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PHOSPHORUS, IRON AND TRACE METAL INTERACTIONS AT THE
SEDIMENT LAYER-WATER COLUMN INTERFACE: THE POTENTIAL
ROLE OF RECOVERED MINE DRAINAGE RESIDUALS

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Abstract

Nutrient enrichment, eutrophication and harmful algal blooms are global environmental concerns. The study site, Grand Lake o' the Cherokees (GLOC) located in northeast Oklahoma, experiences eutrophication due to excess phosphorus (P) loading and resulting severe algal blooms, and elevated sediment trace metal concentrations due to its close proximity to the abandoned Tri-State Lead-Zinc Mining District (TSMD). Mine Drainage Residuals (MDRs), amorphous iron oxyhydroxides recovered from passive treatment systems in the TSMD, may serve as phosphorus sinks for problems in GLOC. In order to understand metal-nutrient interactions at the sediment layer-water column interface at this reservoir and evaluate the P removal performance of MDR amendments, three green house microcosm (GHM) and one field mesocosm studies were conducted in this project.

The first GHM study (Chapter One) focused on impacts from algal blooms and showed that excessive biomass changed P balances between the water column and sediment layer, but did not impact trace metal concentrations in the system, which means that increased algal blooms in the reservoir likely will not result in trace metal release from contaminated sediments into the water column. The second GHM study (Chapter Two) investigated sediment disturbance effects and showed that mixing caused initial P release from sediment into the water column during resuspension, but overall P decreases after redeposition. Throughout the entire process, trace metal concentrations in both the water column and sediment layer were below the corresponding guidelines. The third GHM study (Chapter Three) compared P removal performance from different dosages of MDRs and showed no significant P decreases compared to control treatments in the short-term. However, significant P capture occurred with MDR addition treatments and the control treatments showed significant P release due to biomass death and decay. Overall, MDR additions

served as long-term sinks for internal P loading to prevent labile P releases from biomass decay and decrease the likelihood of future blooms, all without noticeable trace metal release.

The field mesocosm study (Chapter Four) applied three different MDR addition methods (mixed, layered and bagged) and performance was compared to a control treatment. Although by the end of four months all four treatments achieved over 99% P removal, within the first seven days MDR addition treatments had much more rapid and greater P decreases than control due to the quicker P sorption rate and greater P sorption capacity than sediment (30 g/Kg compared to 0.6 g/Kg, respectively). No trace metal release was observed in both water and sediment, and the bagged MDR addition method was recommended for future engineering design of large-scale MDR amendments into eutrophic reservoirs to improve water quality and prevent harmful algal blooms.

Chapter One: Algal Biomass Influences Phosphorus-Metal Interactions at the Sediment-Water Interface in Grand Lake of the Cherokees (Oklahoma, USA)

This chapter has been formatted for submission to Environmental Science and Pollution Research.

Abstract

The objective of this research was to understand how algal blooms impact the nutrient and trace metal cycling processes at the sediment layer-water column interface in a large terminal reservoir, the Grand Lake o' the Cherokees, Oklahoma. The study site has elevated metals concentrations in the sediments from the upstream Tri-State Lead-Zinc Mining District and elevated nutrient concentrations in the water column from agricultural and urban run-off, resulting in eutrophication and substantial algal blooms. It was hypothesized that trace metal release from contaminated sediments to the water column would be driven by increased algal biomass growth. A green house microcosm study was designed with three different biomass treatments: control (no algae addition), low biomass (40 $\mu\text{g/L}$ chlorophyll a) and high biomass (80 $\mu\text{g/L}$) using lake sediment groundwater (as a control) and laboratory-incubated *Microcystis aeruginosa*, one of the dominant blue-green algae in this lake. After 30 days, each of the treatments showed changes in planktonic, attached and benthic chlorophyll-a concentrations, and dominant algal species, and species richness. Soluble reactive phosphorus (SRP) and nitrate nitrogen ($\text{NO}_3\text{-N}$) in the water column showed decreasing trends over time, indicating nutrient uptake by biomass. Iron (Fe), nickel (Ni) and cadmium (Cd) concentrations in all water column samples were below the practical quantitation limit (PQL), while lead (Pb) and zinc (Zn) concentrations ranged from 0.015 to 0.05 mg/L, due to residual contamination from the sediments. Compared to US EPA National Recommended Water

Quality Criteria (NRWQC), Pb concentrations were below the Criteria Maximum Concentration (CMC) but above the Criterion Continuous Concentration (CCC), while Zn concentrations were below both CMC and CCC. At the end of the study, Pb, Zn and Cd concentrations in the sediment showed no significant changes in any treatment, but all treatments had trace metal concentrations above the freshwater sediment quality guideline (SQG) thresholds. However, concentrations were below the Tri-State Mining District (TSMD)-specific SQG thresholds. The results showed that biomass changed nutrient balances between the water column and sediment layer but did not impact trace metal concentrations in the system. It is not likely that increased algal blooms in the lake would result in trace metal release from the contaminated sediments into the water column.

Introduction

In recent decades, anthropogenic activities have detrimentally influenced lake ecosystems by introducing greater nutrient inputs (Chen et al. 2014, Ho et al. 2019, Jiang et al. 2008, Jin et al. 2006, Xie et al. 2003); as the 2012 National Lakes Assessment report showed that 34% of U.S. lakes were classified as eutrophic and 21% were hypereutrophic (EPA 2016) and a more recent study showed that 68% of the large lakes around the world had increased peak summertime algal blooms intensities (Ho et al. 2019). Phosphorus (P) has long been considered as the limiting nutrient in most fresh water ecosystems (Chen et al. 2018, Perkins and Underwood 2001, Sibrell et al. 2009) and it can be introduced into the waters by external loadings such as erosion, runoff and precipitation. Once external P sorbs to sediment particles or is taken up by biomass and deposited in organic matter, internal loading is created from the sediment P sink (Jin et al. 2006, Nikolai and Dzialowski 2014). To improve the trophic status of lakes, control and reduction of external P loading has been most commonly applied; however, the internal P loading can play an

important role in delaying ecosystem recovery and maintaining persistent algal blooms (Chen et al. 2018, Wang et al. 2016, Yao et al. 2016).

Previous studies have shown that the sediment-water interface is the most active site for metal-nutrient interactions (Chen et al. 2014, Jiang et al. 2008, Jin et al. 2006, Song et al. 2013). The release of sediment P can result in elevated concentrations of dissolved P that promote algal blooms and sediment P mobility is greatly impacted by sorption to iron oxides and hydroxides (Chen et al. 2018, Jiang et al. 2008, Wang et al. 2016, Yao et al. 2016). Metal P-binding which controls sediment P bioavailability is dependent on redox and pH conditions (Chen et al. 2018, Wang et al. 2016), which are further mediated by algal growth due to photosynthesis and respiration, as well as temperature and light conditions (Jin et al. 2006, Song et al. 2013, Wang et al. 2016, Xie et al. 2003). Therefore, algal productivity and die off can greatly impact metal/P dynamics at the sediment-water interface.

Grand Lake o' the Cherokees (GLOC) is a large man-made multipurpose reservoir in northeastern Oklahoma operated by the Grand River Dam Authority (GRDA) (Angelo et al. 2007, Morrison et al. 2017a, 2017b). It is a warm monomictic lake with a surface area of 183 km², a mean depth of 11.1 m, a maximum depth of 40.5 m, a mean elevation at 227 m above sea level and a volume of 2.07 km³ (Morrison et al. 2017b, OWRB 2009). It is a eutrophic lake with excess nutrient (P) concentrations and has also experienced seasonal algal blooms which typically occur from mid-spring to mid-autumn (GLWP 2008, Morrison et al. 2017b). According to Morrison et al. (2017b), chlorophyll-a (Chl-a) in vivo concentrations for GLOC varied from 5-40 µg/L in June and 0-15 µg/L in September, depending on the water depth. The nutrient limitation in GLOC varies both spatially and temporally from no nutrient limitation to nitrogen (N) limitation, P limitation, and N and P co-limitation. Internal P loading from anoxic sediments contributes to spatial and temporal

dynamics as it affects water column nutrient concentrations and ratios (Nikolai and Dzialowski 2014). P has been intensively studied for its fate and transport at the sediment-water interface (Hu et al. 2007, Li and Huang 2013, Qin et al. 2004), and for this study, P was chosen as the main nutrient to be examined.

Substantial trace metal mass loading from the abandoned Tri-State Mining District (TSMD) provides another major pollutant load into GLOC. The TSMD now includes several Superfund sites: the Tar Creek Superfund Site in northeast Oklahoma, the Cherokee County Superfund Site in southeast Kansas and two other sites in Jasper and Newton Counties in southwest Missouri (GLWP 2008, Garvin et al. 2017). Elevated concentrations of iron (Fe), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni) and other trace metals have been mobilized from artesian flowing mine water sources, waste rock and tailings runoff and other mining-related disturbances. A recent study (Morrison et al. 2019) showed that the sediment trace metal concentrations in GLOC were around 10.5-3720 mg/kg for Zn, 0.30-22.5 mg/kg for Cd and 7.28-195 mg/kg for Pb. These trace elements may be highly toxic and cause a series of negative impacts on lake ecosystem processes. Since most of these metals readily deposited into lakebed sediments, they can serve as a long-term pollution source providing long-term exposure to the lake ecosystem (Garvin et al. 2017).

Studies performed on seawater systems have shown that algal blooms can impact the trace metal concentrations in the water. Krishnan et al. (2007) showed that greater concentrations of Zn, Cd and Ni, as well as lesser concentrations of Pb, copper (Cu) and cobalt (Co) were observed where blooms occurred, while Cd was released during the biomass decay period. Luengen et al. (2007) showed that during the bloom period, manganese (Mn), Ni and Pb had decreased concentrations due to oxidation, algal uptake and sorption, while during the decay period, Mn, Co, Zn and Pb had increased concentrations due to reductive dissolutions caused by the suboxic conditions created

from decomposing dead biomass. In contrast, studies performed on freshwater systems showed that the eutrophication degree had only negligible effects on the fraction of heavy metals (Lu and Cheng 2011) and algal bloom outbreak as well as decay had only slight effects on heavy metal fractionations in the sediment (Wang et al. 2015).

The aim of this study was to understand how short-term, algal blooms may impact dynamic cycling processes and distribution of P and trace metals at the sediment-water interface in GLOC.

Material and methods

Microcosm setup

The surface sediment used in this study was collected from Sycamore Flats at GLOC (36°44'44.2''N, 94°44'9.6''W, water depth = 1.1 m). About 0.06 m³ of lake sediment was collected using a Ponar dredge; water samples were collected just above the sediment-water interface using a Wildco® horizontal beta sampler at the same site for background water quality characterization. All samples were stored and transported at 4 °C before being delivered to the laboratory. Sediment samples were stored in a walk-in cooler at 4 °C at the laboratory before the incubation experiments.

Because *Microcystis* spp. is a dominant species in GLOC, especially during the blue-green algal blooms (Morrison et al. 2017b, Nikolai and Dzialowski 2014), algal seed (living *Microcystis*) and algal growth medium (Alga-Gro® Freshwater Medium) from Carolina Biological Supply (Burlington, NC) were incubated in the laboratory for approximately four weeks to develop a biomass stock solution for introduction into the microcosms. To control for water quality influences, a local ground water source inoculated with the biomass stock solution was used in the

microcosm study. Regular water samples were collected from both the ground water source and algal stock solution to examine background levels of nutrients.

Green house incubations included three treatments: control (C) with only lake sediment and ground water, low biomass (LB) with lake sediment and ground water with low biomass addition, and high biomass (HB) with lake sediment and ground water with high biomass addition. For this study, the LB treatment use 40 µg/L Chl-a and the HB used 80 µg/L Chl-a. The LB and HB treatments were set up in triplicate, while the C treatment was run in duplicate, for a total of eight experimental vessels. Approximately five kg of homogenized wet lake sediments were added into each 25-L vessel to produce a sediment layer depth of approximately 6.5 cm. Homogenized solutions (ground water for C treatment and ground water mixed with algal stock solutions for LB and HB treatments) were added into each vessel, which produced a water layer depth of approximately around 35 cm, and were allowed to settle for three days without disturbance in order to approach field conditions. Microcosms were incubated in the green house for 30 days at 23 °C to 30 °C. In the results and discussion section, data are presented starting from Day 0, which was three days later after the initial set-up.

Sampling processes

Every three days, water samples were collected about 10 cm above the sediment-water interface in each vessel and analyzed for chlorophyll-a (Chl-a, as phytoplankton), soluble reactive phosphorus (SRP), nitrate-nitrogen (NO₃-N) and a suite of trace metals. Physicochemical water quality data including pH, water temperature (Temp), dissolved oxygen (DO) and oxidation-reduction potential (ORP) readings were collected from each water sample using a YSI 600QS multiparameter datasonde with YSI 650 display between 9:00 and 10:00 in the morning.

Additional ground water was added to the vessels to replenish loss of water due to both sampling and evaporation. Samples of the added ground water were also collected.

Sediment samples were collected at the initial stage and final stage of the study to analyze for Chl-a, nutrient and metals concentrations, as well as other basic sediment quality parameters including moisture content (MC), organic content (OC), particle density and particle size distribution.

At the end of study, due to the appearance of attached algae (periphyton) to the walls and benthic algae on the sediment surface, attached algae (collected from an 8 cm × 10 cm rectangular area on the side wall) and benthic algae (collected from a circular area with a diameter of 3.5 cm from the sediment surface) were sampled for Chl-a analysis.

Chemical analyses

All the Chl-a concentrations (phytoplankton, periphyton and benthic algae) were determined using a hot-ethanol extraction method (Chen et al. 2006). Water samples, or solid samples collected by brush and flushed out with deionized water (Gu et al. 2018), were filtered with Whatman glass microfibre filters (GF/F) and extracted with 90% ethanol in an 85°C water bath for two minutes and at room temperature for five hours, then measured by a spectrometer at 665 nm and 750 nm. The filtered water was used for SRP determination by the ascorbic acid method (EPA Method 365.3), NO₃-N determination by the brucine method (EPA Method 352.1) and dissolved metals analyses via microwave hot HNO₃ digestion (EPA Method 3015) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (EPA Method 6010). Sediment P was extracted with ammonium bicarbonate-diethylenetriaminepentaacetic acid which represented the P fraction bound to Fe, Al and Mn oxides and hydroxides (SSSA, 1996). Sediment metals were extracted through microwave hot HNO₃ digestion (EPA Method 3051) and later analyzed by ICP-

OES (EPA Method 6010). Other sediment parameters were measured through American Society for Testing and Materials methods: ASTM D2974 for moisture content and organic content, ASTM D854 for particle density and ASTM D7928 for particle size distribution.

Statistical analyses

Statistical significance of differences analyses was performed with one-way analysis of variance (ANOVA) using the SPSS 24.0 software. A p value < 0.1 level was considered as significant. When differences between treatments were significant, least significant difference (LSD) tests were performed as a post hoc study. Variations in results were reported in terms of standard deviations (\pm SD).

Results and discussion

Changes in basic water quality data

The changes of water temperature, pH, DO and ORP of the three treatments over the 30-day study period are presented in Figure A 1. There were no significant differences in water temperature, pH and DO among C, LB, and HB treatments. However over time, the pH of all three treatments had an overall increasing trend while the ORP had an overall decreasing trend. DO concentrations fluctuate initially but then came to a relative constant stage after Day 9.

Changes biomass as chlorophyll-a

Over 30 days, all the treatments with various initial biomass concentrations had overall decreasing trends ($p < 0.1$) in Chl-a concentrations, to around 5 $\mu\text{g/L}$ (Figure 1. 1a). It should be noted that on Day 0, the average Chl-a concentrations for control, low biomass and high biomass were 7.2 $\mu\text{g/L}$, 54.7 $\mu\text{g/L}$ and 157.0 $\mu\text{g/L}$, respectively, rather than 0 $\mu\text{g/L}$, 40 $\mu\text{g/L}$ and 80 $\mu\text{g/L}$ as designed. This

was because the first sampling day (Day 0) was three days later after the set-up. The three-day period was provided to allow sediments to settle down and biomass to adapt to the microcosms.

