity	NTU	≤ 5%	> 5% and ≤10%	> 10%

NTU = Nephelometric Turbidity Unit
s.u. = standard unit of pH
μS/cm = microsiemens per centimeter

4 RESULTS

4.1 *In situ* Water Quality Data

4.1.1 Time series

Water temperature and dissolved oxygen rose rapidly after initial inundation of reactor sediments and approached equilibrium by 12 hours (where t_0 = immediately before inundation; t_2, t_6, t_{12}, and t_{24} represent 2, 6, 12, and 24 hours after inundation, respectively; and t_{48}, t_{96}, t_{192}, t_{384} represent 2, 4, 8, and 16 days (48, 96, 192, and 384 hours) after inundation, respectively; see Section 3.1) (Figure 3). Dissolved oxygen concentrations rose within the reactors more rapidly than expected, and thus immediately prior to sampling on day 8 (t_{192}), the reactors were sparged a second time with nitrogen gas (see also Table 2), resulting in a sharp decline in dissolved oxygen visible in the time series (Figure 3). Minimal variation in *in situ* water quality parameters was apparent across treatment and control reactors. Mean water temperatures and pH across all reactors and all sampling times were near the target values (Table 6), with relative deviations from the targets ranging 1.4% to 15%. Dissolved oxygen was more variable during the experiment and was generally greater than 2 mg/L, despite the two sparging events at t_0 and t_{192}. Individual water temperature, dissolved oxygen, and pH data are presented in Appendix A, Table A-1.

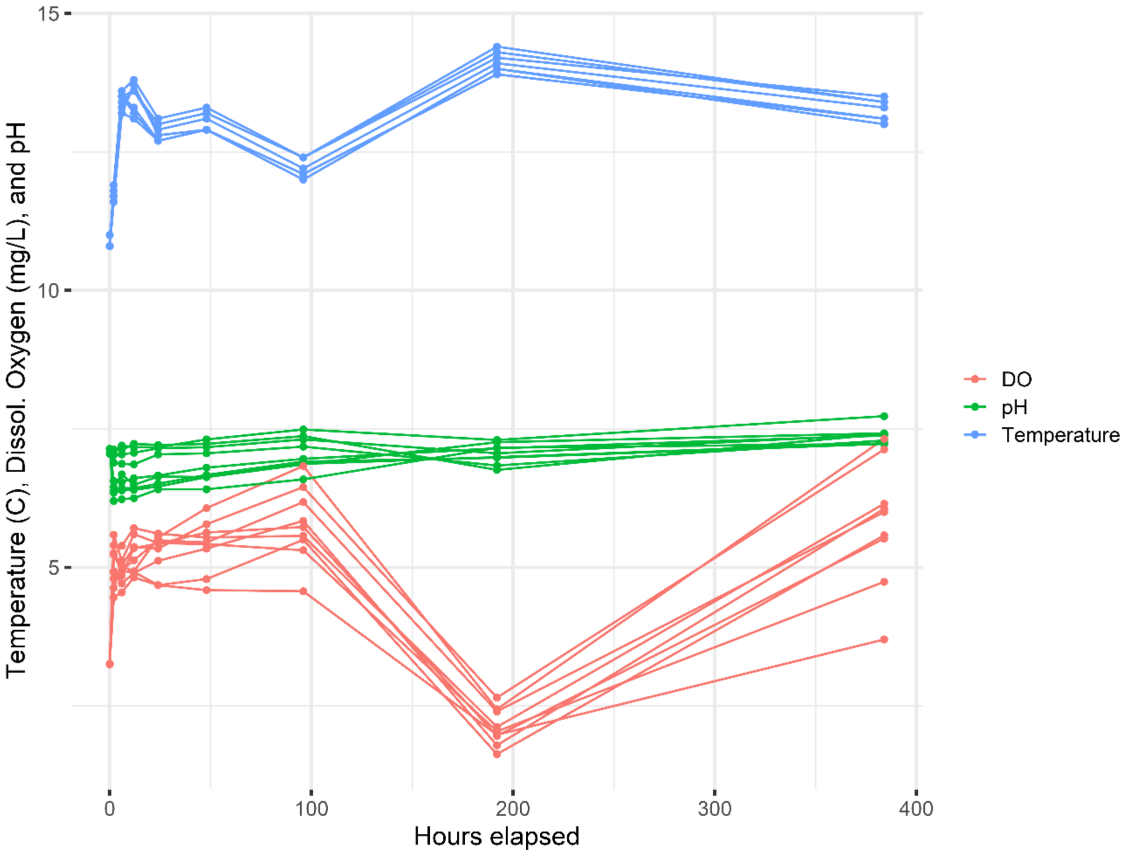


Figure 3. Time series of water temperature, dissolved oxygen, and pH in treatment and control reactors during the experiment.

Table 6. Summary of experimental *in situ* water quality parameter targets and actual values.

Parameter	Target	Actual		Relative difference from target
		Mean	Standard error	
Temperature	15°C	12.8°C	0.11	-15%
Dissolved Oxygen	< 2 mg/L	4.8 mg/L	0.14	> 100%
pH	7 to 7.5 s.u.	6.9 s.u.	0.04	1.4%

Turbidity in each reactor rose rapidly immediately following sediment inundation, and this parameter exhibited an approximately logarithmic decline through the remainder of the experiment (Figure 4). Turbidity measurements were similar at each sampling time across Phoslock™ dosing levels. Turbidity reached values measured in the pre-inundation (t_0) lake water (10 NTU) by the end of the experiment (t_{384}). Individual turbidity data are presented in Appendix A, Table A-1.

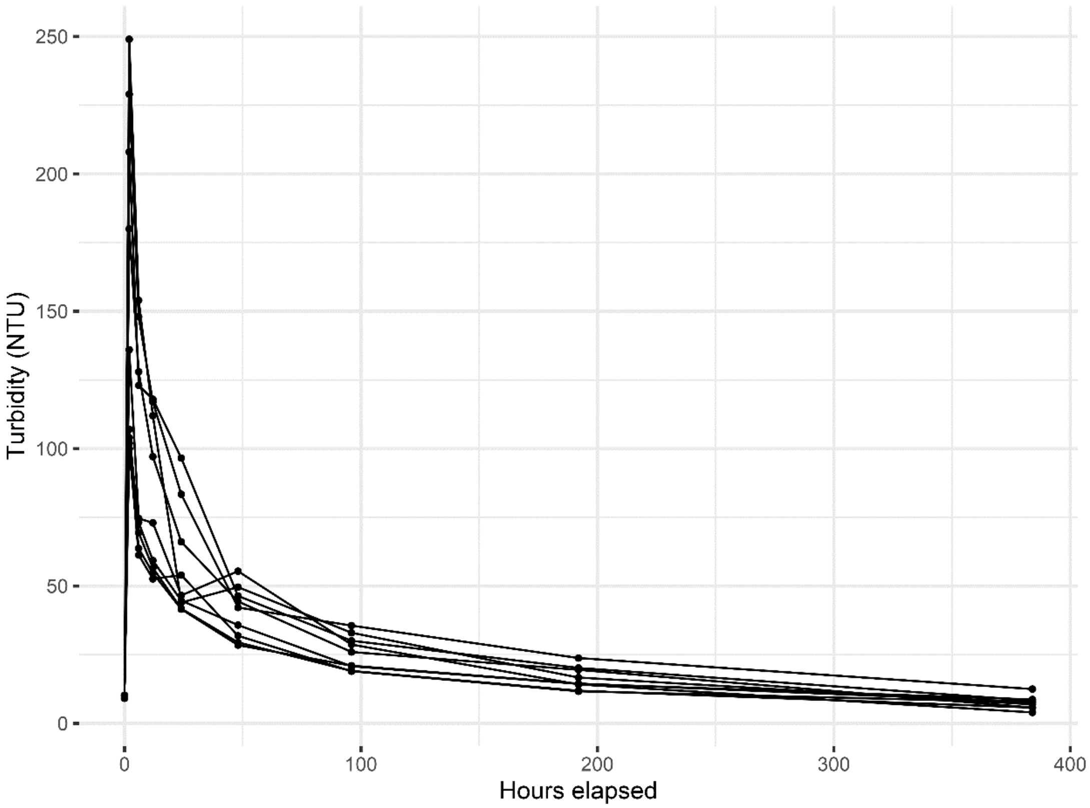
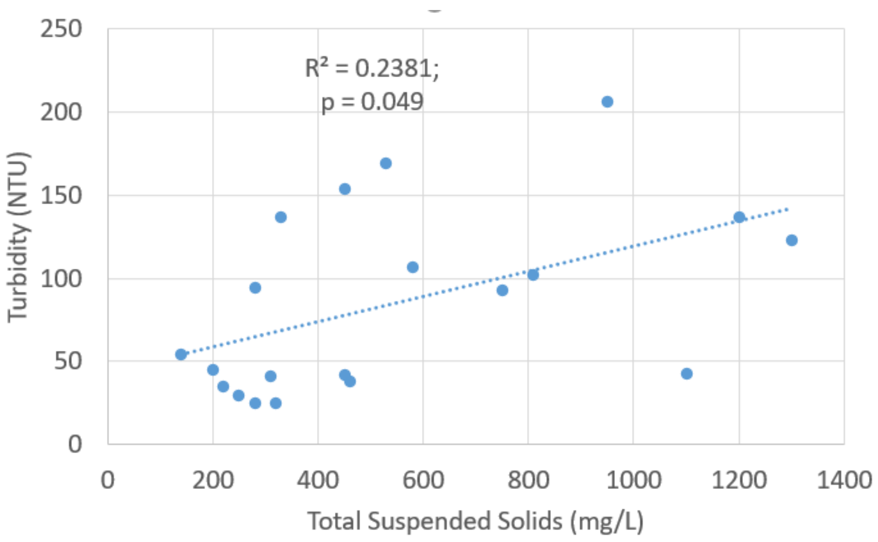


Figure 4. Time series of turbidity in treatment and control reactors during experiment.

Total suspended solids (TSS) and turbidity exhibited a weak relationship (Figure 5). As the statistical correlation was poor ($R^2 = 0.24$), *in situ* turbidity measurements were not used to compute TSS during the experiment. Individual TSS data are presented in Appendix A, Table A-1.



Note: Phase II reactors are included in this relationship.

Figure 5. Relationship of total suspended solids and turbidity in experimental reactors.

4.2 Phosphorus

4.2.1 Soluble reactive phosphorus and total phosphorus Time series

As noted in Section 3.1, the SRP concentration in Upper Klamath Lake waters was measured following collection and found to be relatively low and less than the MRL (< 0.05 mg/L). While SRP was added to the composited lake water to achieve t_0 = 0.05 mg/L prior to filling the reactors (including the controls), results returned from the analytical laboratory indicated that individual t_0 concentrations in all the reactors were < 0.05 mg/L; thus, figures and all calculations used in this report use a value of half the MRL for t_0.