The changes in plankton Chl-a biomass had significant differences among each treatment ($p < 0.01$) (Figure 1. 1b). For C and LB treatments, initial increases in Chl-a mass for the first 3 days was followed by continuous decreases until the end of the study. For HB, a rapid decline was seen on Day 3 (two of the three vessels experienced an unexpected die-off), after which the standard deviations in Chl-a measurements for HB treatment became larger. On Day 6, Chl-a biomass of HB increased, indicating biological re-establishment, which was supported by the observation that biomass re-appeared in the vessels, after which the HB Chl-a mass followed a decreasing trend until the end of study.

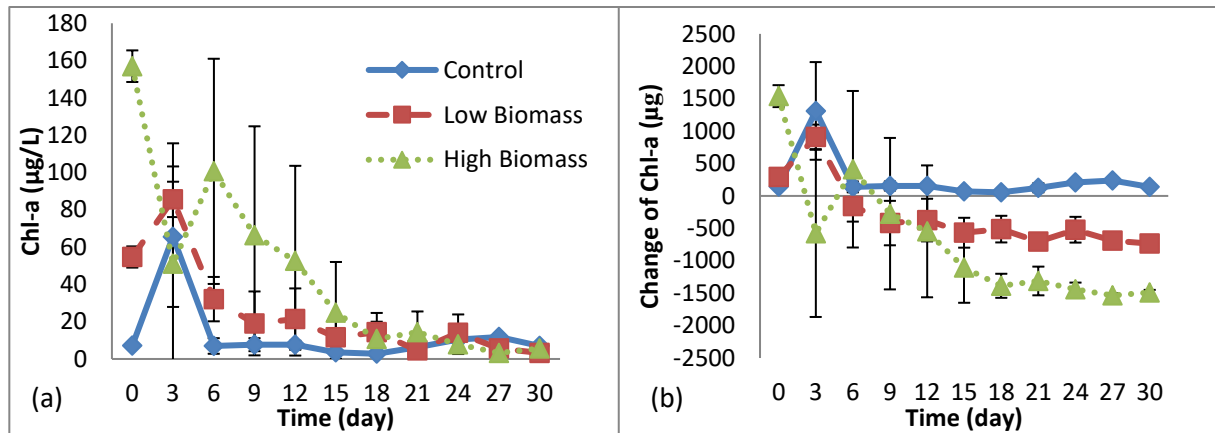


Figure 1. 1. (a) Plankton Chl-a concentration in the water column of three treatments over the 30-day study period. (b) Changes of plankton Chl-a mass for three treatments compared to the set-up condition over the 30-day study period. Data are mean \pm SD.

On Day 30, the Chl-a concentrations of plankton biomass (PB) in the water column, attached biomass (AB) to the side wall and benthic biomass (BB) on the sediment were analyzed to examine biomass distribution (Figure 1. 2). The PB changes were very different among three treatments

($p < 0.01$), while the AB and BB changes showed no significant differences. Results showed that the control treatment with no initial algal addition had an increased plankton biomass, but the two biomass addition treatments experienced die-off of the added algae, which resulted in a decrease in plankton biomass. All treatments had some level of attached and benthic biomass growth, which accounted for 8.0% to 75.6% of the final total biomass. These results supported the previous observation about initial die-off and re-establishment, as the original dominant algae species (plankton) was replaced by new algal species (mainly the filamentous attached algae).

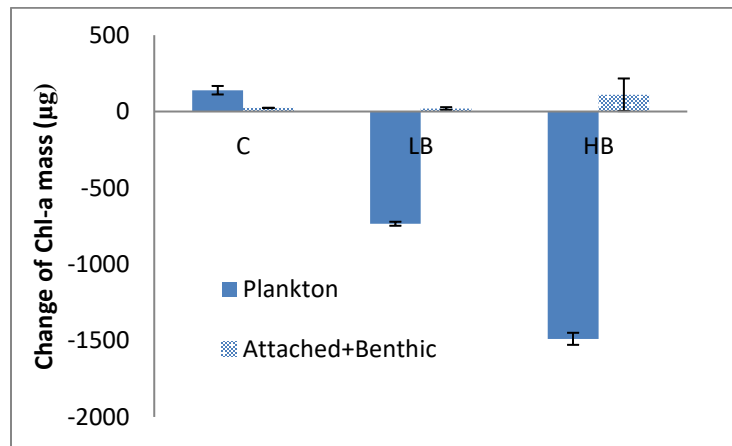


Figure 1. 2. Change of Chl-a mass in each treatment for different biomass treatments over the 30-day study period. Data are mean \pm SD.

Although the three treatments were set up with different initial biomass levels, by the end of the study, all treatments converged to a similar condition, with no significant differences in PB, AB and BB final masses (Figure A 2).

Biomass samples were also analyzed for identification of dominant algal species (Table 1. 1) and species richness (Figure 1. 3). All three treatments had greater final species richness than initial species richness, which showed new algal species were established in the vessels over time. The C treatment had lesser final richness than LB and HB ($p < 0.1$). Also, except for the original added

species (*Microcystis*), the other two major dominant algal species (*Nodularia* and *Mougeotia sp.*) were both filamentous, which agreed with previous observations.

Table 1. 1. Algal species changes in each microcosm vessel,

Vessel	Initial species richness	Final species richness	Dominant algal species
C1	0	5	<i>Microcystis</i>
C2	0	4	<i>Nodularia, Mougeotia sp.</i>
LB1	1	6	<i>Microcystis</i>
LB2	1	7	<i>Pennate diatom</i>
LB3	1	9	<i>Nodularia, Pennate diatom</i>
HB1	1	7	<i>Nodularia</i>
HB2	1	7	<i>Nodularia, Microcystis</i>
HB3	1	10	<i>Nodularia, Mougeotia sp.</i>

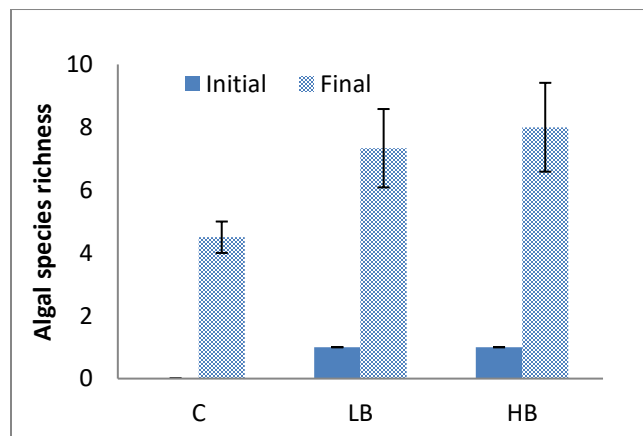


Figure 1. 3. Algal species richness in each treatment. Data are mean \pm SD.

Changes in nutrient concentrations

During this study, SRP and NO₃-N in the water column of each of the treatments showed decreasing trends over time ($p < 0.001$; Figure 1. 4), with no significant differences among each

treatment. The initial and final SRP and NO₃-N concentrations for all three treatments are summarized in Table 1. 2. Ground water was found to contain 0.269-0.766 mg/L for SRP and 1.751-2.365 mg/L for NO₃-N, both of which were greater than the lake water from where the sediments were collected (as 0.138 mg/L for SRP and 1.454 mg/L for NO₃-N). Therefore, this study evaluated the role of added algal biomass under elevated nutrient concentrations.

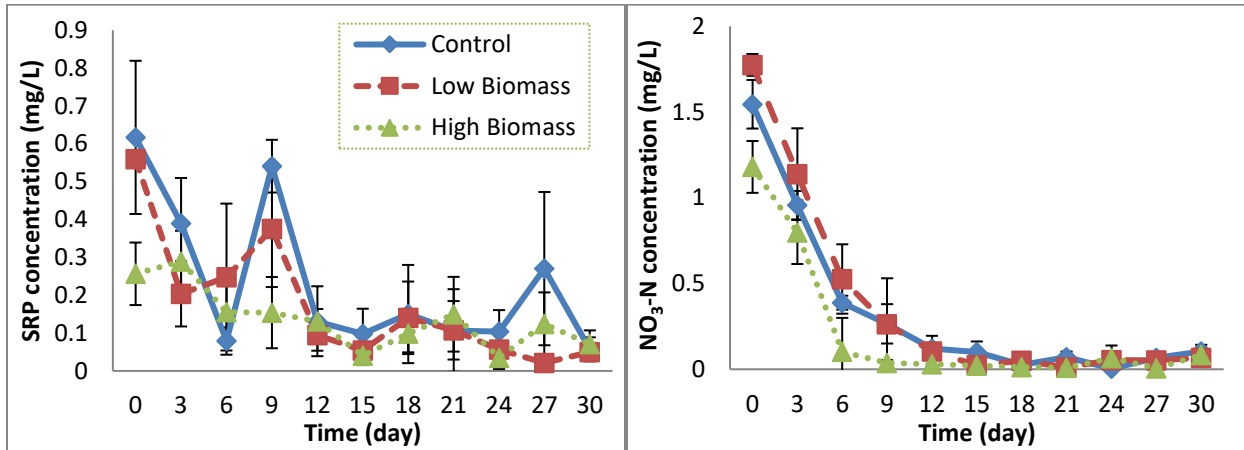


Figure 1. 4. Changes of SRP and NO₃-N concentrations in the water column of three treatments over the 30-day study period. Data are mean \pm SD.

Table 1. 2. Nutrients concentrations for three treatments at beginning and end of study

	Set-up water	Initial			Final		
		C	LB	HB	C	LB	HB
SRP (mg/L)	0.658	0.617	0.560	0.257	0.057	0.049	0.071
NO ₃ -N (mg/L)	1.963	1.545	1.775	1.180	0.105	0.067	0.084

For sediment P concentrations, final sediment concentrations were slightly lesser (17.11 mg/kg for C, 17.84 mg/kg for LB and 17.51 mg/kg for HB), compared to the initial sediment concentration

of 18.01 mg/kg. The statistical analysis showed no significant difference between the initial and final concentrations. Final sediment organic content (OC) values (4.43% for C, 5.10% for LB and 4.32% for HB) were slightly greater than the initial sediment OC of 3.84%. The statistical analysis showed no significant difference between the initial and final concentrations in each treatment, except for the LB treatment.

P masses in the systems before and after the 30-day study period were compared (Table A 1). Both sediment P mass and water P mass showed significant losses ($p < 0.05$), and the lost P mass was assumed to be uptaken by biomass growth.

Relationship between biomass and nutrients

During the 30-day study period, aqueous SRP and NO₃-N concentrations for all treatments decreased and attached and benthic biomass increased. The original hypothesis was treatments with higher initial biomass levels (HB>LB>C) would have less nutrients in the water column. However, since all treatments ended up with abundant algal growth at the end of this short-term study, the statistics showed no significant differences among the three treatments. Figure 1. 1 and Figure 1. 4 showed that C and LB shared similar trends which were different from HB, which could be due to the difference in N:P ratios. According to previous studies (Havens et al. 2003, Smith et al. 1995), lakes with N:P mass ratio < 22:1 are typically dominated by nitrogen-fixing cyanobacteria. The N:P ratio for HB was below this value for the entire study period, while ratios for C and LB were initially above but dropped below this value after Day 6.

After Day 6, the vessels started to exhibit filamentous algal growing and attaching to the walls. Also, algal species identification results at the end of this study showed that *Nodularia* (nitrogen-fixing cyanobacteria) were found in almost every vessel (except for LB1), which indicated that

Nodularia growth became competitive to phytoplankton growth at this N-limiting condition (Oliva et al. 2009). During the 30-day study period, new algal species became dominant and re-established the equilibrium state in these vessels.

All vessels had both decreased water P mass (from 15.17-15.65 mg to 0.51-2.35 mg) and decreased sediment P mass (from 52.22-52.28 mg to 45.24-51.83 mg). Since these were closed systems, the lost P could only be stored in another compartment in each system, e.g., the biomass. Figure 1. 5 showed that with greater biomass loss (HB>LB>C) ($p<0.1$), there was lesser P mass loss from water and sediment (HB<LB<C)($p<0.01$). It was concluded that the dead biomass contributed a fraction of P into the whole system and the growth and death of biomass changed the P distribution, which is in agreement to previous studies (Wang et al. 2016, Xie et al. 2003, Zhu et al. 2013).

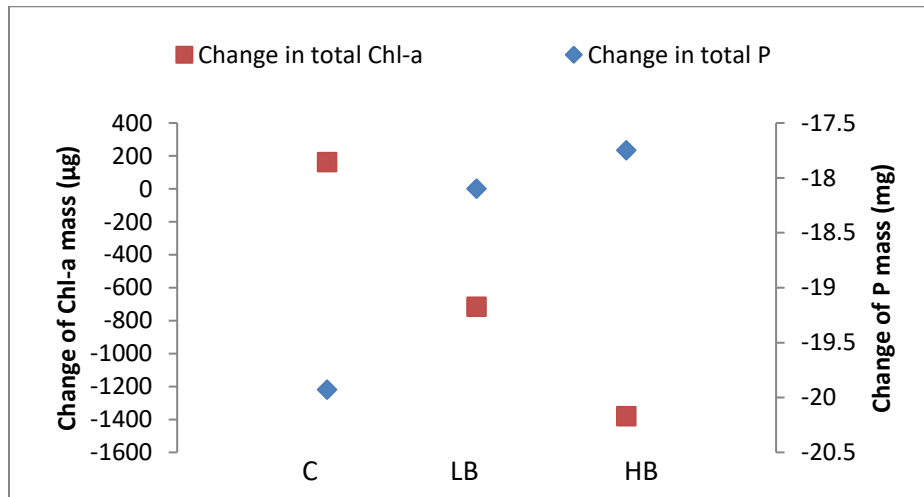


Figure 1. 5. Changes in total P mass and change in total Chl-a mass for three treatments.

The water column pH for all treatments increased from 7.5 to 8.5-9.0 during the 30-day study period, which corresponded to algal growth since photosynthetic processes uptake CO₂ and re-established the carbonate/bicarbonate equilibria (Boers 1991, Wang et al. 2016, Xie et al. 2003).

This biomass growth-mediated increase in pH likely promoted sediment P release. Xie et al.

(2003) showed that algal bloom could result in a significant P release from sediment into the water column, accelerating excess P pollution in the lake water. Other studies have also showed that after bloom peaks, decomposition of accumulated biomass can also greatly impact water quality by decreasing pH and DO, as well as increasing the dissolved inorganic P and N in the water column (Chuai et al. 2011, Xie et al. 2003, Zhu et al. 2013).

Changes in metals concentrations

Within the 30-day study period, iron (Fe), nickel (Ni) and cadmium (Cd) concentrations from all water samples were below the practical quantitation limits (PQL) of 0.0081, 0.0060 and 0.0008 mg/L, while lead (Pb) and zinc (Zn) concentrations were detected from 0.015-0.05 mg/L, due to both the background concentrations in the set-up groundwater (0.029 mg/L for Pb and 0.062 mg/L for Zn) and the residual contamination from the sediments (Figure 1. 6). The sediments were collected close to the TSMD where Pb and Zn were mined and elevated Pb and Zn levels in contaminated sediment and water were not unexpected (Angelo et al. 2007, Garvin et al. 2017).

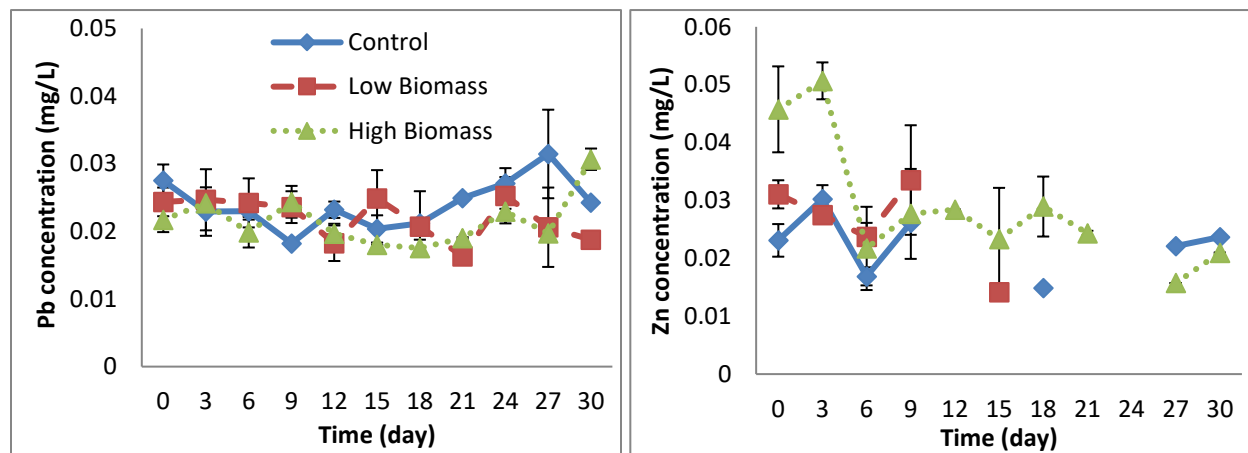


Figure 1. 6. Changes of Pb and Zn concentrations in the water column of three treatments over the 30-day study period. Data are mean \pm SD. Missing points are due to concentrations below the practical quantification limit (PQL).

According to US EPA National Recommended Water Quality Criteria (NRWQC), the hardness-adjusted CMC can be applied to short-term exposures and the CCC can be applied to long-term exposures. The results showed that all Pb concentrations were below the CMC and above the CCC, while all Zn concentrations were below the both CMC and CCC (Table 1. 3).

Table 1. 3. Hardness and hardness adjusted NRWQC ranges for aqueous metal concentrations

	Range of hardness as CaCO ₃ mg/L	CCC (mg/L)		CMC (mg/L)	
		Zn	Pb	Zn	Pb
Control	113.3-320.9	0.130-0.315	0.074-0.224	0.131-0.317	0.003-0.009
Low Biomass	104.5-402.9	0.122-0.382	0.068-0.283	0.123-0.385	0.003-0.011
High Biomass	114.9-328.0	0.132-0.321	0.075-0.229	0.133-0.323	0.003-0.009

For sediment metals concentrations, although the statistical analysis showed no significant difference between initial and final values, initial Fe concentration at 16200 mg/kg was slightly greater than the final Fe concentrations in C, LB and HB at 16000 mg/kg, 15200 mg/kg and 14600 mg/kg, respectively. Sediment concentrations of the other three trace metals (Pb, Zn and Cd), which are major contaminants from the mining district, also showed no significant difference before and after the 30-day study period (Table 1. 4). In addition, multiple sediment quality guidelines (SQGs) for both TSMD-specific and consensus-based freshwater systems were examined (Table 1. 4) including Probable Effects Concentrations (PEC) and Threshold Effect Concentrations (TEC) (Ingersoll et al. 2009, MacDonald et al. 2000).

Table 1. 4. Sediment metal concentrations compared to SQGs

	TSMD PEC (mg/kg)	Consensus- Based TEC (mg/kg)	Consensus- Based PEC (mg/kg)	Initial range of concentrations (mg/kg)	Final range of concentrations (mg/kg)
Zn	2083	121	459	354-480	339-463
Cd	11.1	0.99	4.98	2.09-2.86	2.02-2.90
Pb	150	35.8	128	41.4-45.4	40.7-50.1

When comparing the initial and final sediment metals concentrations for all three treatments to the SQGs, all values were above the consensus-based TEC-SQG and below the TSMD-specific PEC-SQG. However, Zn concentration for the initial set-up and final control treatment had partially exceeded the consensus-based PEC-SQG (with 50% and 17% above PEC-SQG, correspondingly), while the remaining concentrations were all below the consensus-based PEC-SQG. The site-specific study conducted by Ingersoll et al. (2009) also showed that with infrequently exceeded PEC-SQGs, GLOC sediments would not reduce the survival or growth of sediment-dwelling organisms. GLOC elevated sediment metals concentrations might pose adverse effects compared to other freshwater systems; however, these values are likely not elevated enough to frequently cause adverse effects or contribute to toxicity in this specific area.

Relationship between biomass and metals

For water column metal concentrations, there was no change in the percentage exceeding NRWQCs for all three treatments. The growth and death of biomass did not cause an increase in trace metals (Pb, Zn and Cd) into the water column. There was no difference for metal

concentrations in the sediment layer, between the initial and final stages for all three treatments in the percentages exceeding consensus-based TEC-SQG and TSMD-specific PEC-SQG.

For the consensus-based PEC-SQG, there was a decreased percentage of Zn exceedance after the 30-day study period, indicating that different levels of growth and death for the biomass did not increase sediment metal concentrations. Instead, the fact that both LB and HB treatments had 0% exceeding for consensus-based PEC-SQG and C had only 17% after 30 days might indicate that Zn adsorbed, was assimilated by biomass growth, or was complexed by organic matter derived from biomass, which in the long term would eventually deposit into the sediments after complete die-off and decomposition of the biomass (Duan et al. 2014, Wu et al. 2017). Overall, biomass growth in this short-term study did not cause trace metals release into the water column from the sediment layer.

Conclusions

In this study, changes in the biomass activities in this biological highly productive system impacted the nutrient cycling flux between the surface sediment layer and water column. The decrease of P masses from both the water column and sediment layer indicated a fraction of P taken up by biomass growth. After the 30-day study period, algal species richness increased, and the dominant species changed for all three treatments. Changes driven by biological activity such as photosynthesis and respiration caused an increase in pH and a decrease of ORP and indicated that biomass growth could impact internal P loading in this system. Trace metal concentrations in the water column showed no difference over the 30-day period for all three treatments, with Pb concentrations below the CMC and above the CCC and Zn concentrations below both the CMC

and CCC. Sediment metal concentrations also showed no difference before and after the 30-day study period for all treatments, with no exceedance of the TSMD-specific PEC-SQG, and only partial exceedance of the consensus-based PEC-SQG, which indicates no increased risk to the lake ecosystem. Algal blooms in the lake may cause changes in nutrient distributions, however, they will not introduce more trace metals (especially Pb, Cd and Zn) into the water columns from the sediment layer over the short term. In the future, a long-term study is desired to further explore the impacts from decay and decomposition of the algal bloom on the nutrient and metal releases.

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Chapter Two: Sediment Disturbance Effects on Nutrients and Metals in a Reservoir Receiving Both Agricultural Runoff and Hard Rock Mine Drainage

This chapter has been formatted for submission to Lake and Reservoir Management.

Abstract

A green house microcosm study was completed to simulate nutrient/metal interactions at the sediment layer-water column interface in a large Oklahoma reservoir that receives untreated lead-zinc mine waters and agricultural runoff. To evaluate sediment disturbance influences, three different mixing treatments were established in nine 25-L vessels containing lake sediments and water: control (no mixing), low mixing (200 rpm) and high mixing (500 rpm), using overhead blade-stirrers. A two-hour mixing period produced significant ($p < 0.05$) increases in total suspended solids, total phosphorus (P), iron (Fe), nickel (Ni) and zinc (Zn) in the water column, indicating nutrient and trace metal release due to mixing disturbance. During the subsequent 7-day settling period, water column total P, Fe, Ni and Zn concentrations decreased 54.8%, 98.9%, 57.7% and 89.4%, respectively, for the low mixing treatment and 96.7%, 98.7%, 92.1% and 99.0%, respectively for the high mixing treatment, indicating sediment redeposition, metal precipitation, and/or nutrient sorption. After 7 days, sediments showed decreased P and increased metal (Fe, Zn, Cd and Pb) concentrations compared to initial conditions. The growth of algal biomass may have affected P-metal binding, turning bioavailable P into non-bioavailable P and promoting metal sequestration to the sediments with biomass. All aqueous metal concentrations, when compared to US EPA National Recommended Water Quality Criteria, were below both Criteria Maximum

Concentration and Criteria Continuous Concentration guidelines. Sediment metal concentrations were below the site-specific sediment quality guidelines (SQGs) both before and after mixing.

Introduction

Sediment resuspension can impact phosphorus re-distribution between the sediment layer and water column (Ding et al. 2018, Wang et al. 2014, Wu et al. 2013). Re-suspended sediments can serve as an internal nutrient source by releasing excess P into the water column and therefore resulting in eutrophication and severe algal blooms (Xu et al. 2010, Zhang et al. 2014). Sediment mixing events can be generally divided into two types: bioturbation, which may be considered a static release, and hydrodynamic disturbance, a more dynamic release (Qin et al. 2004). Bioturbation is typically caused by a variety of benthic macroinvertebrates or benthivorous fish that change water column turbidity, dissolved oxygen and redox conditions during feeding activities, fecal excretion and decomposition, and other behavior, therefore enhancing concentrations of soluble reactive phosphorous (SRP) and release of total phosphorous (TP) from the sediment (Adamek and Marsalek 2013, Ottolenghi et al. 2002, Boyle et al. 2014). Compared to bioturbation, hydrodynamic disturbance due to turnover, wind, wave, flushing events (e.g., storms and floods) and human activities such as dredging, usually causes greater resuspension of sediments (Hu et al. 2007, Qin et al. 2004, Li and Huang 2013). Depending on different conditions, resuspended sediments may function as an internal source for P release or as a sink for P sorption. P concentrations in the overlying water are often greater than the sorption capacity of sediments, so the sediment will adsorb rather than release P (Cyr et al. 2009, Hu et al. 2007, Qin et al. 2004). Sediment resuspension can enhance P retention by decreasing mobile P fractions and increasing refractory P fractions (Li and Huang 2013). Therefore, dredging the surface layer of sediment has

been applied as an internal P loading control method in many places (Yenilmez and Aksoy 2013, Yu et al. 2017).

Sediment resuspension can also result in trace metal release, which can lead to persistent and toxic pollution of the water column (Prygiel et al. 2015, Botwe et al. 2018). The long-term transport and fate of trace metals depend on their potential mobility during resuspension and on redox-driven biogeochemical transformations (Liu et al. 2019). Studies have shown that the change of anoxic/oxic status during resuspension can result in distinct metal release rates: rapid release from anoxic sediments and gradual release from oxic sediments (Hwang et al. 2011). Redox potential is an important factor for trace metal release and it may have a positive or negative correlation with metal concentrations in the water column. Likely oxide-forming metals (e.g., Fe) show a negative relationship, while likely sulfide-forming metals (e.g., Cu) demonstrate a positive correlation with redox potential (Ye et al. 2013, Gibson et al. 2015). Since sorption to Fe/Mn (hydro)oxides is dominant at the sediment layer/water column interface, the reduction and solubilization of Fe (hydro)oxides can lead to remobilization of other trace metals (Wang and Wang 2017, Liu et al. 2019).

The study site, Grand Lake o' the Cherokees (GLOC) (Figure 2. 1) is a eutrophic reservoir due to agricultural and urban run-off that results- in seasonal algal blooms, which can occur from mid-spring to mid-autumn (Morrison et al. 2017). GLOC is located downstream of the abandoned Tri-State Lead-Zinc Mining District (TSMD), which includes several Superfund sites with the closest being the Tar Creek Superfund Site. Lake sediments have previously demonstrated elevated trace metals concentrations including Fe, Pb, Zn, Cd, Ni and others (Garvin et al. 2017). A study conducted by Morrison et al. (2019) showed trace metal concentrations of 10.5-3720 mg/kg Zn, 0.30-22.5 mg/kg Cd and 7.28-195 mg/kg Pb for sediments in GLOC. Trace metal contamination

emanates from artesian flowing mine water discharges, waste rock and tailings runoff and leachate, and other mining-related disturbances. These contaminant sources enter small tributary streams like Tar Creek, and eventually flow into the Neosho and Spring Rivers which form GLOC behind Pensacola Dam. Once deposited into the lake sediment, trace metals may become a long-term source of exposure and toxicity to the lake ecosystem if disturbed (Garvin et al, 2017).

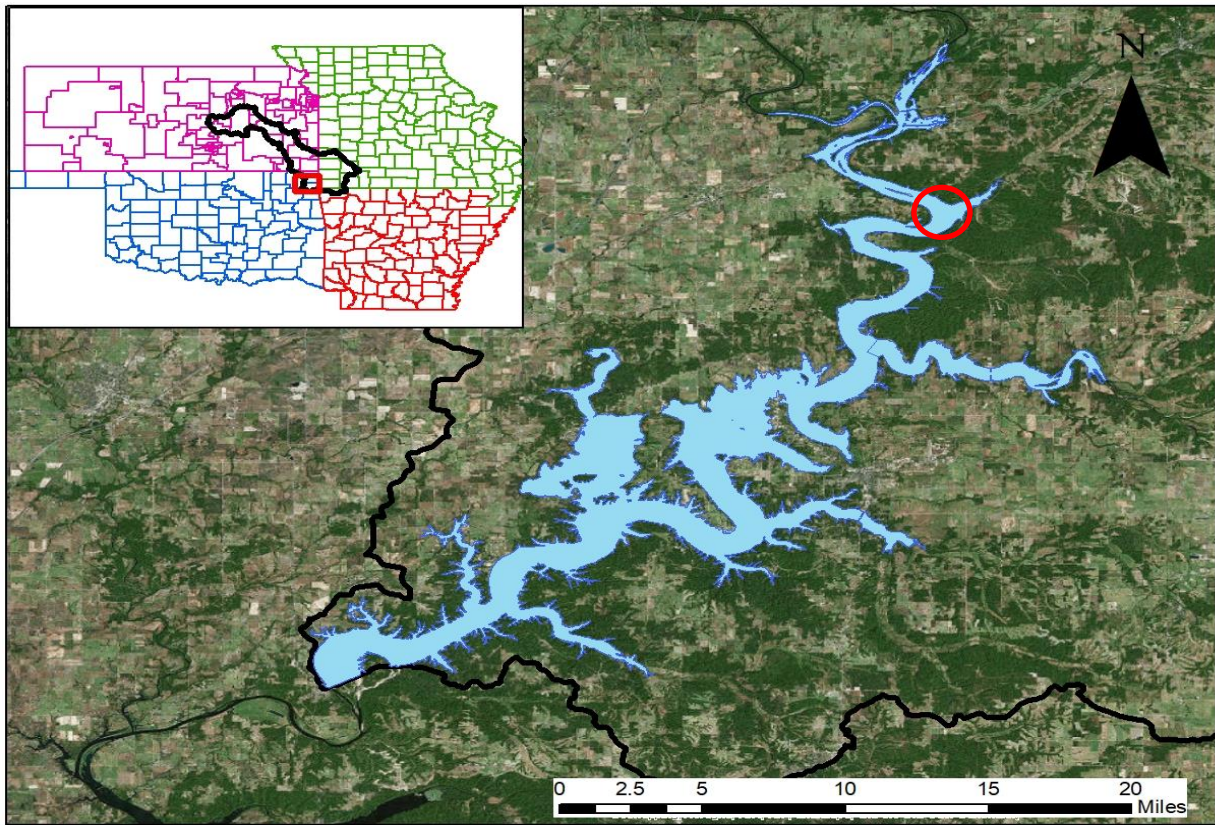


Figure 2. 1. Map of Grand Lake o' the Cherokees (GLOC) showing Sycamore Flats sampling location (red circle). Insert map shows the location of GLOC related to Oklahoma, Kansas, Missouri and Arkansas.

The focus of this study was to simulate the impact of different disturbance types (i.e., “low” mixing caused by bioturbation and “high” mixing caused by hydrodynamic disturbance) on

phosphorus and trace metals relationships between the sediment layer and water column, and to determine if trace metal release occurs during the resuspension process. These disturbance events were simulated in green house microcosms using GLOC sediments.

Study site

Background water quality and sediment samples were collected in GLOC at Sycamore Flats (36°44'44.2''N, 94°44'9.6''W, water depth 1.1 m). Lake sediments were collected using a Ponar dredge, and water samples were collected using a discrete-depth Wildco® horizontal beta water sampler just above the sediment layer/water column interface. After collection, all samples were stored and transported in coolers filled with ice at 4°C before delivery to University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) laboratories.

Materials and methods

Microcosm setup

Study vessels were constructed using 25-L open-mouth bottles by adding 5 kg of homogenized wet lake sediments and 20 L homogenized on-site groundwater. Due to the logistics of transporting large volumes of lake water between sampling sites (GLOC) and the experimental green house (University of Oklahoma Aquatic Research Facility), on-site groundwater was utilized and nutrient and trace metal concentrations were periodically examined; groundwater quality was similar to lake water ($p < 0.05$ for all tested parameters). Three different treatments were used for this study: control (C) treatment with no mixing, low mixing (LM) treatment with 200 rpm mixing (Reynold's number (Re) $\approx 13,500$) and high mixing (HM) treatment with 500 rpm mixing ($Re \approx 33,700$), using

overhead blade-stirrers. Reynold's numbers were calculated from a previous preliminary study. Each treatment included triplicates, which resulted in a total of nine vessels.