In general, SRP concentrations in reactor overlying waters increased in the treatment and control reactors with time (Figure 6). A rapid increase and decrease ("spike") of SRP occurred in most reactors during the first 12 hours (< t_{12}). Concentrations of SRP in the high Phoslock^{TM} treatment reactors returned to below detection after the initial "spike" and remained below detection through t_{96}. By t_{192}, SRP concentrations began to increase in the high Phoslock^{TM} treatment similar to the other treatments and controls. Of the nine reactors, only one control reactor appeared to approach SRP equilibrium by the final sampling time (t_{384}), as evidenced by a flattening of the SRP trend line for this reactor (Figure 6). Individual SRP data are presented in Appendix A, Table A-1.

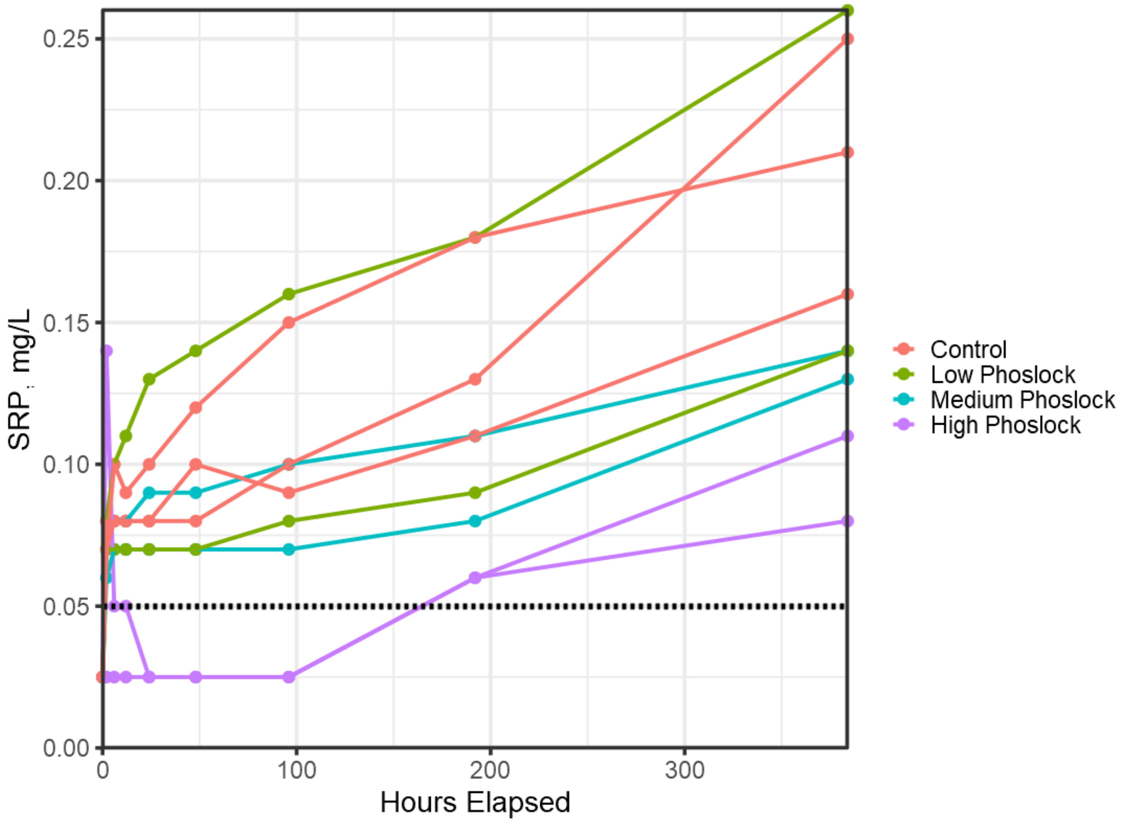


Figure 6. Time series of soluble reactive phosphorus (SRP) in overlying water of treatment and control reactors during the experiment. Colors denote Phoslock^{TM} dosing levels; red = Control (0 g/m^2), green = Low (114 g/m^2), blue = Medium (250 g/m^2), purple = High (389 g/m^2). The dashed blue line indicates the SRP MRL (0.05 mg/L); points below this line are reported as half the MRL.

Total phosphorus (TP) concentrations at t_0 were less than the MRL (< 0.05 mg/L) (see explanation above for SRP), and TP behaved similarly across treatment and control reactors after an initial "spike" of TP that occurred within the first 12 hours of the experiment (Figure 7) in at least one of each Phoslock^{TM} treatment and control reactors. After t_{12}, concentrations of TP rose slowly across reactors, possibly approaching equilibrium. Individual TP data are presented in Appendix A, Table A-1.

Ratios of average SRP to average TP in the overlying water of the treatment and control reactors generally increased over the course of the experiment (Figure 8). The ratio ranged from 0.2 to 0.4 at t_2, with the exception of a high Phoslock^{TM} treatment reactor that exhibited a ratio of 1.0 at t_2. The relatively low ratios at the start of the experiment suggest that the majority of phosphorus in the overlying water column immediately following '"flood up" was particulate phosphorus, including organic and inorganic forms of phosphorus, which would have been removed using a 0.45-µm filter and thus not measured as part of SRP. Note that ratios are not reported for t_0 since all SRP and TP values were reported as less than 0.05 mg/L by the analytical laboratory for the first sample of the experiment. Ratios of average SRP to average TP rapidly increased toward one over time, with most reactors exhibiting values of one by t_{384}, suggesting that most or all of the phosphorus in the overlying water at the end of the experiment was SRP. The fact that some reactors exhibited ratio values greater than one reflects the degree of measurement error in the SRP and/or TP analytical methods.

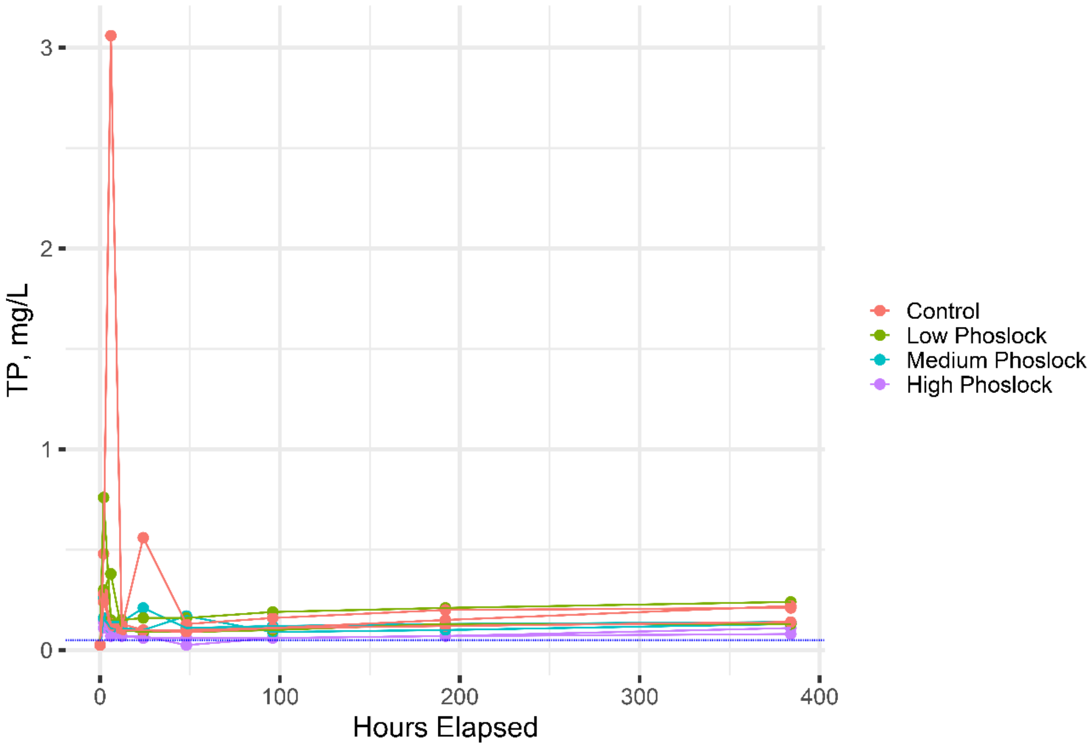


Figure 7. Time series of total phosphorus (TP) in overlying water of treatment and control reactors during experiment. Colors denote Phoslock^{TM} dosing levels; red = control (0 g/m^2), green = low (114 g/m^2), blue = medium (250 g/m^2), purple = high (389 g/m^2). The dashed blue line indicates the TP MRL (0.05 mg/L); points below this line are reported as half the MRL.

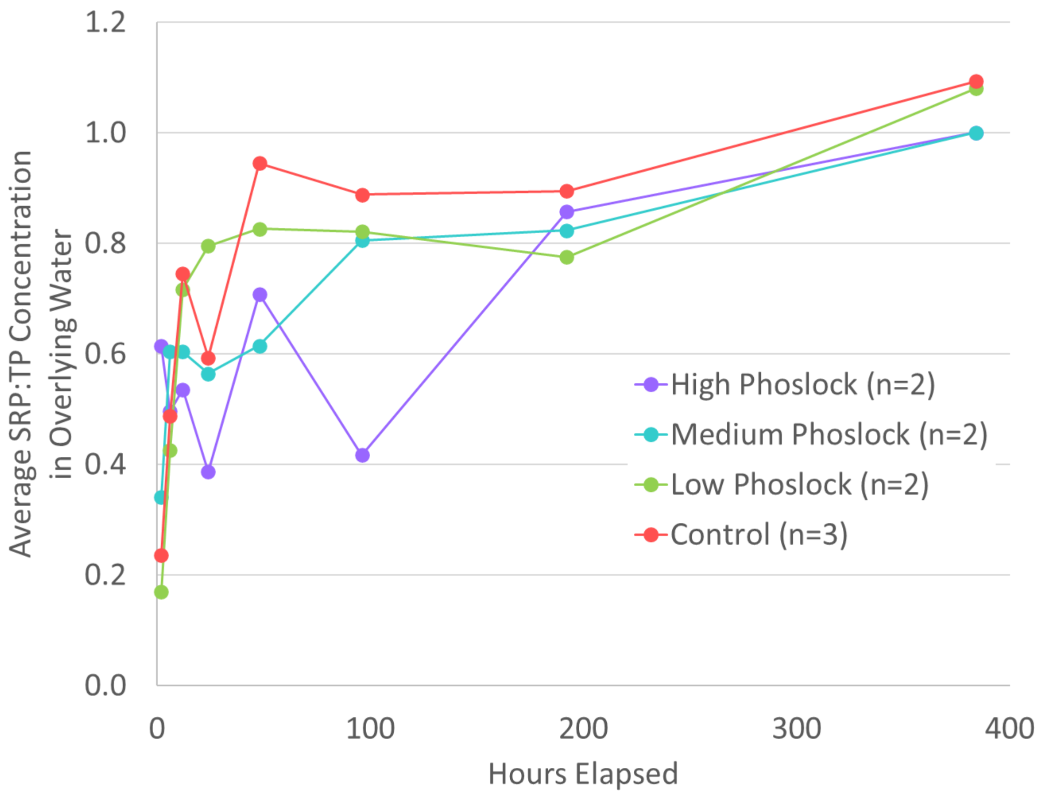


Figure 8. Time series from t_2 to t_{384} of the ratio of average soluble reactive phosphorus (SRP) to average total phosphorus (TP) in overlying water of treatment and control reactors during experiment. Colors denote Phoslock^{TM} dosing levels; red = control (0 g/m^2), green = low (114 g/m^2), blue = medium (250 g/m^2), purple = high (389 g/m^2).