All vessels were set-up in the green house and allowed to equilibrate for about two weeks. The study was conducted in two portions: C vs LM and C vs HM. Each portion lasted seven days. In later data discussion part, C vs LM vs HM were compared together since C had been serving as the control treatment over time for both LM and HM without significant changes.

Sampling processes and Chemical analysis

During each stage, water samples were collected at 0, 1, 2, 3, 4, 8, 24, 48, 72, 120 and 168 hours, where the initial two hours were the mixing period and the latter 7 days were the post-mixing and settling period. Water samples were collected 10 cm above the sediment layer/water column interface for analysis of total suspended solids (TSS) according to the non-filterable residue method (EPA Method 160.2), total phosphorus (TP) and soluble reactive phosphorus (SRP) according to the ascorbic acid method (EPA Method 365.3), nitrate-nitrogen ($\text{NO}_3\text{-N}$) according to the brucine method (EPA Method 352.1) and chlorophyll-a (Chl-a) concentrations according to a hot-ethanol extraction method (Chen et al., 2006), in which the water samples were filtered with Whatman glass microfiber filters (GF/F) and extracted with 90% ethanol in 85°C water bath for 2 minutes and at room temperature for 5 hours, then measured by a Cole-Parmer SQ2800 UV/visible spectrometer at 665 and 750 nm. Total metals (TM) and dissolved metals (DM) samples first underwent microwave hot HNO_3 digestion (EPA Method 3015 using a CEM MARS Xpress Digestion System) and then were analyzed via Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (EPA Method 6010) using a Varian Vista-Pro simultaneous axial ICP-OES for a suite of metals concentrations (silver (Ag), aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg),

lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), silicon (Si) and zinc (Zn)). A YSI 600QS multiparameter datasonde coupled with a YSI 650 display were used to collect and record physicochemical water quality data including pH, pH mV, water temperature (Temp), Resistivity, Salinity, Specific Conductance, Conductivity, Total Dissolved solids (TDS), dissolved oxygen (DO) (in mg/L and % air saturation) and oxidation-reduction potential (ORP), immediately after each water sample collection event. Supplemental groundwater was added to each vessel periodically to maintain water volume/sediment mass ratios. The supplemental groundwater was used to replenish the losses due to both sampling and evaporation. Any additional groundwater was sampled and analyzed.

At the beginning and at the end of study, sediment samples were collected from each vessel for gravimetric analysis of moisture content (MC) and organic content (OC) as loss on ignition through American Society for Testing and Materials methods (ASTM D2974). Sediment P was extracted with ammonium bicarbonate-diethylenetriaminepentaacetic acid, which represented the P fraction bound to Fe, Al and Mn oxides and hydroxides and was analyzed following EPA Method 365.3 (SSSA 1996). Sediment samples for metals analyses underwent microwave hot HNO₃ digestion (EPA Method 3051) and then were analyzed via ICP-OES (EPA Method 6010).

Statistical analyses

SPSS 24.0 software was used to perform all statistical analyses to determine significance of differences. First, a Shapiro-Wilk test was performed to check for normality. If data were found to be normally distributed, independent t-tests were performed; otherwise, Mann-Whitney u-tests were performed. For comparisons among three or more groups, one-way analysis of variance (ANOVA) tests were performed, with least significant difference (LSD) tests performed as a post hoc study. Variations in results were reported as standard deviations (\pm SD).

Results and discussion

Water quality changes

Physicochemical water quality parameters for this study were summarized in Table B 1. Water temperatures for all treatments were similar ($p=0.279$). pH values were circumneutral and ranged from 7.1 to 9.4. Dissolved oxygen concentrations ranged between 11.0 and 18.4 mg/L (136.2 to 233.7 percent saturation), except for the HM treatment during initial mixing when they decreased to < 1 mg/L. ORP values were typically positive, ranging from +62 to +234 mV, again with the exception of values as low as -85 mV during initial mixing.

Changes in total suspended solids and Chl-a

Total suspended solids (TSS) concentrations are shown in Figure 2. 2. Smaller figures were inserted to the upper right corner, showing the entire 168-hour study period, while the original larger figures showed details for the first 8 hours of the study. The insert figures shared the same x-axis and y-axis units as the original figures. And for both inserted and original figures, the y-axis were in log-scale. Although the C treatment values stayed relatively constant over the study periods (6.5-20.2 mg/L), both the LM and HM treatments showed increases during the initial mixing period, then decreasing trends during the remaining period, as expected. The HM treatments had a greater peak concentration (19,166 mg/L) than the LM (204 mg/L) at the end of mixing period (Hour 2), the mean TSS for the HM treatments at the end of study (168 hours) was 21.8 mg/L, but LM treatment TSS concentrations decrease below 20 mg/L within 24 hours. These data indicated that greater disturbance caused more solids to be re-suspended in the water column, which take longer to settle out.

No significant differences ($p=0.528$) or trends over time ($p=0.369$) existed between the mixing treatments and the C treatments for plankton Chl-a concentrations. For all three treatments over

the entire study period, Chl-a concentrations were around $5.43 \pm 1.26 \mu\text{g/L}$. Although biomass growth during the study period might have affected some P fractions, the differences between treatments were not significant.

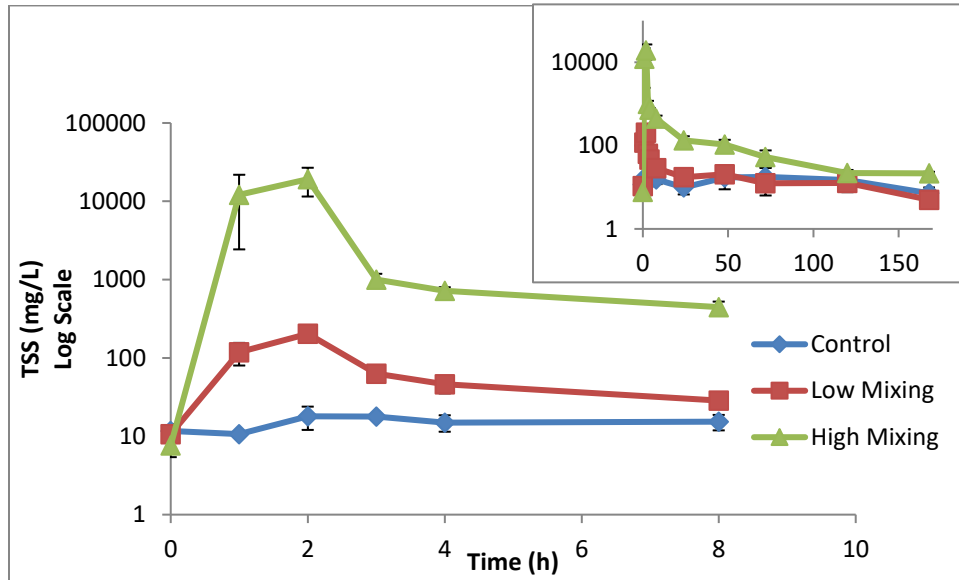


Figure 2. 2. Total Suspended Solids (TSS) of C, LM and HM treatments over study period. Data are mean \pm SD. Original figure shows details of the first 8 hours of the study while insert figure shows entire 168-hour study. Y-axis are in log-scale.

Changes in nutrient concentrations

Soluble reactive phosphorus (SRP) and nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations showed no significant differences among treatments ($p=0.090$ and $p=0.057$, respectively) as well as no significant trends over the study period ($p=0.660$ and $p=0.968$, respectively) (Table 2. 1).

Table 2. 1. Soluble reactive phosphorus (SRP) and nitrate-nitrogen (NO₃-N) concentrations for three treatments over study period. Data shown are mean ± SD.

Treatment	SRP (mg/L)	NO ₃ -N (mg/L)
C	0.132±0.127	0.079±0.038
LM	0.099±0.046	0.105±0.100
HM	0.222±0.168	0.231±0.175

Total phosphorus (TP) concentrations showed trends similar to TSS: lower concentrations in C treatments (0.004-0.105 mg P/L) and initial increases for both mixing treatments, followed by decreases during settling periods (Figure 2. 3). For LM treatments, TP concentration was less than the initial value after 48 hours, while for HM treatments, TP concentrations exceeded initial concentration through the end of study (168 hours). HM disturbances substantially increased TP levels in the water column so much so that they required extended time to settle.

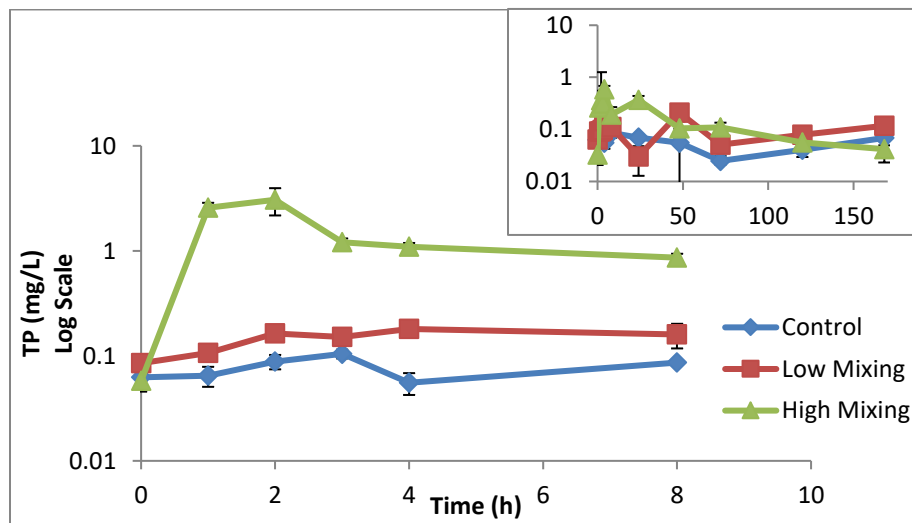


Figure 2. 3. Total Phosphorus (TP) of C, LM and HM treatments over study period. Data are mean ± SD. Original figure shows details of the first 8 hours of the study while insert figure shows entire 168-hour study. Y-axis are in log-scale.

Sediment P concentrations showed significant differences between initial Set-up (S), final C treatment (C), final LM treatment (LM) and final HM treatment (HM) ($p=0.010$). Compared to initial values, concentrations for all final treatments showed decreases in sediment P concentrations (Table 2. 2). However, the LM and HM treatments had greater changes (11.76% decrease for LM and 17.92% decrease for HM) compared to the C treatments with 6.62% decrease). These results indicate that mixing caused more P to be released from the sediment layer into the water column.

Table 2. 2. Initial and final sediment Total Phosphorus (TP) concentrations and percentage changes for different treatments. Data shown are means.

	Sediment P (mg/kg)	Change (%)
Initial Set-up (S)	32.22	---
Final C treatment (C)	30.09	-6.62
Final LM treatment (LM)	28.43	-11.76
Final HM treatment (HM)	26.45	-17.92

Relationship between mixing and TP

To identify the relationships between TP and TSS, linear correlations were applied for comparison on the data (Figure 2. 4). Both the LM and HM treatments had greater R values (0.5216 and 0.9290, correspondingly) than the C treatments ($R=0.0361$). These results agree with the study performed by Ding et al. (2018), who also found a positive correlation between TSS and TP and concluded that the sediment resuspension caused by mixing events could release P from sediment layer into the water column and accelerate nutrient cycling processes (Ding et al. 2018, Qin et al. 2004, Li et al. 2010).

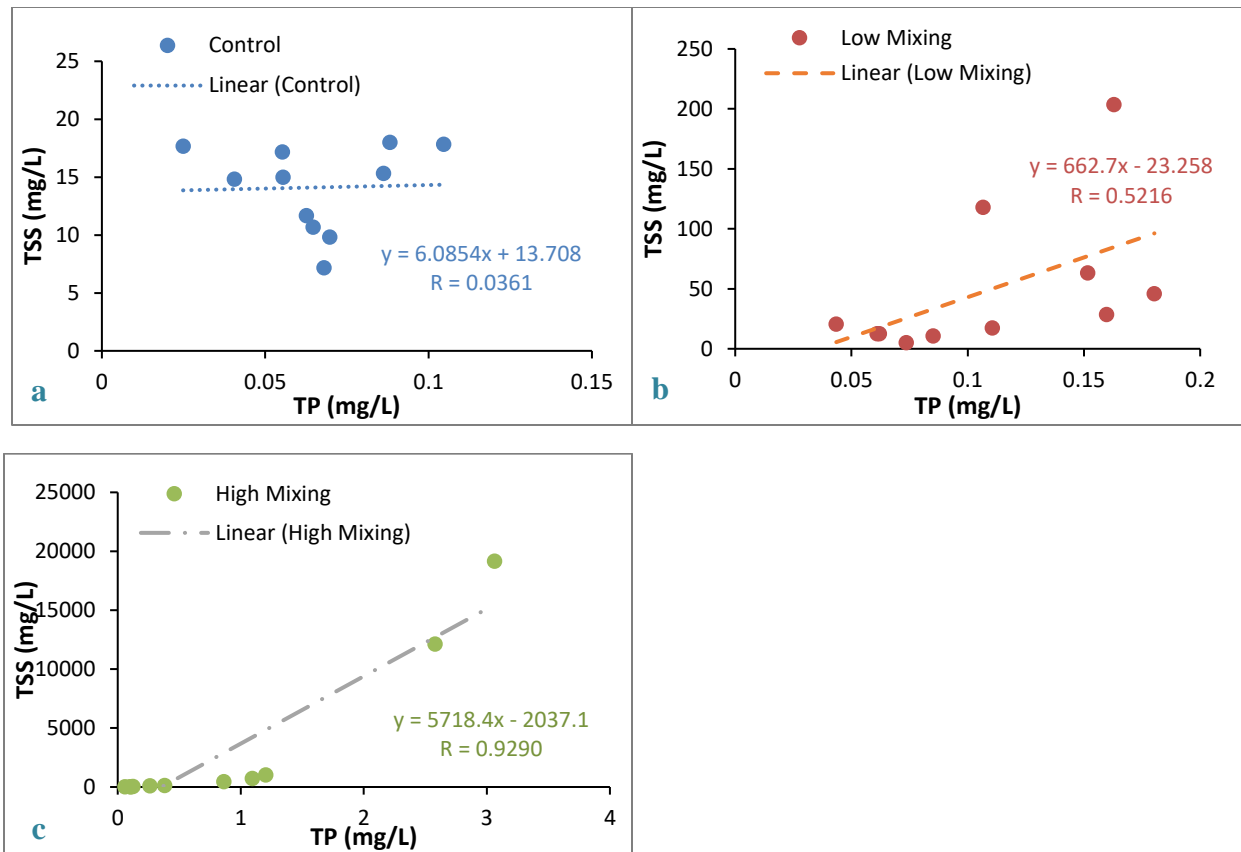


Figure 2. 4. Relationship between Total Phosphorus (TP) and Total Suspended Solids (TSS) of C (a), LM (b) and HM (c) treatments.

Although likely not readily available for biological use, over half of TP can be hydrolyzed into bioavailable organic P (Gao et al. 2006). TP release introduced by mixing events could compensate for the deficiency of nutrients necessary for algal growth and therefore lead to potential algal blooms (Ding et al. 2016, Ding et al. 2017, Ding et al. 2018). In order to control eutrophication and prevent harmful algal blooms, sediment resuspension should be monitored as strong resuspension could promote eutrophication. In this study, the 168 hours (7 days) study time was not long enough to observe the promotion of biomass growth after sediment resuspension and their corresponding P uptake. Therefore, in the future study, a longer study period would be recommended for this long-term monitoring of biomass activity promoted by P cycling processes caused by mixing events.

Changes in aqueous metals concentrations

Dissolved iron (Fe) and zinc (Zn), as well as both dissolved and total arsenic (As), cadmium (Cd) and lead (Pb) concentrations for all water samples were below the practical quantitation limits (PQL) of 0.0081, 0.006, 0.02, 0.0006 and 0.0195 mg/L, respectively. Dissolved manganese (Mn) and nickel (Ni) concentrations were detected between 0.001-0.652 mg/L and 0.008-0.015 mg/L, respectively (Figure 2. 5). For dissolved Mn concentrations, HM showed significant difference than C and LM treatments ($p < 0.0005$ for C vs HM and $p = 0.001$ for LM vs HM), which indicates that high mixing events could cause increased dissolved Mn concentrations while the subsequent settling could reduce the dissolved Mn. For dissolved Ni concentrations, all three treatments had significant differences among each other (all $p < 0.05$), and all treatments stayed relatively constant over time ($p = 0.995$).

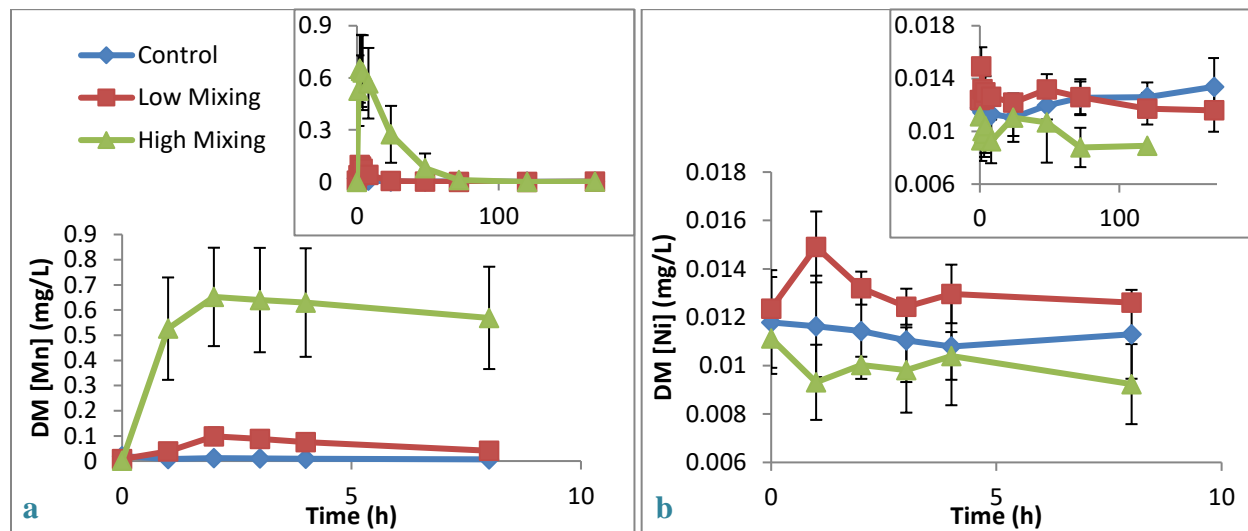


Figure 2. 5. Dissolved Mn (a) and Ni (b) concentrations for C, LM and HM treatments. Data are mean \pm SD. Missing points are due to the concentrations below practical quantification limit (PQL). Original figure shows details of the first 8 hours of the study while insert figure shows entire 168-hour study.

Dissolved metals concentrations were hardness-adjusted to indicate bioavailability and compared to the National Recommended Water Quality Criteria (NRWQC) established by US EPA (USEPA 2002). Results showed that dissolved concentrations over the entire study period were below both the Criterion Maximum Concentration (CMC, which estimates acute toxicity effects) and the Criterion Continuous Concentration (CCC which estimates chronic toxicity effects).

Total metal concentrations were shown in Figure 2. 6. Total Fe, Mn, Ni and Zn concentrations shared trends similar to TSS and TP. Concentrations in C treatments stayed relatively constant, and concentrations in LM and HM treatments increased during the mixing periods and decreased during settling periods. There was a significant difference among all three treatments for total Fe, Mn, Ni and Zn, with $p=0.012$, $p=0.009$, $p=0.001$ and $p=0.032$, respectively. Post-hoc tests also showed that for all these four dissolved metals, HM was significant from C and LM treatments with all $p<0.05$, indicating high mixing events caused greater metal release during resuspension. However, after 7-day of settlement, all HM treatments decreased to similar level as C and LM treatments, indicating the metals precipitated back to sediment with the settling suspended solids.

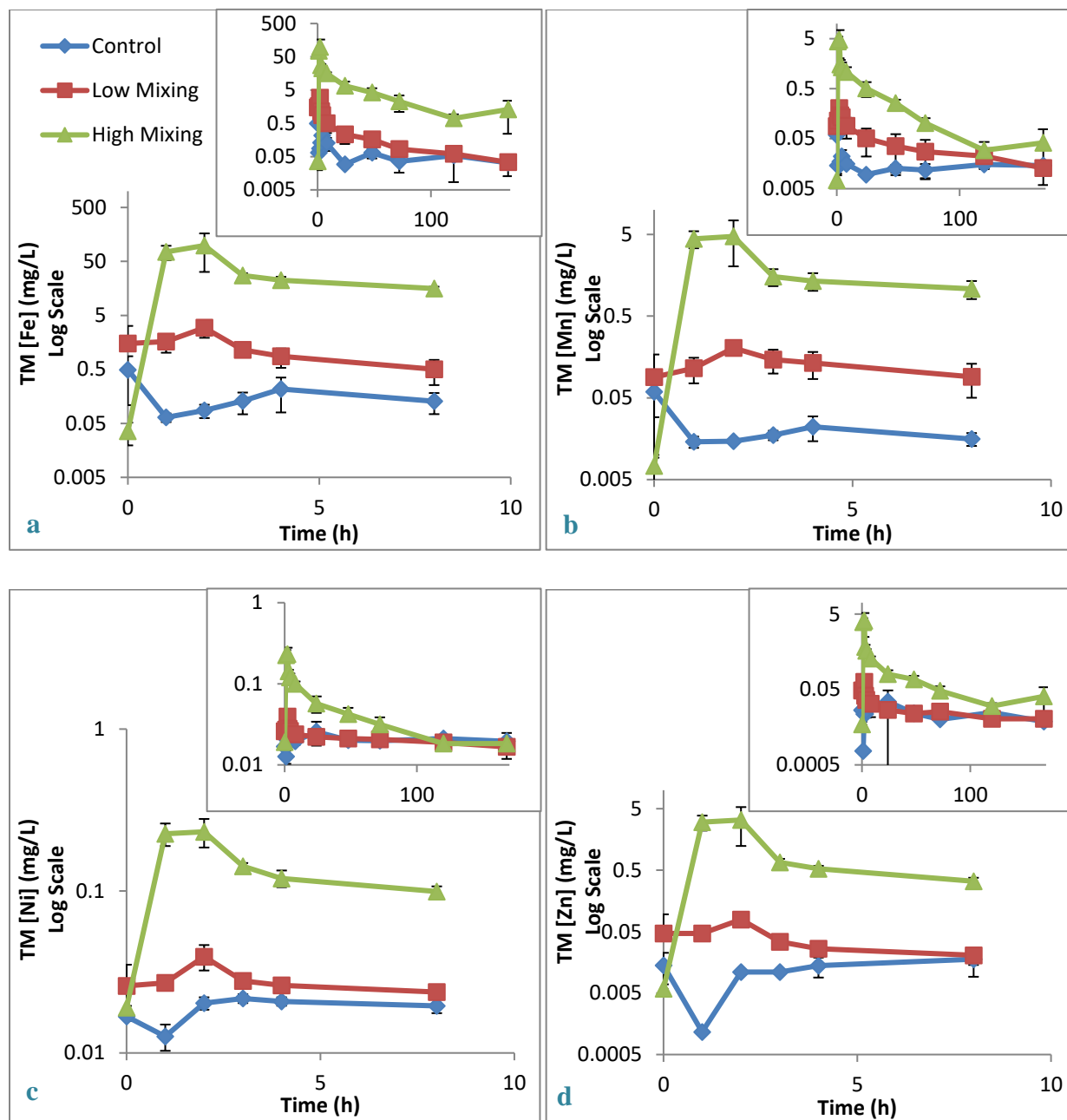


Figure 2. 6. Total Fe (a), Mn (b), Ni (c) and Zn (d) concentrations for C, LM and HM treatments. Data are mean \pm SD. Original figure shows details of the first 8 hours of the study while insert figure shows entire 168-hour study. Y-axis are in log-scale.

Changes in sediment metals concentrations

Sediment metal concentrations are shown in Table 2. 3. Final concentrations for all three treatments had greater concentrations than the initial conditions for all six metals (ANOVA, $p < 0.0005$). Comparing final concentrations, Mn, Cd and Zn showed percentage changes of $C < LM < HM$, indicating that greater mixing would likely result in lower water column concentrations. Ni and Pb showed percentage changes of $LM < C < HM$, indicating small disturbances could cause release of metals from the sediment to water column but that larger disturbances could result in transfer from water back to sediments. Only Fe had $LM < HM < C$, which indicated that mixing caused release of Fe from the sediment layer into the water column and smaller disturbances better facilitate this release.

Table 2. 3. Initial and final sediment metal concentrations and percentage changes for different treatments. Data shown are means.

Treatment		Mn	Ni	Cd	Fe	Pb	Zn
mg/kg							
Initial	S	346.1	9.14	2.39	10354	36.02	291.6
	C	453.0	12.25	3.07	13948	49.23	347.8
Final	LM	455.6	12.15	3.24	13523	48.83	364.4
	HM	486.0	12.81	3.52	13765	50.70	403.1
		Mn	Ni	Cd	Fe	Pb	Zn
% change							
C		30.91	34.00	28.55	34.71	36.68	19.25
LM		31.66	32.86	36.02	30.60	35.57	24.96
HM		40.43	40.11	47.58	32.94	40.77	38.23

Post hoc least significant difference (LSD) tests showed that initial sediment metals concentrations were significantly different ($p < 0.0005$) from all final C, LM and HM treatments. Comparing among final values, HM treatments were significantly different from C treatments for Mn ($p = 0.034$), Cd ($p = 0.001$) and Zn ($p = 0.006$) and also significantly different from LM treatments for Mn ($p = 0.047$), Ni ($p = 0.037$), Cd ($p = 0.021$) and Zn ($p = 0.034$), while C and LM treatments shared no significant differences (all $p > 0.05$).

Sediment metal concentrations were compared to Tri-State Mining District (TSMD) specific Sediment Quality Guidelines (SQGs) (Ingersoll et al. 2009) (Table 2. 4). These SQGs were Probable Effects Concentrations (PECs), above which harmful effects on sediment-dwelling organisms were expected to occur frequently (Ingersoll et al. 2009, MacDonald et al. 2000). Results showed none of the treatments exceeded the TSMD PECs, which indicated no trace metal contamination in sediments before and after mixing.

Table 2. 4. Sediment metal concentration ranges compared to SQGs.

	TSMD PEC (mg/kg)	Initial range of concentrations (mg/kg)	Final range of concentrations (mg/kg)
Zn	2083	272.4-327.6	331.8-434.8
Cd	11.1	2.31-2.46	2.96-3.75
Pb	150	33.7-37.2	46.8-52.3

Relationship between mixing and metals

For total metal concentrations, compared to C treatments, which stayed relatively consistent over the entire study period, both LM and HM treatments showed increasing Fe, Mn, Ni and Zn during mixing periods and subsequent decreases during settling periods. Also, all final sediment metal concentrations were greater than initial values, indicating metal sequestration from the water column into the sediment layer. During mixing, metals buried in the deeper sediment might have been released into water column and later removed into the surface sediment layer. It should be noted that in this study, sediment samples were only collected from the sediment layer surface, therefore, in the future study, sediment samples at various depths could be collected to further identify the transportation of metals between water column and multiple sediment layers during the sediment resuspension processes. Resuspension of sediments may help to remove trace metals from the water column via two proposed processes. First, during resuspension, more fine particles were present in the water column, serving as available sorption sites for both nutrients and metals, and settling to the sediment layer once disturbance ceases (Ding et al. 2018). The second process could be that greater DO was introduced into the water during the mixing period, which may have provided additional oxidation to increase the trace metals adsorption capacity of the suspended sediments which used to be buried deep in anaerobic conditions (Qin et al. 2004, Zhu et al. 2005).

Conclusions

For this study, mixing resulted in the redistribution of P between the water column and the sediment layer and trace metals were removed from the water column into the sediment layer. Final sediments showed decreased P and increased metal concentrations compared to initial set-up values. The presence of algal growth in all treatments during the entire study provided the

potential for biomass to break down metal-P couplings, transform bioavailable P into non-bioavailable P, and allow released trace metals to precipitate to the sediment layer. Compared to C treatments, LM and HM treatments showed significant differences in TP and metals concentrations. Based on the NRWQC, all aqueous metal concentrations for all treatments were below both the CCC and CMC, and based on the SQGs, sediment metals concentrations were below TSMD PECs, which showed mixing not causing trace metal contamination to both water column and sediment layer. Overall, resuspension caused by mixing and subsequent settling helps to release sediment P into the water column and precipitate aqueous trace metals to the sediment layer.

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Chapter Three: The Role of Mine Drainage Residual Addition on Nutrient and Trace Metal Release in Microcosms with Biomass Growth and Decay

This chapter has been formatted for submission to Water, Air, & Soil Pollution.

Abstract

A green house microcosm study investigated the impacts of recovered iron oxyhydroxide mine drainage residuals (MDRs) on phosphorous (P) and trace metal distribution at the sediment layer and water column interface. Each mesocosm included 5 kg of lake sediment and 20 L on-site groundwater. Three treatments were examined with triplicate: Control (C) with no addition; Low MDR (LM) with 0.3 kg MDR; High MDR (HM) with 0.9 kg MDR. During the first 10 days, soluble reactive phosphorous (SRP) and total phosphorous (TP) showed decreasing trends due to uptake by biomass with no significant differences among three treatments. After 75 days, biomass died in all three treatments, P concentrations went down in LM and HM treatments due to MDR sorption, while C treatments showed a P release from dead biomass death and decay. Comparing trace metal concentrations in the water column to the USEPA National Recommended Water Quality Criteria, all samples were below both the hardness-adjusted acute and chronic criteria, except for Pb with regard to the chronic criterion. Compared to site-specific Sediment Quality Guidelines (SQGs), all sediment samples were below Tri-State Mining District (TSMD) specific SQGs.

Introduction

Excess nutrient inputs into water systems have raised concerns about eutrophication and resulting harmful algal blooms (Sibrell et al. 2009, Ho et al. 2019). Phosphorus (P), the common limiting nutrient in freshwater systems, often enters lakes and reservoirs via two distinct loading sources: external and internal (Chen et al. 2018, Perkins and Underwood 2001). External loading mainly includes inputs from flowing waters such as natural rivers and streams, surface run-off and precipitation, while internal loading refers to release from the P sink in sediments (Jin et al. 2006, Nikolai and Dzialowski 2014, Perkins and Underwood 2001). Therefore, eutrophication concerns are often managed by decreasing external P loading by watershed best management practices (Yang et al. 2014) or water treatment (Sibrell and Tucker 2012), while internal sources are often addressed by dredging and removal of P-rich sediment (Yu et al. 2017).

Phosphorus sorbing materials (PSMs) have been investigated to decrease external P loading and control internal P release. Generally, PSMs can be divided into two categories: calcium (Ca) and/or magnesium (Mg) based materials for precipitation of P and iron (Fe) and/or aluminum (Al) based materials for adsorption (Christianson et al. 2017, Penn et al. 2007). Fe/Al salts such as alum (aluminum sulfate) and ferric sulfate have been applied in municipal and industrial wastewater treatment, but the cost of using commercial products for P removal in lakes and reservoirs can be quite expensive (Penn et al. 2007, Sibrell et al. 2009, Sibrell and Tucker 2012). Therefore, a need exists to develop cost-efficient PSMs and corresponding methods to apply them.

Several studies have been conducted to evaluate P removal efficiencies of different industrial waste products including steelmaking slags, fly ash, wood ash, drinking water treatment residues, paper mill sludge, sander dust, mag dust (waste products from building practices, composed mainly of calcium oxide and silicon dioxide) and waste gypsum, all of which demonstrated P removal

potential, but widespread application is restricted by local availability and transportation costs (Drizo et al. 2006, O'Reilly and Sims 1995, Penn et al. 2007, Sibrell et al. 2009, Spears et al. 2013).

Iron and aluminum oxides generated from water treatment at mining sites, known as mine drainage residuals (MDRs), have become another option due to their wide availability (Spears et al. 2013).

Acid mine drainage (AMD) often occurs at abandoned coal and metal mines. Exposure of sulfide minerals (e.g., pyrite, FeS_2) to water and air, which introduces oxygen, results in oxidation reactions producing sulfuric acid and dissolved metal species. Other metals in host rock and adjacent strata (e.g., aluminum (Al), manganese (Mn), zinc (Zn), and lead (Pb)) may dissolve and be released (Stumm and Morgan 1996, Sibrell et al. 2009). Therefore, AMD can cause low pH and elevated ecotoxic trace metal concentrations in receiving water bodies. To sustainably treat AMD without constant chemical and energy inputs, an economical approach including a sequence of ecologically engineered process units has been developed—passive treatment (Hedin et al. 1994, Watzlaf et al. 2004, Hedin 2008, Nairn et al 2009). Passive treatment systems improve water quality by acid neutralization, metal retention and alkalinity generation (Oxenford 2017). The oxidation ponds and wetlands of these systems produce MDRs rich in iron oxyhydroxides (Hedin 2008, Sibrell et al. 2009).