4.2.2 Flux of soluble reactive phosphorus and total phosphorus across the sediment-water interface

For SRP and TP, the flux across the sediment-water interface was calculated as the difference between the final water column concentration at t_{384} and the water column concentration at t_6 (SRP) and t_{12} (TP), assuming that any change in SRP or TP concentrations over the course of the experiment was the result of flux from the sediments into the overlying water. Flux was computed using starting values 6–12 hours after inundation to eliminate the transient "spike" from the calculation (see also Section 5.1). Calculated fluxes were converted to daily areal rates (i.e., mg SRP or TP per m^2 per day) for reporting purposes. The flux of both SRP and TP across the sediment-water interface was positive in all treatment and control reactors during the experiment (Figure 9 and Figure 10). Fluxes were the highest in the non-amended control (0 grams per square meter [g/m^2]) and the low Phoslock^{TM} dosing level (114 g/m^2), and they were lowest in the high Phoslock^{TM} dosing level (389 g/m^2). Although the aforementioned general pattern is visually apparent in the data, variability in SRP and TP fluxes within each of the Phoslock^{TM} dosing levels and the control reactors was high (Table 7). A one-way analysis of variance (ANOVA) test conducted for each distribution of calculated SRP and TP flux data confirmed that fluxes of SRP and TP were not significantly different across treatments (Table 7), which was in part a function of the degree of replication used in this experiment. In general, mean SRP fluxes were greater than mean TP fluxes for the treatment and controls (Table 7).

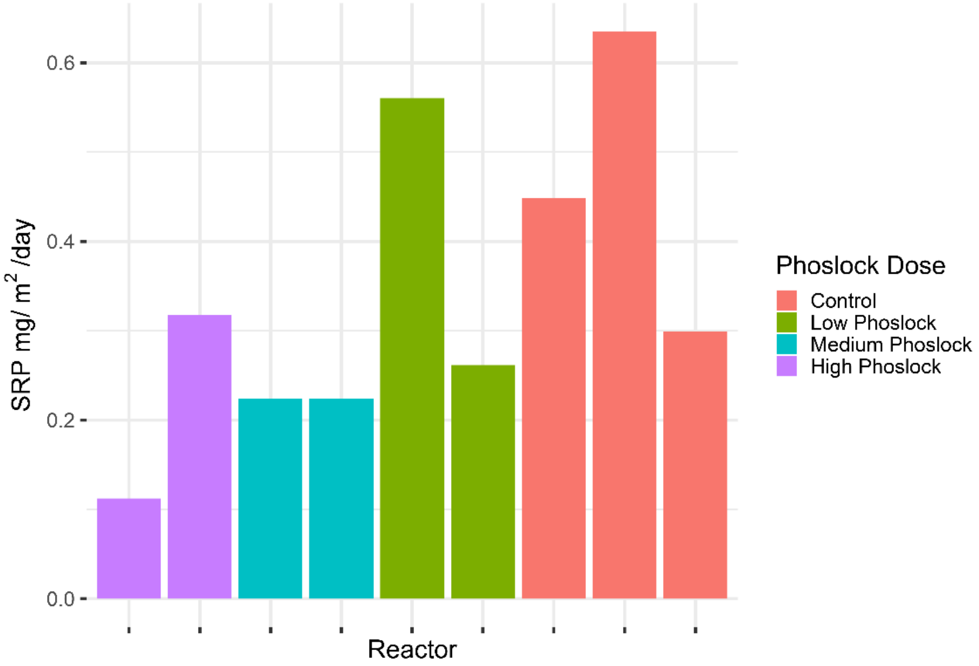


Figure 9. Estimated flux of soluble reactive phosphorus (SRP) from sediments to overlying water from t_6 (6 hrs) to the end of the experiment, t_{384} (16 days), scaled to daily rates over 1 square meter. Colors denote Phoslock^{TM} dosing levels; red = control (0 g/m^2), green = low (114 g/m^2), blue = medium (250 g/m^2), purple = high (389 g/m^2).

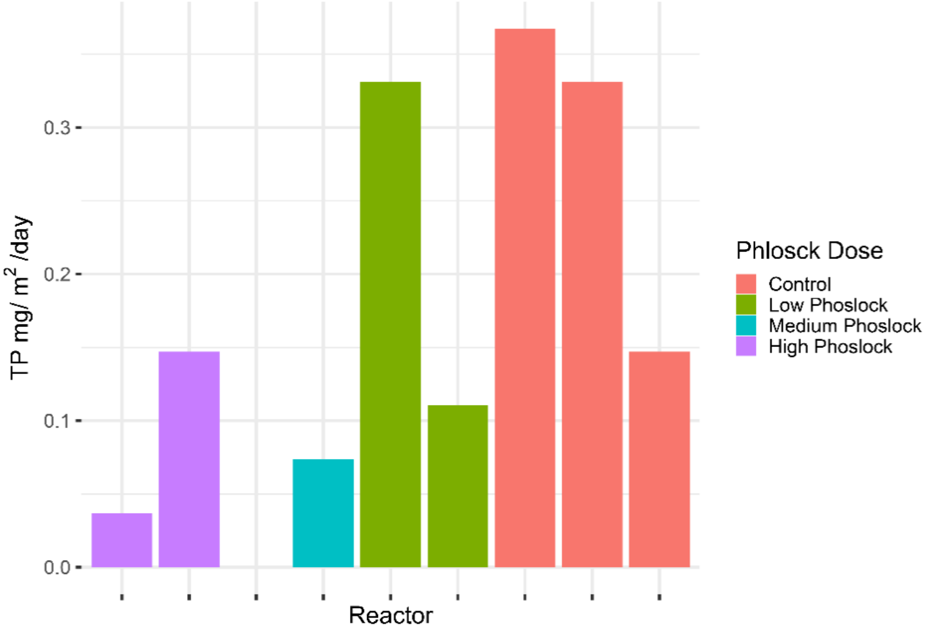


Figure 10. Estimated flux of total phosphorus (TP) from sediments to overlying water from t_3 (12 hrs) to the end of the experiment, t_{384} (16 days), scaled to daily rates over 1 square meter. Colors denote Phoslock^{TM} dosing levels; red = control (0 g/m^2), green = low (114 g/m^2), blue = medium (250 g/m^2), purple = high (389 g/m^2).

Table 7. Soluble reactive phosphorus (SRP) and total phosphorus (TP) flux replicates (n) mean, variance, and ANOVA results for experimental reactors by Phoslock™ treatment.

Analyte	Treatment	Number of Replicates	Mean (mg/m²/day)	Variance	Degrees of freedom	F	p
Soluble Reactive Phosphorus (SRP)	High Phoslock™	2	0.27	0.0004	3	2.17	0.21
	Medium Phoslock™	2	0.42	0.00005			
	Low Phoslock™	2	0.61	0.006			
	Control	3	0.65	0.002			
Total Phosphorus (TP)	High Phoslock™	2	0.22	0.0015	3	1.52	0.32
	Medium Phoslock™	2	0.22	< 0.00001			
	Low Phoslock™	2	0.41	0.003			
	Control	3	0.45	0.002			

4.2.3 Phoslock™ sorption capacity for soluble reactive phosphorus and total phosphorus at the sediment-water interface nearest the Phoslock™ layer

Soluble reactive phosphorus (SRP) sorption capacity of the added Phoslock™ could not be calculated as planned because overlying water SRP did not appear to reach equilibrium concentrations (Figure 6), suggesting that reactor sediments had the potential to release additional SRP. Overlying water TP also did not appear to reach equilibrium concentrations over the course of the 16-day experiment (Figure 7), although the majority of the phosphorus present in the overlying water later in the experiment was SRP (Figure 8) suggesting that the lack of equilibrium for TP was driven largely by SRP release from the sediments.

Total phosphorus measured in the composite sample of homogenized sediment prior to t_0 was 270 milligrams per kilogram (mg/kg) (n =1). Final sediment TP (t_{384}) in the top 1 cm of sediment (i.e., at the sediment-water interface) was lower than the initial (t_0) sediment TP in most reactors, with no apparent relationship to Phoslock™ dosing level (Table 8).

Table 8. Sediment total phosphorus (TP) in reactors immediately before inundation (t_0) and at the end of experiment (t_{384}).

Phoslock™ dosing level	Initial t_0 sediment TP (mg/kg)	Final t_{384} sediment TP (mg/kg)
High Phoslock™	270	150
		150
Medium Phoslock™		220
		300
Low Phoslock™		140
		190
Control		240
		320
		270

Near-bottom water TP collected 1 cm above the sediment surface at the end of the experiment (t_{384}) was higher in all reactors than TP collected in the middle of the overlying water column at the same time sampling point (Table 9). A one-way ANOVA found no significant difference in the difference across treatments. Near-bottom water was assumed to contain an accumulation of Phoslock^{TM} relative to the rest of the water column, which as described in Section 3.1, could not be sampled discretely.

Table 9. Difference in overlying water TP and near-bottom water TP, 1 cm above sediment surface, at t_{384}.

Phoslock^{TM} Dosing Level	Overlying (mid-column) TP (mg/L)	Near-bottom TP (mg/L	Near-bottom minus overlying TP (mg/L)
High Phoslock^{TM}	0.08	0.17	0.09
	0.11	0.22	0.11
Medium Phoslock^{TM}	0.14	0.75	0.61
	0.13	0.3	0.17
Low Phoslock^{TM}	0.24	0.47	0.23
	0.13	0.37	0.24
Control	0.21	0.27	0.06
	0.22	0.51	0.29
	0.14	0.22	0.08

4.3 Lanthanum

4.3.1 Dissolved lanthanum time series

Dissolved lanthanum concentrations in reactors diverged in response to the Phoslock^{TM} treatment, where control reactors showed minimal or no increase in dissolved lanthanum, and treatment reactors exhibited rapid initial increases of dissolved lanthanum and relatively higher equilibrium concentrations (Figure 11). Equilibrium conditions were obtained in high Phoslock^{TM}, medium Phoslock^{TM}, and two control reactors by t_{192} (4 days). High Phoslock^{TM} dose reactors approached a dissolved lanthanum equilibrium concentration near 155 micrograms per liter (µg/L); medium Phoslock^{TM} dose reactors approached equilibrium concentrations between 45 and 60 µg/L; low Phoslock^{TM} dose reactors approached equilibrium concentrations at 12 and 15 µg/L; and two of three control reactors approached equilibrium concentrations of less than 0.5 µg/L. Somewhat elevated concentrations of dissolved lanthanum were detected during the experiment in one of three control reactors, with t_{384} at approximately 8 ug/L or approximately 50% of the low Phoslock^{TM} dose reactors (Figure 11).