Sibrell et al. (2009) processed MDRs from six different coal mine drainage sites in PA, composed primarily of Fe and Al oxyhydroxides, with minor amounts of gypsum and unreacted calcite MDRs. After drying and palletization, they performed phosphorus adsorption capacity (PAC) tests which achieved as high as 20,000 mg/kg MDR. Their column tests also showed rapid sorption with 60-90% P removal within the first five minutes of contact time. Stripping tests with 76% P removed showed that this P-sorbing material can be regenerated in the long term. Wei et al. (2008) performed batch studies with MDR treating secondary wastewater effluents and built Freundlich

isotherm sorption models to estimate the PAC range based on different effluent concentrations. They concluded over 98% P removal efficiency and no appreciable trace metal leaching over a typical pH range of 6-8. The study carried out by Han et al. (2005), instead of direct use of MDRs, used modified lignocellulosic fibers with surface-precipitated AMD materials to remove at least 40% of P from water with a 59 mg/L influent P concentration. Their study showed that the sorption capacity of such modified fibers was higher than other conventional adsorbents and a pseudo second-order kinetic model fitted well for sorption of P onto the modified media. Heal et al. (2005) tested the P removal performance of MDR in waste water in both laboratory experiments, which achieved a 90% P removal rate, and field investigations where MDR added into a constructed horizontal flow wetland achieved a mean P removal efficiency of $27 \pm 28\%$ during a 15 month monitoring period. They found that hydraulic design was key to high P removal as they noticed short-circuiting flow limited the full P removal capacity of the MDR. Followed up with the previous study, Dobbie et al. (2009) conducted two long-term field studies (three years and nine months) and concluded that MDR treatment systems had considerable potential to remove P with a lifetime estimated to be ten times longer than other tested substrates, with no observed toxic metals releases.

Most of the MDR P-removal studies were based on wastewater with much higher levels (often around 10 mg/L) than eutrophic lake water. Therefore, the high sorption performance achieved at such elevated P levels may not apply to eutrophic natural water conditions (around 1 mg/L). Most of the cited studies were performed in flow through columns, batches and experimental wetlands; very little research has been done on direct application of MDR in lakes and reservoirs. Trace metal leaching examinations mainly focused on the water column without much investigation into the sediment layer. This study aimed to estimate the MDR-enhanced P removal performance at

natural water concentrations, evaluate trace metal changes in the water column and sediment layer and potentially provide P control guidelines for lake and reservoir management.

Material and methods

Study site description

Grand Lake o' the Cherokees (GLOC) is a large eutrophic multipurpose reservoir (surface area approximately 19,000 ha) which experiences seasonal algal blooms (Morrison et al. 2017). Historically, P has been an important excess nutrient in this watershed, and internal P loading contributes to seasonal changes in TN:TP ratios such that limiting nutrients change (Nikolai and Dzialowski 2014).

Background water quality and sediment samples were collected in GLOC at Sycamore Flats (36°44'44.2''N, 94°44'9.6''W, water depth = 1.1 m). Water samples were collected using a depth-discrete horizontal water sampler just above the sediment layer-water column interface and lake sediments were collected using a Ponar dredge. After collection, all samples were stored and transported in coolers filled with ice at 4°C before delivery to the University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) laboratories.

Phosphate sorbing material: Mine Drainage Residuals

The headwaters of GLOC are located approximately 33 km downstream (via Tar Creek and the Neosho River) from the center of the Tar Creek Superfund Site, the northeast Oklahoma portion of the now derelict Tri-State Lead-Zinc Mining District (TSMD) (Figure 3. 1). Currently, four National Priority List (NPL) Superfund Sites are located in TSMD, besides Tar Creek, there are the Cherokee County Superfund Site in southeast Kansas and two other superfund sites in Jasper

and Newton Counties in southwest Missouri (Garvin et al. 2017). The entire TSMD drains to GLOC through the Neosho and Spring Rivers.

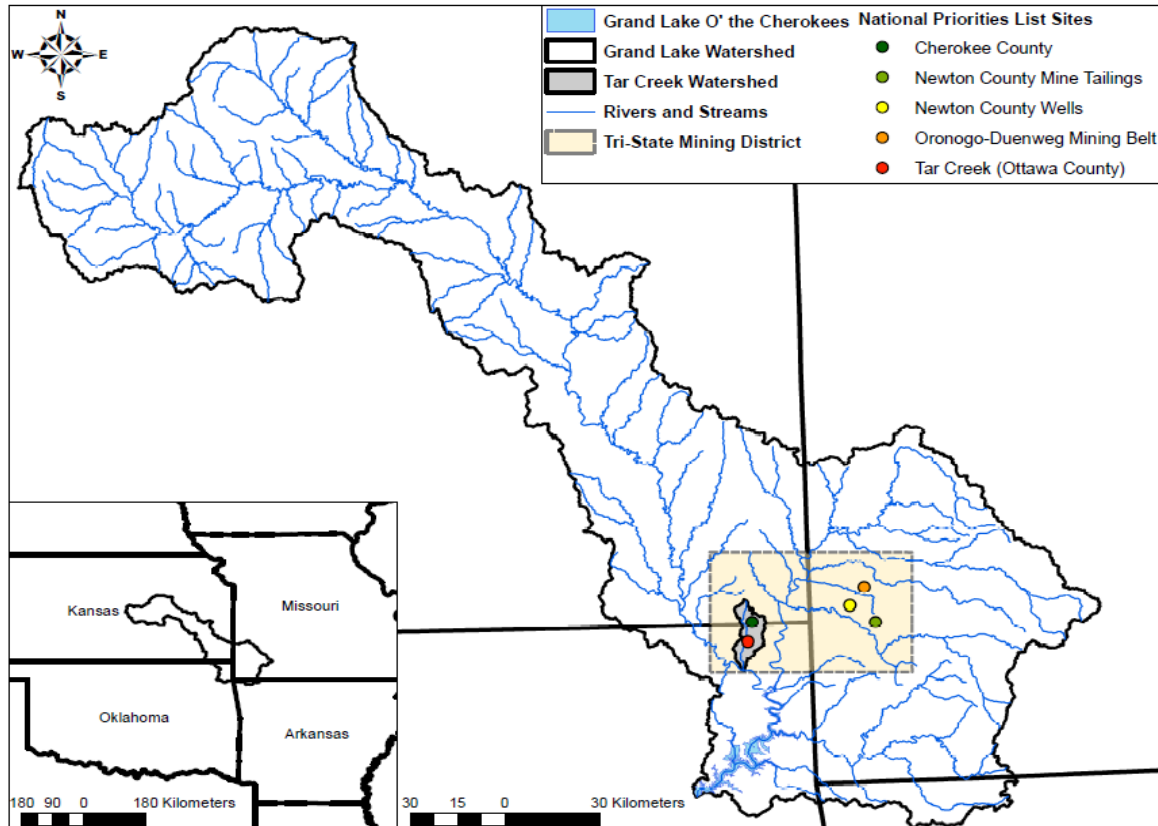


Figure 3. 1. Location of GLOC watershed and its surrounding major river basins and NPL Superfund Sites

At the Tar Creek Superfund Site, the Mayer Ranch passive treatment system (MRPTS) has received artesian flows of net alkaline mine water since late 2008. Iron is successfully retained in the oxidative process units (including an oxidation pond and two surface flow wetland units) and 99% overall iron removal is achieved, from 175 ± 25 to 0.65 ± 0.98 mg Fe/L (n = 184). Approximately 57,000 kg iron is retained annually (Oxenford 2016, Nairn et al. 2018). MDR used in this study was collected in the MRPTS oxidation pond with characterization listed in Table 3. 1 (Oxenford 2016).

Table 3. 1. Characterization of MDR collected from MRPTS oxidation pond (Oxenford 2016)

Crystallinity (%)	Mean particle size (µm)	D60/D10	Specific Surface Area (m ² /g)	Color	Organic Content (%)	Mineral phase
17.4	11.7	14.3	244	Yellowish Red	4.3	Goethite

Microcosm set-up

Green house microcosms were set-up at the University of Oklahoma Aquatic Research Facility using 25-L vessels with 5 wet kg lake sediment and 20 L ground water. To avoid long-distance transport of lake water on site ground water was used and periodic sampling showed the quality to be similar to lake water. Three treatments were established in this study: control (C) with only lake sediment and ground water; low MDR addition (LM) with lake sediment, ground water and low dose of 0.3 kg dry MDR addition; and high MDR addition (HM) with lake sediment, ground water and high dose of 0.9 kg dry MDR addition. The ratios of 1:10 and 3:10 MDR to lake sediment (dry weight:dry weight) was selected based on previous preliminary studies. MDR was added on top of the lake sediment layer without mixing to imitate the future application of dosing MDR into eutrophic lakes.

Each treatment included triplicates, which resulted in a total of nine experimental vessels. After set-up, all vessels were allowed to settle and equilibrate for two days before the first set of sample collections.

Sampling process and chemical analysis

Water samples were collected at Days 0, 1, 2, 4, 6, 8, 10 (short-term) and Day 40, 75, 102 and 138 (long-term). Samples were taken at 10 cm above the sediment layer and water column interface

using a siphoning technique. All samples were analyzed for total phosphorus (TP) and soluble reactive phosphorus (SRP) using the ascorbic acid method (EPA Method 365.3) as well as nitrate-nitrogen ($\text{NO}_3\text{-N}$) using the brucine method (EPA Method 352.1). Although no biomass was added into any treatments, algal biomass blooms and decay were observed during the study, therefore chlorophyll-a (Chl-a) was analyzed using a hot-ethanol extraction method (Chen et al. 2006), in which the water samples were filtered with Whatman glass microfiber filters (GF/F) and extracted with 90% ethanol in an 85°C water bath for 2 minutes and at room temperature for 5 hours, then measured by a Cole-Parmer SQ2800 UV/visible spectrometer at 665 and 750 nm. Total metals (TM) and dissolved metals (DM) samples first underwent microwave hot HNO_3 digestion (EPA Method 3015 using a CEM MARS Xpress Digestion System) and were analyzed via Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (EPA Method 6010) using a Varian Vista-Pro simultaneous axial ICP-OES for a suite of trace metals: silver (Ag), aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), silicon (Si) and zinc (Zn). A YSI 600QS multiparameter datasonde coupled with a YSI 650 display were used to collect and record basic water quality data including pH, pH mV, water temperature (Temp), Resistivity, Salinity, Specific Conductance, Conductivity, Total Dissolved solids (TDS), dissolved oxygen (DO) (in mg/L and % air saturation) and oxidation-reduction potential (ORP), immediately after each water sample collection event. Supplemental ground water was added to the vessels to replenish loss of water due to sampling and evaporation. Samples of any supplemental ground water were collected and analyzed.

Sediment and MDR samples were collected at the initial stage (before set-up) and final stage (after last set of water sample collections) of the study and measured gravimetrically for moisture content

(MC) and organic content (OC) through American Society for Testing and Materials methods (ASTM D2974). Sediment P was extracted with ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA) (Kuo 1996), which represented the P fraction bound to Fe, Al and Mn oxides and hydroxides and was analyzed following EPA Method 365.3 (SSSA 1996). Sediment samples for metals analyses underwent microwave hot HNO₃ digestion (EPA Method 3051) and then were analyzed via ICP-OES (EPA Method 6010), similar to water samples.

Statistical analysis

Statistical significance of differences analyses was performed with one-way analysis of variance (ANOVA) using SPSS 24.0 software. A p-value < 0.05 level was considered significant. When differences between treatments were significant, least significant difference (LSD) tests were performed as a post-hoc study. Variations in results were reported in terms of standard deviations (\pm SD).

Results and discussion

Basic water quality parameters and Chl-a

No biomass growth was observed at the set-up stage of the study and no algal biomass was added into treatments during the entire study period. However, algal biomass blooms and decay were observed during the study. Over the study period, water temperatures ranged from 21.3 to 27.2° C with no significant differences among the three treatments ($p=0.934$), but significant initial decreasing and later increasing trends over time ($p<0.0005$). pH ranged between 6.9-7.7 during the first 8 days and 8.2-10.0 from Day 10 to Day 138 with no significant differences among

treatments ($p=0.974$) and significant increasing trends over time ($p<0.0005$). ORP ranged between 189-242 mV during the first 8 days and 32-234 mV from Day 10 to Day 138 with no significant differences among treatments ($p=0.923$) but significant decreasing trends over time ($p<0.0005$).

DO concentration, ranged between 7.0-27.6 mg/L (Figure C 1), showed no significant differences among treatments ($p=0.660$), and a significant increasing trend over the first 4-6 days followed by a decreasing trend until Day 138 ($p<0.0005$). During the first 6 days, the time to peak DO concentration appeared to be delayed by greater MDR addition (C<LM<HM) which indicated DO concentrations may have been suppressed by MDR additions.

Chl-a concentrations, ranged between 1.4-121.8 $\mu\text{g/L}$ (Figure C 2), showed no significant differences among treatments ($p=0.976$), and no significant trends over time ($p=0.080$). MDR addition treatments had lesser peak Chl-a concentration (LM) or both lesser peak Chl-a concentration and delayed peak over time (HM), which indicated the MDR addition may have inhibited initial algal biomass growth.

Nutrient concentrations in water and sediment

$\text{NO}_3\text{-N}$ concentrations ranged from 1.36 to 0.02 mg/L with no significant differences among three treatments ($p=0.714$) and significant decreasing trends over time ($p<0.0005$). SRP concentrations ranged from 0.001 to 0.678 mg/L (Figure 3. 2. a), and TP concentration ranged from 0.018 to 0.525 mg/L (Figure 3. 2. b). Smaller figures were inserted to the upper right corner, showing the entire 138-day study period, while the original larger figures showed details for the first 10 days of the study. The insert figures share the same x-axis and y-axis units as the original figures. From Day 0 to Day 75, both SRP and TP showed no significant differences among three treatments ($p=0.876$ and $p=0.137$, respectively), but significant decreases over time (both $p<0.0005$). This indicated

that during the initial biomass growth period, added MDR did not result in significant water column P concentration changes compared to C treatments. However, from Day 75 to Day 138, both SRP and TP showed significant differences among the three treatments ($p=0.003$ and $p=0.001$, respectively), with C treatments showing significant increases in both SRP and TP ($p=0.010$ and $p=0.014$, respectively) while LM and HM treatments showed no significant changes in both SRP and TP ($p=0.127$ and $p=0.759$ for LM, $p=0.208$ and $p=0.123$ for HM, respectively). This indicated that during the biomass decay period, while the LM and HM treatments had relatively constant SRP and TP concentrations, C treatments showed increasing SRP and TP concentrations, which indicates that added MDR sorbed P released from dead and decomposing biomass before it was released into the water column.

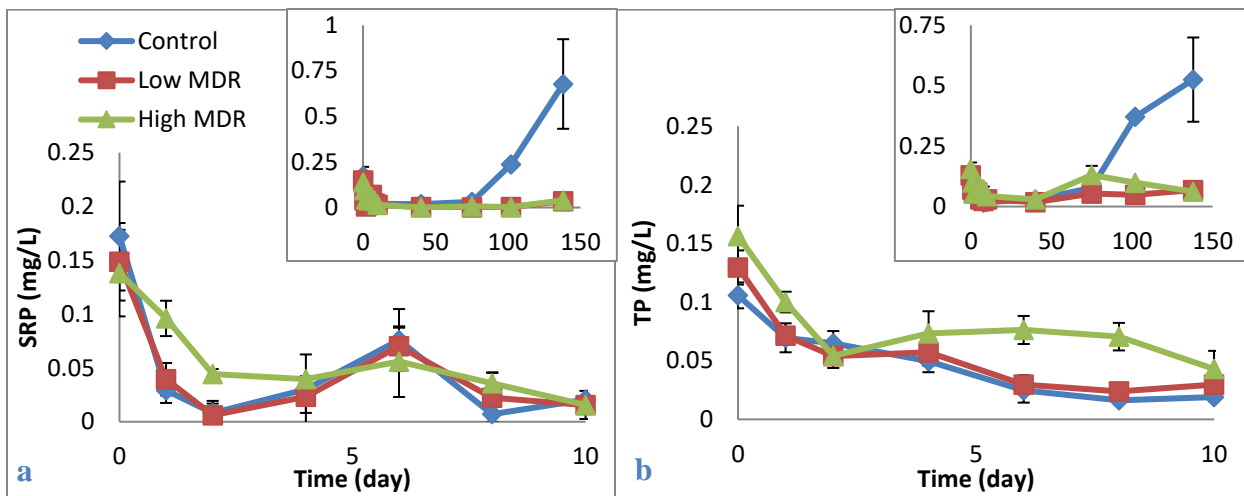


Figure 3. 2. Soluble Reactive Phosphorus (SRP) (a) and Total Phosphorus (TP) (b) concentrations of three treatments over the study time. Data are mean \pm SD. Original figure shows details of the first 10 days of the study while insert figure shows entire 138-day study period.