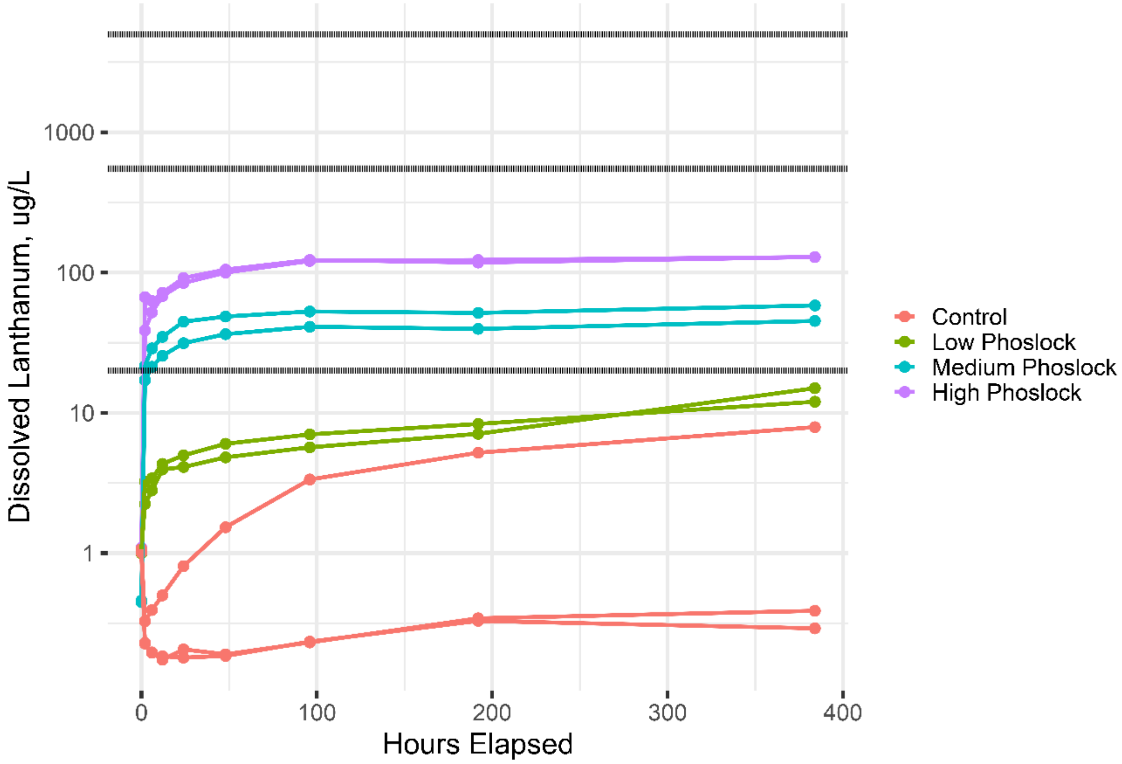


Figure 11. Time series of dissolved lanthanum in overlying water of treatment and control reactors during the experiment. Colors denote Phoslock^{TM} dosing levels; red = control (0 g/m^2), green = low (114 g/m^2), blue = medium (250 g/m^2), purple = high (389 g/m^2). Dashed lines at 20, 552, and 5,000 µg/L indicate lanthanum LC50 values for rainbow trout eggs, *Daphnia magna*, and common carp (*Cyprinus carpio*), respectively.

4.3.2 Flux of dissolved lanthanum across the sediment-water interface

The flux of dissolved lanthanum across the sediment-water interface was computed as the difference between the final water column concentration at t_{384} and the initial water column concentration at t_0, assuming that any change in dissolved lanthanum concentrations over the course of the experiment were the result of flux from the sediments into the overlying water. Calculated fluxes were converted to daily rates (i.e., µg La per square meter per day [µg/m^2/d]) for reporting purposes. Variability in dissolved lanthanum fluxes within each of the Phoslock^{TM} dosing levels and the control reactors generally was lower than the variability between the treatments and controls (Figure 12), and the magnitude of the dissolved lanthanum fluxes was positively related to the amount of Phoslock^{TM} added to the reactor. Despite low replication, a one-way ANOVA test was conducted on calculated dissolved lanthanum flux data, followed by a post-hoc Tukey test to determine which treatment types differed significantly from each other. ANOVA results also suggest that the flux of dissolved lanthanum was significantly different across Phoslock^{TM} treatments (Table 10; p-value < 0.001), and each treatment was significantly different from the others (all $p < 0.001$), except for the control and low Phoslock^{TM} treatments ($p = 0.22$).

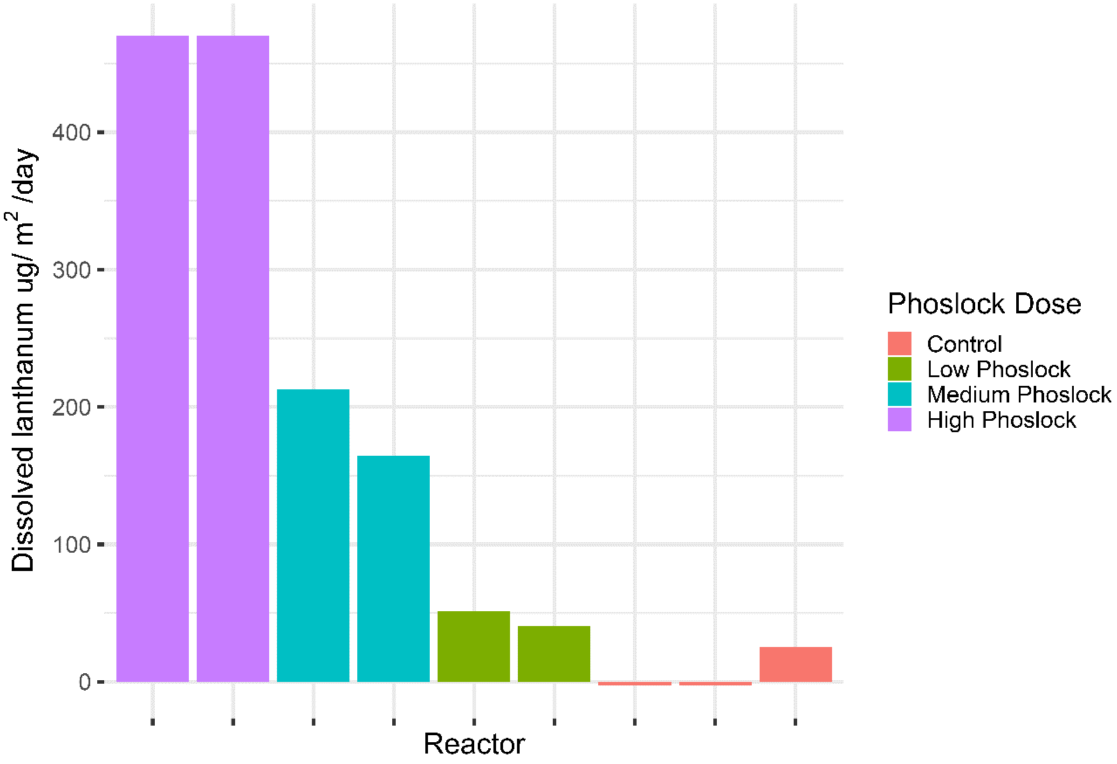


Figure 12. Calculated flux scaled to daily rates over 1 square meter of dissolved lanthanum from Phoslock^{TM}-sediment slurry into overlying water from t_0 to t_{384} (16 days). Colors denote Phoslock^{TM} dosing levels; red = control (0 g/m^2), green = low (114 g/m^2), blue = medium (250 g/m^2), purple = high (389 g/m^2).

Table 10: Dissolved lanthanum flux replicates (n) mean, variance, and ANOVA results for experimental reactors by Phoslock^{TM} treatment.

Group	**Count**	**Mean (µg/m^2/day)**	**Variance**	**Degrees of Freedom**	**F**	**p**
High Phoslock^{TM}	2	470.3	0.09	3	279.6	< 0.00001
Medium Phoslock^{TM}	2	188.6	24.09			
Low Phoslock^{TM}	2	45.9	5.39			
Control	3	6.7	9.25			

4.3.3 Comparison of lanthanum in water to toxicity thresholds

Observed lanthanum concentrations in reactor overlying waters did not exceed compiled toxicity thresholds except for the 0.02 mg/L threshold listed for rainbow trout (*Oncorhynchus mykiss*) eggs (Table 11) in the high and medium Phoslock^{TM} dosing levels (Figure 11). Following the LC50 for *Oncorhynchus mykiss* eggs, the second lowest LC50 compiled was for *Daphnia magna* (Bogers 1995a), which was more than three times greater than the highest lanthanum concentration measured in this experiment. Note that with the exception of Bogers (1995a) where no temperature was reported, the LC50 values summarized in Table 11 were determined using 20 °C test conditions, as compared with 5, 15, and 25 °C incubations used in this experiment. All measured lanthanum concentrations were also lower than those reported as having growth effects on *Microcystis aeruginosa* (1.0–2.5 mg/L for 7- to 20-day static exposure periods; Jin et al. 2009 and Ooserthout and Lurling 2013, as cited in Herrmann et al. 2016) and growth effects on the green algae *Scenedesmus sp.* (1.0–16.0 mg/L for various static exposure periods; Bogers 1995, Jin et al. 2009, and Ooserthout and Lurling 2013, as cited in Herrmann et al. 2016). Concentrations of lanthanum in the high Phoslock^{TM} treatment may overlap with some ecological endpoints for the zooplankton *Daphnia magna* (immobilization, reproduction) (0.099–100 mg/L or greater; Seyfried 2007, Hoger 2009, and Lürling and Tolman 2010, as cited in Herrmann et al. 2016) and additional ecological endpoints (immobilization, NOEC) for fish species (< 0.600–> 0.127 mg/L Stauber and Binet 2000 and Stauber 2000, as cited in Herrmann et al. 2016).

Table 11. Lanthanum reported LC50 values for static exposure tests on zooplankton and fish species.

Species Common Name	Species Scientific Name	Compound[a]	Exposure time	Hardness (mg $CaCO_3$/L)	pH value [s.u.]	Temperature [°C]	LC50 [mg/L]	Reference as cited in Herrmann et al. (2016) [b]
Zooplankton type	*Daphnia magna*	$LaCl_3$	21 days	250	7.0–8.4	20–21	0.552	Bogers (1995a)
Zooplankton type	*Daphnia magna*	La (P)	48 hours	128	6.8–8.3	20±2	> 63.3[c]	Watson-Leung (2009)
Rainbow trout	*Oncorhynchus mykiss* (egg)	–	28 days	104	7.0–7.8	–	0.02	Birge et al. (1979)
Zebrafish	*Danio rerio*	La_2O_3	96 hours	250	7.3–7.8	24±1	> 100.0[d]	Bazzon (2000)
Common carp	*Cyprinus carpio*	$LaCl_3$	21 days	218	6.3–8.2	19.5–21.0	> 5.0	Bogers (1995b)

[a] La(P) – application of Phoslock^{TM}.

[b] Bazzon, M. 2000. Fish acute toxicity test to zebra fish Danio rerio. OECD Guideline: Method 203, INERIS, Verneuil-en-Halatte, France, 2000, report no.: BA842. Report date: 30.07.2007.

Birge, W.J., J.A. Black, A.G. Westerman. 1979. Evaluation of aquatic pollutants using fish and amphibian eggs as bioassay organisms W.S. Nielsen, G. Migaki, D.G. Scarpelli (Eds.), Animal as Monitors of Environmental Pollutants, National Academy of Sciences, Washington, D.C., pp. 108-118.

Bogers, M. 1995a. Daphnia Magna, Reproduction Test with Lanthanum (La), Report No.: 139499. Testing Laboratory: NOTOX B.V., Owner company: Kemira Pernis B. V, 's-Hertogenbosch, Rotterdam.

Watson-Leung, T. 2009. Phoslock^{TM} Toxicity Testing with Three Sediment Dwelling Organisms (*Hyalella azteca, Hexagenia spp.* and *Chironomus dilutus*) and Two Water Column Dwelling Organisms (Rainbow Trout and *Daphnia magna*), Ontario Ministry of the Environment, Etobicoke.

Bogers, M. 1995b. Lanthanum (La): Prolonged toxicity study with carp in a semi-static system, Report no.: 139488. Testing laboratory: NOTOX B. V. 's-Hertog enbosch, The Netherlands. Owner company: Kemira Pernis B. V. Rotterdam, The Netherlands.

[c] Dissolved La concentration series varied over the course of the experiment.

[d] Test conducted with saturated La solution.

4.3.4 Lanthanum in sediments

Total lanthanum in composite (n=3) sediment cores (1 cm diameter, 10 cm depth) ranged 1.0 to 2.4 mg/kg across the treatment and control reactors at t_0. Sediment concentrations were approximately 70 to 1,000 times higher in the treatment reactors at t_{384}, ranging 135 to 1,520 mg/kg, and sediment concentrations were also higher in each of the control reactors at t_{384}, ranging 3.6 to 30.2 mg/kg, with one of three control reactors exhibiting an increase of 30 times the initial total lanthanum concentration (Table 12). Note that the latter control reactor exhibited a small decrease in water dissolved lanthanum over the course of the experiment (Table 12), and the control reactor that exhibited the highest lanthanum equilibrium concentration shown in Figure 11 exhibited a relatively small increase in sediment total lanthanum (Table 12). To investigate the potential for a relationship between the change in sediment total lanthanum and the change in dissolved lanthanum in the overlying water column of the experimental reactors over the course of the experiment, the difference between t_0 and t_{384} sediment total lanthanum was plotted against the difference between t_0 and t_{384} dissolved lanthanum in the reactor overlying water (Figure 13).

Table 12. Total lanthanum (La) in reactor sediments at t_0 and t_{384}.

Phoslock™ dosing level	**Sediment Total La (mg/kg)**			**Water Dissolved La (mg/L)**		
	Initial t_0	**Final t_{384}**	**Difference**	**Initial t_0**	**Final t_{384}**	**Difference**
High Phoslock™	2.4	887.0	884.6	0.001	0.129	0.128
	1.5	1520.0	1518.6	0.001	0.129	0.128
Medium Phoslock™	1.8	548.0	546.2	0.000	0.058	0.058
	1.8	488.0	486.2	0.000	0.045	0.045
Low Phoslock™	2.0	135.0	133.1	0.001	0.015	0.014
	1.5	151.0	149.5	0.001	0.012	0.011
Control	1.6	3.6	2.1	0.001	0.000	-0.001
	1.0	30.2	29.2	0.001	0.000	-0.001
	1.3	5.3	4.0	0.001	0.008	0.007

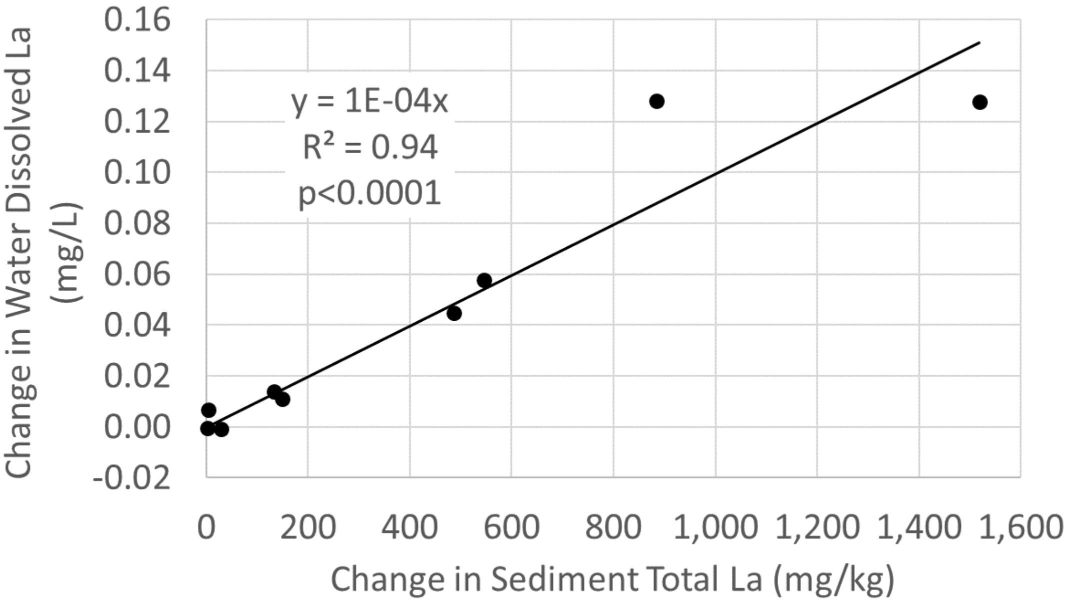


Figure 13. Change in dissolved lanthanum (La) in reactor overlying water as a function of the change in sediment total La over the course of the experiment (t_0 to t_{384}).

5 DISCUSSION

5.1 Hypothesis 1

Direct application of Phoslock^{TM} to the wetland sediment surface prior to inundation will increase sediment binding capacity for SRP relative to non-amended sediments and will reduce the amount of SRP that fluxes out of the sediments as a response to inundation.

While the study results indicate a high degree of variability in measured SRP fluxes across the sediment-water interface of the experimental reactors, positive fluxes occurred in all treatment and control reactors, with the highest observed fluxes in the non-amended control (0 g/m^2) and the low Phoslock^{TM} dosing level (114 g/m^2), and the lowest observed fluxes in the high Phoslock^{TM} dosing level (389 g/m^2; Figure 9). This pattern would be apparent regardless of the systematic treatment of values less than the MRL for SRP and TP as one-half of the MRL, or 0.025 mg/L. In the high Phoslock^{TM} dosing level (389 g/m^2), SRP flux into the overlying water column appears to have been inhibited early in the experiment, but the effect was relatively short-lived as average SRP concentrations in the water column of the high Phoslock^{TM} reactors (0.095 mg/L) were 45 to 70 percent of average concentrations in the medium (0.135 mg/L) and low (0.020 mg/L) Phoslock^{TM} dosing levels at t_{384} (Figure 6). The variability across replicates means that Hypothesis 1 is not statistically supported. The results of this study do show differences between the treatment and control reactors. This observed variability indicates that 1) higher doses of Phoslock^{TM} may be required to achieve a statistically significant reduction in SRP flux relative to the non-amended control, and/or 2) a greater level of replication is necessary to better understand the degree to which Phoslock^{TM} treatment affects SRP flux for the sediments used in this experiment. Given the observed variability, and assuming normality of the underlying distribution of SRP results, replication of five reactors per Phoslock^{TM} treatment would have been necessary to demonstrate statistical significance between Phoslock^{TM} dosing levels ranging 0 g/m^2 to 389 g/m^2 for a statistical power of 0.8 and for the sediments used in this experiment. Further, the apparently transient effect of Phoslock^{TM} on sediment phosphorus binding in the high Phoslock^{TM} dosing level also suggests that higher doses of Phoslock^{TM} may be required to achieve the desired effect.

The application method for Phoslock^{TM} used in this experiment is likely an important source of the observed variability in SRP (and TP) fluxes over time and across reactors. To simulate a potentially low-cost application method for Phoslock^{TM} in wetland restoration projects in the Upper Klamath Basin, Phoslock^{TM} was added as a slurry on top of "field-condition" wetland sediments (i.e., no purposeful drying or wetting of sediments was conducted prior to their use) in the treatment reactors at the beginning of the experiment, after which Upper Klamath Lake water was added to all reactors to simulate "flood up" of a restoration site. Even at the high Phoslock^{TM} dosing level (389 g/m^2) used in this experiment, the Phoslock^{TM} "slurry" was completely aqueous, and as such it rapidly dispersed into the sediment profile when applied to sediments that were damp at the time of collection. Additionally, at "flood up," a large fraction of the "field condition" sediment became suspended in the water column of the reactors, mixing the Phoslock^{TM} particles into the water column and throughout the exposed upper layer of the sediment as this material re-settled in an uncontrolled, heterogeneous manner. Several hours later, horizontal and vertical heterogeneity of the re-settled Phoslock^{TM} in the upper sediment profile of each reactor may have resulted in inefficient binding of SRP to the lanthanum-infused clay, allowing SRP to flux out of sediments and into the overlying water column, even in the high Phoslock^{TM} dosing level (389 g/m^2) after 8 days (Figure 6).

Geurts et al. (2011) report a similar inefficiency of phosphorus binding to lanthanum-modified bentonite-clay that was mixed into sandy soils and peat soils in experimental reactors before the soils were re-wetted or shallowly flooded. Geurts et al. (2011) indicate that sandy soils subjected to Phoslock^{TM} additions at 5:1 La:P exhibited lower SRP release into overlying waters relative to 1:1 La:P treatments (which corresponds to the low dosing level [114 g/m^2] used in this study), whereas SRP concentrations in waters overlying peat soils increased with the higher 5:1 La:P Phoslock^{TM} dosing level. In contrast to Geurts et al. (2011), our study results suggest that Phoslock^{TM} addition can be effective for reducing SRP release from peat soils, although variability in the binding capacity for SRP across the amended sediment surfaces may be high.