It had been noticed that for some sampling events, SRP concentrations were greater than TP concentrations, likely due to leakage of SRP from damaged biomass cells during filtering processes. Tarapchek et al. (1982) also observed SRP release from fragile biotic and abiotic

particulate materials during filtration processes. In this study, filtrate from Chl-a determinations was used for SRP analyses and high vacuum pressures in the filtering system may have resulted in release of P into the filtrate.

Sediment P concentrations for lake sediments and MDRs were compared between the initial and final stages (Table 3. 2). P concentrations in lake sediments showed no significant difference among the four groups including initial set up conditions ($p=0.356$) and the LSD post-hoc tests showed no treatment was different from the other ($p>0.05$). P concentrations in MDRs showed significant differences among the three groups ($p=0.001$) and the LSD post-hoc tests also showed treatments were different, except between LMDR and HMDR ($p<0.0005$ for all, except $p=0.919$ for LMDR vs HMDR).

Table 3. 2. Initial and final sediment phosphorus concentrations and percentage changes for different treatments. Data shown are means.

		P concentration (mg/kg)	Change (%)
Initial	Set-up Sediment (SS)	32.55	NA
	Set-up MDR (SMDR)	2.52	NA
Control sediment (CS)		33.56	3.09
Final	Low MDR addition sediment (LMS)	32.19	-1.12
	High MDR addition sediment (HMS)	37.53	15.28
	Low MDR addition MDR (LMDR)	25.18	899
	High MDR addition MDR (HMDR)	24.84	885

Before set-up, the initial lake sediment (SS) had around 12 times greater P concentration than the MDR (SMDR). By the end of the 138-day study, P concentrations in the lake sediments were all around 33 mg/kg, with 3.09%, -1.12% and 15.28% change, respectively. However, P concentrations in the final MDRs increased from 2.52 to around 25 mg/kg, which were 10 times greater. The increased final P concentrations in MDRs indicate that added MDR sorbed P from this system.

Change of P mass in the three components of the study system (water column, sediment layer and MDR layer, if applicable) were compared for all nine vessels (Table 3. 3). It must be noted that the water P masses were calculated based on the SRP concentrations (due to previously identified problems), while sediment P and MDR P masses were calculated based on the AB-DTPA extracted P. Therefore, a mass balance was not applicable on these data. Compared to C, both LM and HM showed decreased water P mass and increased MDR P mass, demonstrating that added MDR arrested P release into the water column. Also, HM treatments had greater increases in total P mass, which indicated the added MDR served as a P sink in this system.

Table 3. 3. Change of P mass in three components of each vessel before and after the 138-day study period.

	Change of water P (mg)	Change of MDR P (mg)	Change of sediment P (mg)	Change of total P (mg)
C1	3.84	NA	20.93	24.78
C2	13.61	NA	5.89	19.50
C3	15.68	NA	-17.76	-2.08
LM1	-2.27	5.58	4.99	8.30
LM2	-1.65	7.78	-6.30	-0.16
LM3	-1.08	7.03	-1.98	3.97
HM1	-0.83	19.05	21.32	39.54
HM2	-1.34	25.65	16.57	40.87
HM3	-2.17	15.55	6.90	20.28

Metal concentrations in water and sediment

For all dissolved metals (DM) samples, Fe, As and Cd concentrations were below the practical quantitation limits (PQLs) of 0.003 mg/L, 0.02 mg/L and 0.0006 mg/L, respectively. Compared to hardness adjusted National Recommended Water Quality Criteria (NRWQC) (U.S.EPA 2014), dissolved metal concentrations were below both the acute Criterion Maximum Concentration (CMC) and the chronic Criterion Continuous Concentration (CCC), except for Pb with regard to the CCC. Also, compared to National Secondary Drinking Water Regulations (NSDWRs) (U.S.EPA 2008), dissolved metals concentrations were below Secondary Maximum Contaminant

Levels (SMCLs) for Fe, Mn and Zn, which were 0.3 mg/L, 0.05 mg/L and 5 mg/L, respectively. That is to say, compared to C, both LM and HM treatments did not cause excess trace metals release. The majority of trace metal concentrations were below relevant criteria, therefore, concerns about trace metal contamination to the water column from added MDRs were likely minimal, which was also supported by the study by Sibrell et al. (2009).

For total metals (TM) concentrations, As and Cd concentrations for all samples were below the practical quantitation limit (PQL) of 0.02 mg/L and 0.0006 mg/L, respectively. Measurable concentrations of Fe, Ni, Pb and Zn concentrations were plotted over time (Figure 3. 3). For Ni and Zn, there were no significant differences among the three treatments ($p=0.893$ and $p=0.865$, respectively), but significant decreasing trends over time ($p<0.0005$ and $p<0.0005$, respectively). For Fe and Pb, there were no significant trends over time ($p=0.609$ and $p=0.838$, respectively), but significant differences among the three treatments ($p=0.020$ and $p<0.0005$, respectively). LSD post-hoc tests showed C treatments were significantly different from HM ($p=0.006$) for Fe and different from LM and HM ($p=0.001$ and $p<0.0005$, respectively) for Pb. It should be pointed out that metals data were not collected on Day 102 and Day 138, due to the observed relatively constant concentrations.

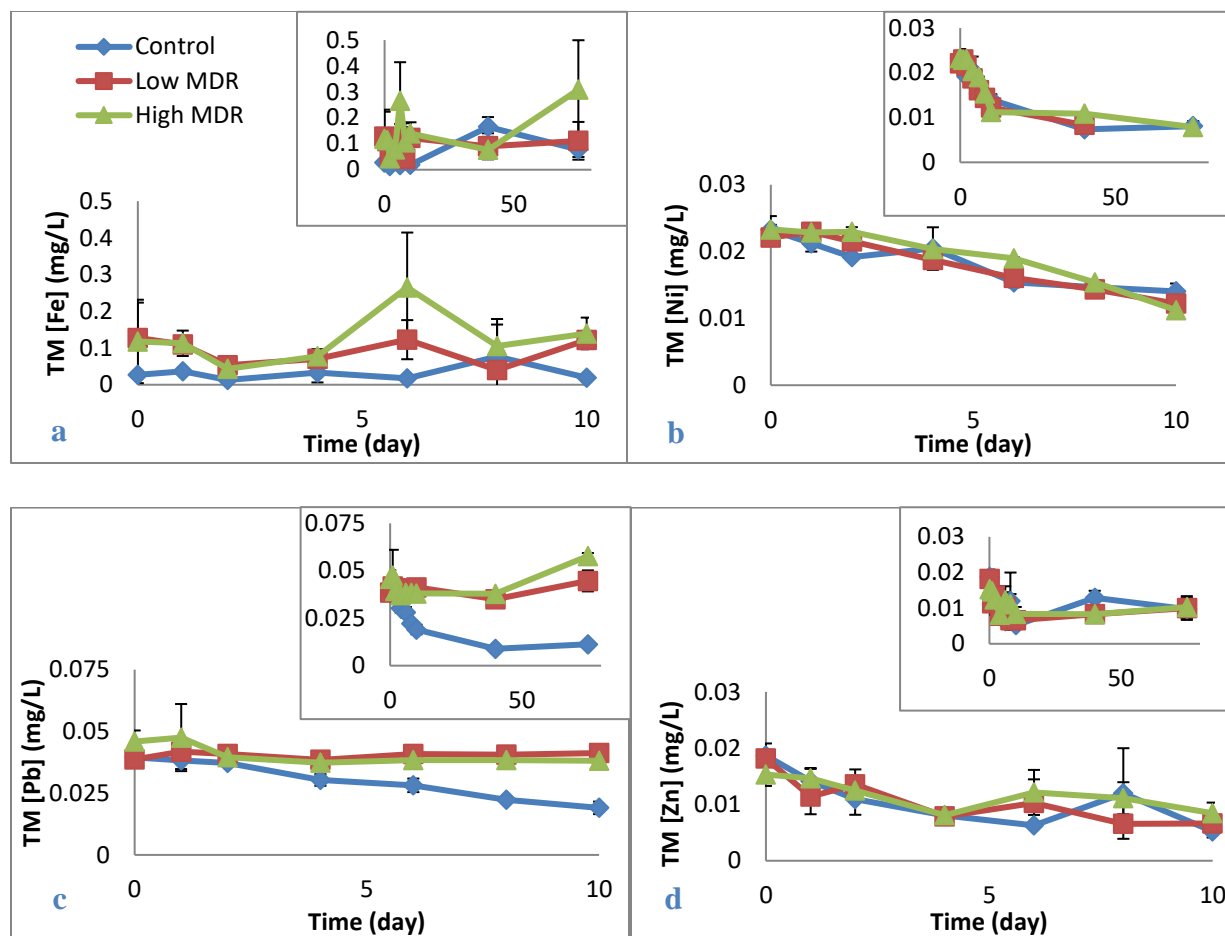


Figure 3. 3. Total Metal (TM) concentrations for Fe (a), Ni (b), Pb (c) and Zn (d) of three treatments over the study time. Data are mean \pm SD. Original figure shows details of the first 10 days of the study while insert figure shows first 75 days of the study.

During the first 10 days, HM showed a peak total Fe concentration at Day 6, and all total Fe concentrations for LM and HM were above C, except for LM at Day 8, indicating that MDR addition treatments, not surprisingly, resulted in increased Fe concentrations. HM treatments also showed increased TP concentrations during the first 10 days, indicating that biomass might interfere with metal-nutrient relationships by breaking Fe-P bonds and causing Fe and P release into the water column. During the later biomass decay period, a decrease of total Fe concentration was seen after Day 40 for C, but increases were realized for LM and HM. Control treatments

showed increasing P concentrations after Day 40, while LM and HM treatments stayed relatively constant. These data indicated that settled dead biomass may promote formation of Fe-P couples and LM and HM treatments with abundant Fe-binding sites captured released P from biomass decomposition, while C treatments did not provide enough iron material for P sorption and showed elevated P levels in the water column. Perkins and Underwood (2001) found Chl-a to be significantly correlated to Fe-bound P in the water column, which indicates the link between algal biomass and available P from internal loading sources. Wang et al. (2019) also observed that settled cyanobacteria/organic matter promoted the formation of Fe-P binding and enhanced the sediment P sink. These authors concluded that an effective future bloom control method was to remove the current bloom biomass and dredge P-rich sediments, a costly endeavor.

Regarding Pb concentrations, compared to C treatments which showed decreasing trends, LM and HM treatments stayed relatively consistent with greater total Pb concentrations at the end of study, which meant MDR addition may have caused some level of trace metal release. For Ni and Zn, all treatments showed decreasing trends over time, which may be attributed to absorption from biomass growth and adsorption on the dead biomass materials (Fielding 2017).

Sediment metal concentrations, for both lake sediments and MDR, were compared between initial and final stages (Table 3. 4). For lake sediment, there were significant differences among the four groups for As, Mn, Ni, Cd, Fe, Pb and Zn ($p < 0.0005$, $p = 0.001$, $p = 0.002$, $p = 0.028$, $p = 0.010$, $p = 0.001$, $p = 0.002$, respectively), and LSD post-hoc tests also showed S and C treatments were significantly different from LM and HM treatments ($p < 0.05$) for all metals. For MDR, there was no significant difference among the three groups for all studied metals, except for Mn ($p = 0.004$), and LSD post-hoc tests which showed every treatment was different from the others for Mn ($p = 0.001$ for SMDR vs LMDR, $p = 0.049$ for SMDR vs HMDR, $p = 0.017$ for LMDR vs HMDR).

Table 3. 4. Initial and final metal concentrations in sediments and MDR and percentage changes for different treatments. Data shown are means. (SS = Set-up Sediment, SMDR = Set-up MDR, CS = Control Sediment, LMS = Low MDR addition Sediment, HMS = High MDR addition Sediment, LMDR = Low MDR addition MDR, HMDR = High MDR addition MDR.)

Treatment		As	Mn	Ni	Cd	Fe	Pb	Zn
mg/kg								
Initial	SS	4.40	537.2	11.5	3.50	13758	51.0	390.5
	SMDR	382.7	280.3	285.6	58.5	483228	803.7	10119
Final	CS	4.40	487.4	12.1	3.40	14123	53.2	407.3
	LMS	15.2	400.6	25.2	5.60	31063	84.4	781.9
	HMS	22.4	359.3	27.4	6.20	35175	86.5	780.8
	LMDR	368.4	747.5	296.2	52.6	434621	783.7	9610
	HMDR	377.7	480.7	287.0	58.2	478393	815.6	9447
		As	Mn	Ni	Cd	Fe	Pb	Zn
% change								
	CS	0.99	-9.26	5.18	-2.77	2.66	4.26	4.30
	LMS	246.83	-25.41	118.39	58.38	125.78	65.28	100.22
	HMS	410.67	-33.11	138.12	76.35	155.67	69.43	99.94
	LMDR	-3.73	166.67	3.74	-10.04	-10.06	-2.50	-5.03
	HMDR	-1.29	71.48	0.51	-0.47	-1.00	1.47	-6.64

At the initial set-up, As, Ni, Cd, Fe, Pb and Zn concentrations were greater but Mn concentration were lesser in MDRs than in lake sediments. Elevated trace metal concentrations in LM and HM

sediments were due to contact with MDRs as the corresponding concentrations in LMDR and HMDR all slightly decreased in final samples. Mn appeared to be exported from lake sediment to MDRs, as increases were seen in LMDR and HMDR, with decreases in C, LM and HM. These metal concentrations changes between lake sediments and MDRs were likely due to both ion exchange and likely inevitable contamination at final solid sample collection, meaning some MDR mixed into lake sediment samples and vice versa.

Sediment metal concentrations were compared to the Sediment Quality Guidelines (SQGs) specific to the TSMD (Ingersoll et al. 2009). Table 3. 5 lists metals concentrations compared to Probable Effects Concentrations (PECs), above which harmful effects on sediment-dwelling organisms were expected to occur frequently.

Table 3. 5. Solid metal concentration ranges compared to SQGs.

	Zn	Pb	Cd
TSMD PEC (mg/kg)	2083	150	11.1
Range of conc. for SS (mg/kg)	387-395	49.4-53.0	3.4-3.6
Range of conc. for CS (mg/kg)	366-437	51.0-54.9	2.6-4.5
Range of conc. for LMS (mg/kg)	686-845	78.6-90.0	4.1-6.4
Range of conc. for HMS (mg/kg)	563-909	67.6-96.8	4.5-7.1
Range of conc. for SMDR (mg/kg)	9447-10517	765.0-849.0	55.6-62.3
Range of conc. for LMDR (mg/kg)	9068-10217	743.7-812.5	48.5-57.7
Range of conc. for HMDR (mg/kg)	7975-10221	692.9-892.9	51.2-61.9

For both initial and final lake sediments, results showed none of the treatments exceeded the TSMD PECs. For MDRs (SMDR/LMDR/HMDR), results showed all of the treatments exceeded

the TSMD PECs, which was not unexpected since MDRs were precipitated from mine drainage that contains elevated toxic trace metals. It is natural that MDRs have high trace metal concentrations. The fact that sediment after addition of MDRs were still less than SQGs supported the future application of MDR dosing to achieve P removal in eutrophic reservoirs and withdrawing after saturation with P. During the entire period when MDRs were in contact with the water column and sediment layer, no significant trace metal release was observed, therefore, indicating MDR is a safe P-sorbing material. The reason to refer to site-specific SQGs rather than consensus-based SQGs is that GLOC has been receiving metal contaminated water and sediments since completion of the Pensacola Dam in 1940 (TSMD mining peaked in the 1920s but continued until the late 1960s). However, GLOC sediments show no significant correlation between toxicity to amphipods and site-specific-SQGs for these metals (Ingersoll et al. 2009). In their toxicity studies of GLOC sediments, the authors concluded that infrequently exceeding the SQGs would likely still not result in death or inhibit growth of amphipods.