Water column temperature and pH were less variable than dissolved oxygen through the course of the experiment (Table 5) and did not appear to be a source of variability in the SRP or TP flux results. Dissolved oxygen varied during the experiment, and despite pre-sparging the reactor water, which was undertaken to support SRP release after "flood up" (Section 3.1), and the careful and gentle transfer of water into the reactor containers to minimize mixing, dissolved oxygen rose rapidly after t_0 (where t_0 = immediately before inundation; t_2, t_6, t_{12}, and t_{24} represent 2, 6, 12, and 24 hours after inundation, respectively; and t_{48}, t_{96}, t_{192}, t_{384} represent 2, 4, 8, and 16 days (48, 96, 192, and 384 hours) after inundation, respectively; see Section 3.1) from 1 mg/L to 3.3 mg/L, on average. The rapid increase in dissolved oxygen was likely due to some degree of physical mixing that occurred during "flood up" and the fact that the reactors were initially open to the atmosphere. The latter was done to approximate wetland field conditions where water column depths are typically less than three feet deep (i.e., the reactors contained overlying water of 32 cm depth or just over one foot), supporting natural water column and sediment reaeration rates that have the potential to be higher than deeper water columns in lakes and reservoirs. While wetlands are often characterized by low oxygen and low redox potential at or near the organic carbon-rich sediment-water interface, the rapidly increasing dissolved oxygen between sampling times for this experiment suggests relatively low rates of heterotrophic microbial activity in the reactor sediments, even after 16 days, which is somewhat surprising given the high degree of organic matter typical in wetland sediments surrounding Upper Klamath Lake (e.g., Aldous et al., 2005). A less active microbial community in the reactor sediments may have been due to naturally lower activity in winter sediments (i.e., collected in December), where a target 15°C water temperature was not sufficient to support a degree of microbial activity that could maintain dissolved oxygen less than 2 mg/L. However, despite the rapid increase in dissolved oxygen in the pre-sparged water, SRP increased steadily in the overlying water column in the control and low Phoslock^{TM} dosing level (Figure 6), suggesting that there was a reservoir of phosphorus in the sediments that was not bound to iron hydroxides, manganese compounds, or metal oxides under the relatively higher redox conditions (i.e., SRP) and this phosphorus diffused through sediment pore waters and into the overlying water over the course of the experiment. It is also possible that some orthophosphorus in sediment microsites was bound in iron, manganese, and/or metal colloidal materials and the low levels of DO did not completely suppress redox-mediated release of this form of phosphorus from sediments. Reactors were loosely covered after t_{24} and sparged a second time immediately prior to t_{192} due to concerns about whether the steadily increasing dissolved oxygen would inhibit SRP release; however, concentrations of phosphorus in the overlying water were only slightly elevated at t_{384} relative to t_{192} such that the loose cover and/or second sparging appears to have been unnecessary from an SRP-release perspective. Further, elevated SRP (Figure 6) and an increasing ratio of SRP to TP (Figure 8) at t_{384} despite oxic (3.70 mg/L to 7.32 mg/L) overlying water suggests that SRP continued to diffuse into the water column regardless of dissolved oxygen concentrations in the overlying water, potentially because dissolved oxygen concentrations in sediment pore waters and particle microsites were still sufficiently low to support release of orthophosphorus from mineral and/or metal surfaces and eventual diffusion across the sediment-water interface and/or there was a reservoir of unbound SRP that diffused into the overlying waters. Overall, while dissolved oxygen concentrations in the reactor water columns did not remain low or zero during the experiment, the increase over time did not appear to be a source of variability in continuing SRP release across the reactors.

The minimum (0.11 milligram per square meter per day [mg/m^2/d]) and maximum (0.63 mg/m^2/d) SRP fluxes measured in this experiment (see Table 7) were roughly 15 to 100 times lower than fluxes measured using sediment cores collected from restoration and undisturbed wetlands around Upper Klamath Lake (Table 13; see Figure 1 for sampling locations reported in Aldous et al. [2005] and Graham et al. [2005]). The sediment cores used in the Aldous et al. (2005) and Graham et al. (2005) study were subjected to dry, moist, and wet conditions over several weeks during mid-July to mid-September (i.e., summer to early fall) before being flooded with Upper Klamath Lake water, so the experimental conditions were not exactly analogous to the conditions in this study. Despite the much higher SRP fluxes reported by Aldous et al. (2005) and Graham et al. (2005), sediment TP in their study ranged from 750 to 1,106 mg/kg, or approximately 2 to 9 times greater than the minimum and maximum sediment TP values measured in this experiment, suggesting that sediment TP content is not likely to be the only explanation for the generally low potential for SRP release apparent in our experiment. The ambient temperatures for the Aldous et al. (2005) and Graham et al. (2005) sediment incubations were not reported, but their experimental cores were maintained outside during summer and early fall in the Upper Klamath Basin when air temperatures typically reach 25°C to 35°C and microbial activity is expected to be substantially greater than that of sediments collected in winter and subsequently incubated at a 15°C target temperature, as was the case for this experiment. Higher microbial activity would support higher rates of mineralization of organic phosphorus to orthophosphorus, and thus increase SRP in overlying waters, whereas lower microbial activity under lower temperatures would support lower mineralization rates and lower relative concentrations of SRP in overlying waters. Water temperature variability as part of Phase II of this study is currently being analyzed to determine whether and to what degree SRP fluxes are affected by temperature across multiple Phoslock^{TM} dosing levels.

Table 13. Soil bulk density, total phosphorus (TP), and SRP fluxes associated with sediments from wetland sites located around Upper Klamath Lake. Data from Aldous et al. (2005) and Graham et al. (2005). U = undisturbed wetlands; R = restoration wetlands as defined by Aldous et al. (2005).

Wetland site name	Bulk density [a] (g/cm^3)	Total soil P [a] (ug/cm^3)	Total soil P [a] (mg/kg)	SRP flux after 24 hours (Mean± SE) (mg/m^2/d)	SRP flux after 4 days (Mean± SE) (mg/m^2/d)
Hank's Marsh (U)	0.13	97	750	18.10±7.61 (dry); 0 (moist, flooded)	10.30±3.55 (dry); 0 (moist, flooded)
Sesti Tgawaals Wildlife Area [b] (U)	0.15	148	985		
Upper Klamath Lake National Wildlife Refuge (U)	0.15	125	832		
Agency Lake Ranch (R)	0.24	236	983	32.07±11.99 (dry); 15.03±4.93 (moist); 55.52±16.84 (flooded)	26.63±7.86 (dry); 8.56±2.73 (moist); 19.93±5.60 (flooded)
Caledonia Marsh at Running Y Ranch (R)	0.38	302	796		
Williamson River Delta (R)	0.32	354	1,106		

[a] Soil samples were taken from the upper 10 cm of the soil profile. Values are means of three replicates.

[b] Sesti Tgawaals Wildlife Area was formerly called Squaw Point and is noted as such in Aldous et al. (2005).

In summary, measured SRP fluxes across the sediment-water interface of the experimental reactors suggest that direct application of Phoslock^{TM} to the surface of dewatered wetland sediments from the Upper Klamath Basin increased sediment binding capacity for SRP relative to non-amended sediments following flooding with Upper Klamath Lake water. However, there was a high degree of variability in SRP fluxes across low, medium, and high Phoslock^{TM} dosing levels as well as the non-amended controls, and given the low degree of experimental replication, Hypothesis 1 is not accepted as statistically significant. Additional replication as part of Phase II of this study is currently being analyzed to determine whether statistical significance can be supported for Hypothesis 1.

High vertical and horizontal heterogeneity in Phoslock^{TM} coverage at the sediment-water interface may have increased variability in sediment binding capacity across reactors and suggests that 1) areal dosing levels achieving La:PO_4 molar ratios greater than either 1:1 or 2.2 (i.e., used as a sediment capping dose for reservoirs) are likely to be required; and 2) a field-scale application method that sprays or otherwise places a water-based slurry on top of drained or otherwise dewatered sediments or soils in an agricultural field may result in too much mixing and uneven settling of Phoslock^{TM} once the restoration site is flooded. Using Phoslock^{TM} bulk pricing of $2/kg, an application method(s) that maximizes Phoslock^{TM} efficiency would reduce the overall costs of restoration, but costs may approach $5,000 per acre if La:$PO_4$ molar ratios greater than 2.2 are required (Table 14).

Table 14. Estimated cost of Phoslock™ application to a 100-acre wetland for various doses considered in this and other studies.

Phoslock™ areal dosing level (g/m^2)	Relationship to experimental Phoslock™ dosing levels	La:PO4 molar ratio	Rationale for including in cost calculations	Approximate cost ($) for surface application to a 100-acre wetland[1]
114	Low dose used in this experiment	1.0	1:1 La:P (molar basis)	$ 203,000
250	Medium dose used in this experiment	2.2	Sediment capping dose (Ross et al. 2008)	$ 446,000
389	High dose used in this experiment	3.4	100:1 Phoslock™: bioavailable P (mass basis) = 3.4 La:P (molar basis)	$ 694,000
564	Not used in this experiment	5.0	Geurts et al. (2011)	$ 1,006,000

[1] Assumes $2 per pound Phoslock™, which is on the high end of current bulk pricing estimates.

5.2 Hypothesis 2

Application of Phoslock™ to the wetland sediment surface prior to inundation will not result in a release of potentially toxic levels of lanthanum (La) as a response to inundation.

Dissolved lanthanum concentrations in the Phoslock™ treatment reactors followed distinct patterns of rapid initial increase, followed by an approach to equilibria of increasing concentrations with increased Phoslock™ dosing. Dissolved lanthanum in two of three control reactors remained closest to zero (Figure 11). However, the form of the lanthanum measured is unclear; conversations with the analytical laboratory following the reactor incubations indicated that nanoparticle rhabdophane (LaP) may have been present in the water samples and able to pass through the 0.45-µm filters used to sample dissolved lanthanum, and thus this inert compound could be part of the "dissolved" lanthanum signal. While nanoparticle rhabdophane is reported in the scientific literature related to industrial and material manufacturing (e.g., Diaz-Guillén et al. 2007, Roncal-Herrero et al. 2011) and at least one publication on mining-contaminated wetland soil (Le Pape et al. 2020), detection of this form of lanthanum would require high-resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) and/or single particle inductively coupled plasma mass spectrometry (ICP-MS) at a substantial additional cost per sample. Further, 0.45-µm filtration is the standard operational definition of dissolved lanthanum represented in the existing lanthanum toxicity literature, and the possibility of nanoparticle rhabdophane or other nanoparticle forms of lanthanum is not discussed (Herrmann et al. 2016). While it is possible that nanoparticle rhabdophane was present in the numerous past toxicity studies conducted and reported in the scientific literature, any effects on test biota were presumably inherently captured in those study results, although they could not be differentiated from the effects of other measurable forms of lanthanum. Similarly, if nanoparticle rhabdophane appeared as some fraction of dissolved lanthanum in our analysis, then true free lanthanum (La^{3+}) concentrations were substantially lower than what was measured. As a conservative assumption, this discussion assumes that all lanthanum measured in water was present in a free, dissolved form.

The slight increase in total lanthanum in reactor sediments over the course of the experiment in two of the control reactors (Table 12) suggests the possibility of low-level contamination in the controls, perhaps due to Phoslock^{TM} dust. While the reactors were assembled in an outdoor area with plenty of ventilation, and the Phoslock^{TM} slurry was prepared with careful attention to material isolation, it is possible that minute amounts of dust from the Phoslock^{TM} storage container found their way into the indoor air and/or the surfaces of the control reactors during the experimental incubation period (but after t_0 sampling). While this seems unlikely, the propensity for fine Phoslock^{TM} dust to deposit in areas other than the intended application spot may be a consideration for field-scale application. The 30-fold increase in total lanthanum in reactor sediments over the course of the experiment in one of the control reactors (Table 12) suggests the possibility of more significant contamination during t_{384} sediment sample collection or at the analytical laboratory, although a subsequent review of the sampling protocols and coordination with the laboratory also indicates that either of these events was unlikely. Additional replication as part of Phase II of this study is currently being analyzed to determine whether other control reactors also experienced an increase in total sediment lanthanum over the course of the experiment that could help explain the aforementioned results.

Dissolved lanthanum concentrations in the water overlying the sediment reactors were below most LC50 toxicity thresholds compiled from literature and likely to be most relevant to the Upper Klamath Basin (Table 11). The only threshold exceeded was that for rainbow trout eggs, at 0.02 mg/L for a 28-day exposure period. Both high and medium Phoslock^{TM} treatment lanthanum concentrations exceeded 0.02 mg/L lanthanum by t_{12} and did not decline below that concentration for the duration of the experiment. Rainbow trout, and a subspecies redband trout (*Oncorhynchus mykiss newberrii*), are found in Upper Klamath Lake. Redband trout are an Oregon state sensitive vulnerable species and a cultural and subsistence resource for The Klamath Tribes. Additionally, the endangered Lost River sucker (*Deltistes luxatus*) and shortnose sucker (*Chasmistes brevirostris*) reside in Upper Klamath Lake. Rainbow and redband trout, as well as both sucker species, spawn in coarser gravel substrates in tributaries to Upper Klamath Lake (e.g., Williamson River)[1] rather than in peat-based wetland sediments (or agricultural soils slated for restoration to wetlands adjacent to Upper Klamath Lake), and thus the potential for Phoslock^{TM}-associated lanthanum toxicity to the egg life-history stage for these fish, or other freshwater fish that exhibit similar habitat preferences, may be limited in relation to restoration of Upper Klamath Lake fringe wetlands. However, additional study of lanthanum toxicity thresholds for juvenile trout and/or suckers that may use vegetated shoreline and wetland habitat along the lake edges may be warranted, given that some restored wetlands could be open to the lake or may exchange water with the lake during rearing periods. Further consideration of Phoslock^{TM} use in constructed DSTWs along tributaries to Upper Klamath Lake, including Sevenmile Creek, Wood River, and Sprague River, may also be prudent if such use would increase potential for lanthanum exposure to the trout egg life-history stage in adjacent spawning areas.

The remaining lanthanum toxicity thresholds in Table 11 were at least three times greater than the maximum lanthanum concentration measured in this experiment. Measured lanthanum concentrations were approximately an order of magnitude lower than thresholds reported to affect algal growth, such as 1.0–2.5 mg/L for 7- to 20-day static exposure periods to *Microcystis aeruginosa* (Jin et al.[2009 and Ooserthout and Lurling 2013 as cited in Herrmann et al. 2016). However, high Phoslock^{TM} treatment lanthanum concentrations were greater than the no observed effect concentration (NOEC) for *Daphnia magna* reproduction (0.099 mg/L; Lürling and Tolman 2010, as cited in Herrmann et al. 2016). Note that while not directly related to Hypothesis 2, application of lanthanum-modified bentonite clay (i.e., Phoslock^{TM}) has been reported to decrease

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[1] A subset of suckers spawn at freshwater springs located along the eastern shore of Upper Klamath Lake from April through May (Hewitt et al. 2017).

cyanotoxin concentrations in water, where laboratory-scale applications of relatively high concentrations (50, 100, and 200 mg/L) of lanthanum-modified bentonite clay significantly reduced dissolved microcystin (MC-LR) at 500 µg/L (p=0.002; Laughinghouse et al. 2020).

There are currently no regulatory thresholds for lanthanum. Herrmann et al. (2016) propose a water quality criterion of 4 µg/L based on a Predicted No Effect Concentration (PNEC), which is derived by dividing the lowest reported No Observed Effect Concentration (NOEC) for aquatic organisms (i.e., *Daphnia carinata*; Barry and Meehan 2000, as cited in Herrmann et al. 2016)) by 10. However, Herrmann et al. (2016) note that due to the wide range of background lanthanum concentrations, a PNEC of 4 µg/L may be too low in some areas and further studies and region-specific assessments of freshwater effects are needed to more definitively select a water quality criterion. For example, native water in control reactors exceeded the 4 µg/L threshold by t_{192} and t_{384} in two samples, while many additional control reactor samples were in the range of 1–3 µg/L. Notably, *Daphnia sp.* were observed in all reactors, including the high Phoslock^{TM} treatments, becoming visible around t_{192} and still present in large numbers at t_{384}. No treatment or control reactors exceeded the 552 µg/L LC50 value for a 21-day exposure of *Daphnia magna* to $LaCl_3$ (Table 11, Figure 11).

Overall, application of Phoslock^{TM} to sediment surfaces prior to inundation did not result in a release of lanthanum, as either free dissolved or rhabdophane, at concentrations expected to be acutely toxic to a range of aquatic organisms represented in the published scientific literature (i.e., cyanobacteria, zooplankton, freshwater fish), with the exception of the LC50 for rainbow trout eggs in the high and medium Phoslock^{TM} reactors. Thus, based on the available evidence, Hypothesis 2 is accepted for aquatic biota in general at the lowest Phoslock^{TM} dose used in this study and with a caveat for the medium and high Phoslock^{TM} doses. Future studies should consider lanthanum toxicity testing for wetland-based aquatic species to determine whether exposure to concentrations similar to those reported in this study have the potential to be problematic across multiple life-history stages.

5.3 Additional Discussion

As noted in Section 3.1, organic debris at the sediment water interface interfered with formation of a distinct slurry layer and did not allow discrete sampling of this layer. Instead, TP was measured in the top 1 cm of sediment and the 1-cm layer of near-bottom water at the end of the experiment to assess how much phosphorus may have been captured by Phoslock^{TM} near the sediment-water interface (Table 2). Comparisons between the composited subsample of homogenized sediment TP at the beginning of the experiment and individual sediment TP samples from the top 1 cm of the sediment profile at the end of the experiment indicate that the final sediment TP (t_{384}) was lower than the initial (t_0) sediment TP in most reactors, with no apparent relationship to Phoslock^{TM} dosing level (Table 8). While lower sediment TP at t_{384} as compared to t_0 could be interpreted as an average net flux of phosphorus out of the sediments and into the overlying water column, it is more likely that any comparisons between sediment TP at the beginning and end of the experiment are too coarse to be meaningful due to the heterogeneity of sediment TP, even if the comparisons were to involve individual sediment samples from the same reactor. While the sediment TP data do not elucidate the amount of phosphorus bound by Phoslock^{TM} at the sediment-water interface in the treatment reactors, they do allow for comparisons to TP measured in other Upper Klamath Basin wetland sediments, as discussed above. Further, TP concentrations in near-bottom water at t_{384} were higher than TP concentrations in the overlying water column (Table 9), with a maximum of 0.09 mg TP in the mid-water column (i.e., 15 cm depth) and a maximum of 0.17 mg TP in the 1-cm near-bottom water layer (0.23 L). These data suggest that phosphorus adsorption to Phoslock^{TM} may have occurred at least in part in the near-bottom layer of the water column, rather than solely within reactor sediments.

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APPENDIX A RAW DATA AND QUALITY CONTROL INFORMATION

Table A-1: *In situ* and water column grab sampling data for reactor experiments.

Sample Number	Phoslock Level	Date & Time	Time step (hours)	Temperature (°C)	Turbidity (NTU)	DO (mg/L)	pH	Soluble Reactive Phosphorus (mg/L)	Total Phosphorus (mg/L)	Dissolved Lanthanum (µg/L)
0	High Phoslock	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	1.04
0	High Phoslock	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	1.09
0	Medium Phoslock	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	0.449
0	Medium Phoslock	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	0.458
0	Low Phoslock	1/5/2021, 1300	0	11	9.16	3.3	7.05	0.025	0.03	1.06
0	Low Phoslock	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	0.996
0	Control	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	1.01
0	Control	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	1.07
0	Control	1/5/2021, 1300	0	10.8	10.2	3.3	7.14	0.025	0.03	1.06
1	High Phoslock	1/5/2021, 1523	2	11.9	102	4.6	6.35	0.14	0.14	38.7
1	High Phoslock	1/5/2021, 1523	2	11.6	107	4.8	6.38	0.025	0.11	66.9
1	Medium Phoslock	1/5/2021, 1523	2	11.6	229	4.5	6.2	0.08	0.26	21.6
1	Medium Phoslock	1/5/2021, 1523	2	11.7	208	4.9	6.56	0.06	0.16	17.1

Sample Number	Phoslock Level	Date & Time	Time step (hours)	Temperature (°C)	Turbidity (NTU)	DO (mg/L)	pH	Soluble Reactive Phosphorus (mg/L)	Total Phosphorus (mg/L)	Dissolved Lanthanum (µg/L)
1	Low Phoslock	1/5/2021, 1523	2	11.6	249	5.6	6.89	0.08	0.76	2.24
1	Low Phoslock	1/5/2021, 1523	2	11.7	180	5.4	7.03	0.07	0.30	3.25
1	Control	1/5/2021, 1523	2	11.9	100	5.3	7.11	0.07	0.28	0.229
1	Control	1/5/2021, 1523	2	11.9	136	5.2	7.13	0.08	0.48	0.227
1	Control	1/5/2021, 1523	2	11.8	104	4.9	6.45	0.07	0.24	0.327
2	High Phoslock	1/5/2021, 2030	6	13.2	61.3	5.0	6.39	0.05	0.07	52
2	High Phoslock	1/5/2021, 2030	6	13.3	69.4	4.9	6.43	0.025	0.09	62.7
2	Medium Phoslock	1/5/2021, 2030	6	13.2	148	4.6	6.23	0.08	0.14	28.8
2	Medium Phoslock	1/5/2021, 2030	6	13.5	123	4.9	6.54	0.07	0.11	21.3
2	Low Phoslock	1/5/2021, 2030	6	13.5	154	5.1	6.87	0.10	0.15	2.8
2	Low Phoslock	1/5/2021, 2030	6	13.5	128	5.4	7.04	0.07	0.38	3.41
2	Control	1/5/2021, 2030	6	13.6	63.7	5.0	7.2	0.10	0.13	0.196
2	Control	1/5/2021, 2030	6	13.5	74.6	4.9	7.12	0.08	3.06	0.195
2	Control	1/5/2021, 2030	6	13.4	73.2	4.7	6.68	0.08	0.12	0.393
3	High Phoslock	1/6/2021, 0230	12	13.7	52.6	4.9	6.4	0.05	0.07	68
3	High Phoslock	1/6/2021, 0230	12	13.7	56.6	5.1	6.43	0.025	0.07	71.7

Sample Number	Phoslock Level	Date & Time	Time step (hours)	Temperature (°C)	Turbidity (NTU)	DO (mg/L)	pH	Soluble Reactive Phosphorus (mg/L)	Total Phosphorus (mg/L)	Dissolved Lanthanum (μg/L)
3	Medium Phoslock	1/6/2021, 0230	12	13.1	117	4.8	6.25	0.08	0.14	34.8
3	Medium Phoslock	1/6/2021, 0230	12	13.6	118	5.4	6.61	0.07	0.11	25.5
3	Low Phoslock	1/6/2021, 0230	12	13.3	112	5.6	6.86	0.11	0.15	3.95
3	Low Phoslock	1/6/2021, 0230	12	13.2	97.1	5.7	7.07	0.07	0.10	4.33
3	Control	1/6/2021, 0230	12	13.8	54.7	5.4	7.17	0.09	0.11	0.174
3	Control	1/6/2021, 0230	12	13.6	73	4.9	7.23	0.08	0.13	0.184
3	Control	1/6/2021, 0230	12	13.6	59.3	4.9	6.49	0.08	0.10	0.5
4	High Phoslock	1/6/2021, 1430	24	12.8	54	5.5	6.46	0.025	0.06	84.4
4	High Phoslock	1/6/2021, 1430	24	12.8	41.8	5.5	6.51	0.025	0.07	91.5
4	Medium Phoslock	1/6/2021, 1430	24	12.7	83.4	4.7	6.41	0.09	0.21	44.7
4	Medium Phoslock	1/6/2021, 1430	24	13	96.6	5.4	6.66	0.07	0.10	31.4
4	Low Phoslock	1/6/2021, 1430	24	12.7	44	5.4	7.04	0.13	0.16	4.11
4	Low Phoslock	1/6/2021, 1430	24	12.7	66.1	5.6	7.15	0.07	0.09	4.98
4	Control	1/6/2021, 1430	24	13.1	41.6	5.3	7.17	0.10	0.56	0.206
4	Control	1/6/2021, 1430	24	13	46.6	4.7	7.21	0.08	0.10	0.18
4	Control	1/6/2021, 1430	24	12.9	44.7	5.1	6.64	0.08	0.10	0.808

Sample Number	Phoslock Level	Date & Time	Time step (hours)	Temperature (°C)	Turbidity (NTU)	DO (mg/L)	pH	Soluble Reactive Phosphorus (mg/L)	Total Phosphorus (mg/L)	Dissolved Lanthanum (µg/L)
5	High Phoslock	1/7/2021, 1430	48	12.9	31.9	6.1	6.63	0.025	0.06	100
5	High Phoslock	1/7/2021, 1430	48	12.9	29.5	5.5	6.67	0.025	0.03	105
5	Medium Phoslock	1/7/2021, 1430	48	12.9	42.2	4.8	6.41	0.09	0.11	48.6
5	Medium Phoslock	1/7/2021, 1430	48	13.2	46.4	5.6	6.8	0.07	0.17	36.4
5	Low Phoslock	1/7/2021, 1430	48	12.9	49.6	5.4	7.06	0.14	0.16	4.82
5	Low Phoslock	1/7/2021, 1430	48	12.9	44.4	5.5	7.17	0.07	0.09	6.02
5	Control	1/7/2021, 1430	48	13.3	28.5	5.8	7.31	0.12	0.13	0.19
5	Control	1/7/2021, 1430	48	13.2	55.4	4.6	7.23	0.08	0.10	0.185
5	Control	1/7/2021, 1430	48	13.1	35.8	5.3	6.63	0.10	0.09	1.53
6	High Phoslock	1/9/2021, 1400	96	12.1	19	6.8	6.87	0.025	0.06	121
6	High Phoslock	1/9/2021, 1400	96	12.1	19.1	6.2	6.91	0.025	0.06	123
6	Medium Phoslock	1/9/2021, 1400	96	12.1	35.6	5.5	6.59	0.10	0.12	52.8
6	Medium Phoslock	1/9/2021, 1400	96	12.4	30.1	5.7	6.96	0.07	0.09	41.1
6	Low Phoslock	1/9/2021, 1400	96	12	33	5.3	7.18	0.16	0.19	5.68
6	Low Phoslock	1/9/2021, 1400	96	12	26	5.6	7.31	0.08	0.10	7.02
6	Control	1/9/2021, 1400	96	12.4	21	6.5	7.49	0.15	0.16	0.231

Sample Number	Phoslock Level	Date & Time	Time step (hours)	Temperature (°C)	Turbidity (NTU)	DO (mg/L)	pH	Soluble Reactive Phosphorus (mg/L)	Total Phosphorus (mg/L)	Dissolved Lanthanum (µg/L)
6	Control	1/9/2021, 1400	96	12.4	28.7	4.6	7.37	0.10	0.11	0.234
6	Control	1/9/2021, 1400	96	12.2	20.8	5.8	6.86	0.09	0.11	3.35
7	High Phoslock	1/13/2021, 1430	192	13.9	11.7	2.4	6.99	0.06	0.07	123
7	High Phoslock	1/13/2021, 1430	192	13.9	11.9	2.4	6.98	0.06	0.07	118
7	Medium Phoslock	1/13/2021, 1430	192	13.9	23.8	1.6	7.16	0.11	0.13	51.6
7	Medium Phoslock	1/13/2021, 1430	192	14.2	20.2	2.0	7.15	0.08	0.10	39.7
7	Low Phoslock	1/13/2021, 1430	192	14	16.7	2.0	6.84	0.18	0.21	7.09
7	Low Phoslock	1/13/2021, 1430	192	14	19.5	2.1	7.06	0.09	0.13	8.34
7	Control	1/13/2021, 1430	192	14.4	14.5	2.7	7.3	0.18	0.20	0.343
7	Control	1/13/2021, 1430	192	14.3	14.2	2.0	6.76	0.13	0.15	0.329
7	Control	1/13/2021, 1430	192	14.1	14.4	1.8	7.26	0.11	0.12	5.2
8	High Phoslock	1/21/2021, 1430	384	13.1	7.66	7.3	7.24	0.08	0.08	129
8	High Phoslock	1/21/2021, 1430	384	13.1	5.76	6.0	7.23	0.11	0.11	129
8	Medium Phoslock	1/21/2021, 1430	384	13.1	12.5	5.6	7.23	0.14	0.14	58.3
8	Medium Phoslock	1/21/2021, 1430	384	13.5	8.32	5.5	7.38	0.13	0.13	45.2
8	Low Phoslock	1/21/2021, 1430	384	13.1	6.93	4.7	7.29	0.26	0.24	15

Sample Number	**Phoslock Level**	**Date & Time**	**Time step (hours)**	**Temperature (°C)**	**Turbidity (NTU)**	**DO (mg/L)**	**pH**	**Soluble Reactive Phosphorus (mg/L)**	**Total Phosphorus (mg/L)**	**Dissolved Lanthanum (µg/L)**
8	Low Phoslock	1/21/2021, 1430	384	13	5.76	6.2	7.4	0.14	0.13	12
8	Control	1/21/2021, 1430	384	13.4	7.78	7.1	7.73	0.21	0.21	0.388
8	Control	1/21/2021, 1430	384	13.4	4	3.7	7.41	0.25	0.22	0.291
8	Control	1/21/2021, 1430	384	13.3	8.71	6.1	7.42	0.16	0.14	7.91

Note: Values of SRP and TP shown as 0.025 mg/L were reported by the analytical laboratory as below the reporting limit of 0.05 mg/L. These values are represented as 0.5 x the reporting limit for analysis purposes.

Table A-2: Pre-sampling *in situ* water quality sonde calibration log.

Parameter	**1/5/2021**			
	Std. Value	**Std. Temp (°C)**	**Pre-Cal Value**	**Post-Cal Value**
DO (%)	100%	10.1	104.7%	100.1%
DO (mg/L)	11.39 mg/L	10.1	11.93 mg/L	11.35 mg/L
pH 4	pH 4	10.0	4.07	3.92
pH 7	pH 7	10.0	7.03	7.13
pH 10	pH 10	13.8	9.98	10.10
Turbidity (NTU)	10	-	9.8	9.63
	20	-	20	19.8
	100	-	101	98.7
	800	-	789	796

Table A-3: Pre-sampling *in situ* water quality sonde calibration checks.

Calibration Check 1/6/2021

Parameter	Std. Value	Std. Temp (°C)	Value	Re-Cal Yes or no?	Post-Cal Value	MQO Code
DO (%)	100%	13.8	102.2%	no	N/A	A
pH 4	pH 4	13.2	4.02	no	N/A	A
pH 7	pH 7	13.1	7.13	no	N/A	A
pH 10	pH 10	13.1	10.15	no	N/A	A
Turbidity (NTU)	10	-	9.80	no	N/A	A

Calibration Check 1/7/2021

Parameter	Std. Value	Std. Temp (°C)	Value	Re-Cal Yes or no?	Post-Cal Value	MQO Code
DO (%)	100%	12.5	101.3%	no	N/A	A
pH 4	pH 4	12.5	4.03	no	N/A	A
pH 7	pH 7	12.5	7.04	no	N/A	A
pH 10	pH 10	12.5	10.11	no	N/A	A
Turbidity (NTU)	10	-	9.89	no	N/A	A

Calibration Check 1/13/2021

Parameter	Std. Value	Std. Temp (°C)	Value	Re-Cal Yes or no?	Post-Cal Value	MQO Code
DO (%)	100%	13.1	101.9%	no	N/A	A
pH 4	pH 4	13.1	4.02	no	N/A	A
pH 7	pH 7	13.1	7.11	no	N/A	A
pH 10	pH 10	13.1	10.07	no	N/A	A
Turbidity (NTU)	10	-	9.85	no	N/A	A

Calibration Check 1/21/2021

Parameter	Std. Value	Std. Temp (°C)	Value	Re-Cal Yes or no?	Post-Cal Value	MQO Code
DO (%)	100%	13.6	100.7%	no	N/A	A
pH 4	pH 4	13.6	4.04	no	N/A	A
pH 7	pH 7	13.6	7.09	no	N/A	A
pH 10	pH 10	13.6	10.09	no	N/A	A
Turbidity (NTU)	10	-	9.91	no	N/A	A