Conclusions

In this study, MDR additions did not show significant decreases in aqueous P levels in the water column during the short-term (first 10 days biomass growth period) compared to the control treatment. In the long-term (days 11-138, biomass decay period), LM and HM treatments showed relative constant levels of P and Fe, while C treatments demonstrated significant P release into the water column. MDR additions appear to serve as a long-term internal P loading control method to prevent labile P release back into water column after algal bloom decay which could enhance potential future blooms. The monitoring of aqueous metal concentrations and comparison to NRWQCs and NSDWRs showed limited concerns for trace metal release from MDR additions,

with only Pb above one criterion. Sediment metal concentrations for all samples were below the TSMD site-specific SQGs, indicating that there was no significant toxicity introduced to the sediment layer after MDR addition. Metal concentrations in MDRs, however, exceeded TSMD site-specific SQGs. Future studies may be performed in development of P sorption isotherms for MDRs to better understand maximum P removal rates amendment of MDRs to further decrease trace metal (especially Pb) release and engineering designs for practical MDR addition practices.

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Chapter Four: Recovered Mine Drainage Passive Treatment Residuals Address Reservoir Sediment Nutrient and Trace Metal Pollution: A Field Mesocosm Study at Grand Lake o' the Cherokees, Oklahoma

This Chapter has been formatted for submission to Ecological Engineering

Abstract

Grand Lake o' the Cherokees, Oklahoma is a large multipurpose reservoir that receives both elevated metals concentrations from the upstream Tri-State Lead-Zinc Mining District (TSMD) and excess nutrients from its agricultural watershed along with significant internal phosphorus (P) legacy loads. Mine drainage residuals (MDRs), amorphous iron oxyhydroxides recovered from passive treatment systems, may serve as phosphorus sinks. To evaluate the role of MDRs on reservoir sediment dynamics, a field mesocosm study (20-L vessels) was designed with four different mine drainage residuals (MDR) treatments: sediment control (no addition), mixed (MDR mixed with sediment), layered (MDR on top of sediment, no mixing) and bagged (MDR inside a fine mesh bag on top of sediment, no mixing) with phosphorus-spiked water. Soluble reactive P (SRP) and total P (TP) concentrations demonstrated decreasing trends and the control treatment showed greater concentrations than all MDR treatments. P adsorption capacity (PAC) was determined to be approximately 0.7 mg/g and >30 mg/g for sediments and MDR, respectively. At Day 135, both SRP and TP reached >99% removal for all four treatments. Aqueous lead and cadmium concentrations were below detection limits and zinc concentrations were below the National Recommended Water Quality Criteria. Sediment lead, zinc and cadmium concentrations were below the TSMD-specific sediment quality guidelines, except for final Mixed MDR

treatment sediment with 16.7% of samples exceeding both Cd and Pb criteria. Results showed that MDRs removed excess P from the water column and by using the recommended bagged addition method, trace metal release to both the water column and sediment layer were minimized.

Introduction

Excessive inputs of phosphorus (P) into freshwater systems have raised concerns in recent years due to its contribution to eutrophication and harmful algal blooms (Chen et al. 2014, Xie et al. 2003, Yao et al. 2016). Compared to external P loading, which refers to imported P from runoff, erosion and precipitation that can be controlled by addressing point and non-point sources, internal P loading, which refers to release from sediment P sinks, can be more difficult to control (Chen et al. 2018, Jin et al. 2006, Nikolai and Dzialowski 2014). Under different environmental conditions, e.g., variability in temperature, oxidation-reduction potential, biomass growth, and lake mixing status, a dynamic equilibrium exists between sediment-sorbed P releases into the water column and aqueous P capture by sediment particles (Chen et al. 2014, Chen et al. 2018, Wang et al. 2016, Yao et al. 2016). Therefore, an effective method to maintain sediment P sinks (and minimize P release) will help to control internal P loadings. Dredging has been applied as a common method to remove nutrient-rich sediment contributing to internal P loading (Bormans et al. 2016, Liu et al. 2016, Yu et al. 2017). However, phosphorous sorbing materials (PSMs) may provide an effective alternative. The application of PSM to eutrophic lake and reservoir systems could help with internal P load reduction.

The most studied PSMs can be separated into two groups: calcium (Ca) and/or magnesium (Mg) based materials for P removal via precipitation and iron (Fe) and aluminum (Al) based materials

for P removal via adsorption (Christianson et al. 2017, Penn et al. 2007). Mine drainage residuals (MDRs), the amorphous iron oxyhydroxides generated from treatment of metal-rich mine waters, also commonly referred to as ochre in the UK, have specifically raised interest from many researchers due to their wide availability and minimal cost (Dobbie et al. 2009, Heal et al. 2005, Penn et al. 2007, Spears et al. 2013). Multiple studies have examined phosphorus adsorption capacity (PAC) of MDRs to evaluate maximum P mass taken up per unit mass of MDR. Results varied based on the different composition of MDRs collected from various mine sites: 8 to 10 mg P/g from Zeng et al. (2004), 9.89 to 31.97 mg P/g from Wei et al. (2008), and 1.82 to 23.9 mg P/g from Sibrell et al. (2009). Most of the PAC data demonstrate that MDR are promising PSMs for future applications.

Most current studies on MDR P-removal applications were focused on treatment of relatively high P concentration municipal wastewaters (>20 mg P/L) (Heal et al. 2005, Wei et al. 2008) or dairy manure (180-400 mg P/L) (Sibrell et al. 2015). Many of these studies were performed on the laboratory scale: batch studies by Zeng et al. (2004), a continuous stirred tank reactor study by Wei et al. (2008) and a fixed bed study by Sibrell and Tucker (2012). Several field studies examined various flow-through structures: a MDR-filled trough at the Leitholm wastewater treatment plant (UK) (Heal et al. 2005), a tank containing MDR pellets at the Windlestone wastewater treatment plant (UK) (Dobbie et al. 2009), a partially buried ditch filled with MDR at the University of Maryland Eastern Shore research farm (MD, USA) (Penn et al. 2007) and manure amendment with MDR at Orner dairy farm (PA, USA) (Sibrell et al. 2015). Some studies explored more complex MDR applications such as coating MDR on lignocellulosic fibers to increase sorption capacity (Han et al. 2005) and mixing MDR with anaerobic digested sewage sludge to recover and reuse P (Shepherd et al. 2016). Overall, however, there is a lack of research targeting

P removal at lower concentrations and direct applications of MDR to eutrophic lentic ecosystems (such as ponds, lakes and reservoirs) where internal loading plays a major role. One of the studies performed by Perkins and Underwood (2001) showed that direct dosing of ferric sulfate into a reservoir (Alton Water, UK) successfully sequestered the excess reactive P in this system, controlled internal P loadings and limited algal growth. This study used refined chemical salts, but provided a template for the possible application of MDR as PSM by direct dosing into a lake or reservoir. However, given the presence of trace metals in MDRs, the water column and sediment layers must be monitored for potential ecotoxic trace metal release.

Therefore, this study investigated the practicality of direct MDR application onto the sediment surface in eutrophic water systems. A field mesocosm study was conducted to compare P sorption performance and trace metal release over time among different MDR addition treatments. Additionally, a laboratory PCA study was performed to provide information about long-term P-removal feasibility. At the end, suggestions are offered for future practical applications of using MDR for internal P control at lakes and reservoirs.

Material and methods

Study site description

Grand Lake o' the Cherokees (GLOC) is a large man-made multipurpose eutrophic reservoir operated by Grand River Dam Authority (GRDA) in northeastern Oklahoma, which experiences periodic seasonal harmful algal blooms (Morrison et al. 2017). Also, due to its proximity to the derelict Tri-State Lead-Zinc Mining District (TSMD), it has received water and sediments with elevated concentrations of iron (Fe), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni) and other

trace metals for decades, posing long-term toxicity risks to surrounding ecosystems (Garvin et al. 2017).

The field mesocosm study site, GRDA-operated Duck Creek (DC) nursery ponds, is located on the Duck Creek arm of GLOC near Cleora, Oklahoma. Background water quality and sediment samples were collected in DC at established runoff-dominated ponds that periodically receive overflow from GLOC (36°34'15.0''N, 94°57'50.0''W, nominal water depth 2 ft). Pond sediments were collected using a stainless-steel shovel, and water samples were collected using an extended pole sampler into 250-mL HDPE bottles. Metal samples were preserved by adding trace metal grade HNO₃ to pH<2 to prevent dissolved metals precipitating out; other nutrient and Chl-a samples did not have additional preservation. After collection, all these preliminary site study samples were stored and transported in coolers filled with ice at 4°C before delivery to University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) laboratories. All the preliminary site study samples were analyzed in CREW laboratories, while the some of the later field study samples were analyzed in the GRDA Ecosystem and Education Center (EEC) laboratory.

MDR Characterization

The TSMD includes four USEPA Superfund Sites in Oklahoma (Tar Creel Superfund Site), Kansas (Cherokee County) and Missouri (Oronogo-Duenweg and Newton County Mines). In Oklahoma, the Mayer Ranch passive treatment system (MRPTS) was constructed and has been operated by OU CREW for since 2008. This system was designed to treat approximately 1000 L/min of net alkaline ferruginous lead-zinc mine water through both aerobic (e.g., iron oxidation, hydrolysis, precipitation and settling of iron oxyhydroxides) and anaerobic (i.e., bacterial sulfate reduction for trace metal sulfide precipitation). MDRs used in this field study were collect from

the MRPTS oxidation pond process unit. Previous studies characterized the MDR from MRPTS and found the major chemical and physical properties listed in Table 4. 1 (Oxenford 2016).

Table 4. 1. Characterization of MDR collected from MRPTS oxidation pond (Oxenford 2016)

Crystallinity (%)	Mean particle size (μm)	D60/D10	Specific Surface Area (m^2/g)	Color	Organic Content (%)	Mineral phase
17.4	11.7	14.3	244	Yellowish Red	4.3	Goethite

Field mesocosm set-up

In the field, 24 of 20-L vessels were set-up in this study for four treatments: sediment control (no MDR addition), mixed (MDR mixed with sediment), layered (MDR on top of sediment, no mixing) and bagged (MDR inside a fine mesh bag on top of sediment, no mixing). Each vessel received 5 kg wet lake sediments, 0.5 kg wet MDR (none for control) and 16 L lake water. Each treatment had six replicates. All 24 vessels were randomly placed in six plastic-lined, wood-framed boxes, designed as a temperature control. Since the field study was set up in the summer, diurnal temperature fluctuations and substantial evaporation rates were taken into consideration. Water levels outside the vessels but inside the box were maintained slightly lower than water level inside the vessels.

All vessels were spiked with a KH_2PO_4 stock solution to an initial P concentration of approximately 12 mg/L. This value was selected to examine a worst case scenario, but were still much lower than most previous MDR-P sorption studies.

Sampling process and chemical analysis

Water samples were collected at Hour 0, Hour 6, Day 1, Day 2, Day 7 (one week), Day 78 (two months) and Day 135 (four months). Samples were taken 10 cm above the sediment layer and water column interface using a siphon technique. Nutrient analysis for field study water samples were performed at the GRDA EEC laboratory using a Lachat QuickChem 8500 Flow Injection Analysis System following the ascorbic acid method for SRP and TP (EPA Method 365.3) and the sulfanilamide/NED method (EPA Method 353.2) for NO_2+NO_3 and TN. Chl-a concentrations were measured by a Turner Designs Trilogy Laboratory Fluorometer following the acetone extraction method (U.S. EPA, 2013). Metal samples were transported back and analyzed at the CREW laboratory. All total metals (TM) and dissolved metals (DM) samples first underwent microwave hot HNO_3 digestion (EPA Method 3015 using a CEM MARS Xpress Digestion System) and were analyzed via Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (EPA Method 6010) using a Varian Vista-Pro simultaneous axial ICP-OES for a suite of trace metals: silver (Ag), aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), silicon (Si) and zinc (Zn). A YSI 600QS multiparameter datasonde coupled with a YSI 650 display were used to collect and record basic water quality data including pH, pH mV, water temperature (Temp), Resistivity, Salinity, Specific Conductance, Conductivity, Total Dissolved solids (TDS), dissolved oxygen (DO) (in mg/L and % air saturation) and oxidation-reduction potential (ORP), immediately after each water sample collection event.

Sediment and MDR samples were collected at the initial stage (before set-up) and final stage (after last set of water sample collections) of the study. All these solid samples were transported back to

the CREW laboratory and measured gravimetrically for moisture content (MC) and organic content (OC) as loss on ignition following American Society for Testing and Materials methods (ASTM D2974). Sediment P was extracted with ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA) (Kuo, 1996), which represented the P fraction bound to Fe, Al and Mn oxides and hydroxides and was analyzed following EPA Method 365.3 (SSSA 1996) on a SEAL Analytical Discrete Analyzer AQ300. Sediment samples for metals analysis underwent microwave hot HNO₃ digestion (EPA Method 3051) and then analysis via ICP-OES (EPA Method 6010).

Phosphorus adsorption capacity test

Phosphorus adsorption capacity tests for initial MDR and sediment samples were conducted in the CREW laboratories. In each case, 0.5 g of dry sample and 100 mL of various P solutions (using anhydrous KH₂PO₄) were added into sealed 250-mL glass Erlenmeyer flasks. P concentrations of 0, 1, 5, 10, 50, 100, 250, 500, 750, 1000, 1500, 2000, 3000 and 4000 mg/L were used for MDR and concentrations of 0, 5, 10, 50, 100, 200, 400 and 600 mg/L were used for sediment samples. Incubation temperatures were ambient laboratory temperature (approximately 20°C). All vessels were placed on an orbital shaker at 100 rpm for 24 hours. After incubation, samples were filtered through 0.45-µm syringe filters into clean sample cups and analyzed for soluble reactive phosphorus (SRP). Samples from the PAC tests were analyzed in CREW laboratories using a SEAL Analytical Discrete Analyzer AQ300, following the ascorbic acid method for SRP (EPA Method 365.3).

Statistical analysis

Statistical significance of differences was analyzed with one-way analysis of variance (ANOVA) using SPSS 24.0 software. A p-value < 0.05 level was considered to be significant. When

differences between treatments were significant, least significant difference (LSD) tests were performed as a post-hoc study. Variations in results were reported in terms of standard deviations (\pm SD).

Results and discussion

Basic water quality parameters

Over the four month field study, seasonal and weather variability impacted water quality for the four treatments: control sediment (C), layered MDR addition (L), mixed MDR addition (M) and bagged MDR addition (B) over time (Table 4. 2).

Table 4. 2. Basic water quality parameters during study period for each of four treatments. Data shown are means \pm standard deviations.

	Temp ($^{\circ}$ C)	pH	DO (mg/L)	ORP (mV)
C	7.4 \pm 0.2 - 29.1 \pm 1.2	6.6 \pm 0.1 - 8.0 \pm 0.5	7.8 \pm 0.4 - 11.7 \pm 0.6	22.4 \pm 8.8 - 192.7 \pm 31.3
L	7.4 \pm 0.2 - 29.6 \pm 2.1	6.6 \pm 0.1 - 7.8 \pm 0.5	7.2 \pm 0.5 - 13.0 \pm 0.6	23.1 \pm 4.4 - 212.3 \pm 18.3
M	7.3 \pm 0.3 - 29.4 \pm 1.0	6.7 \pm 0.1 - 8.1 \pm 0.5	7.3 \pm 0.4 - 13.3 \pm 0.6	24.8 \pm 6.5 - 211.3 \pm 13.2
B	7.3 \pm 0.2 - 29.8 \pm 1.9	6.8 \pm 0.1 - 8.3 \pm 0.3	7.1 \pm 0.6 - 14.9 \pm 0.7	25.7 \pm 3.7 - 200.5 \pm 26.4

Chl-a concentrations in the water column

No algal biomass was added to the treatments during the entire study period. Due to the extreme weather conditions and site access limitations from regional flooding, there was about one-month period between the set-up date (August 20th, 2019) and the first sampling date (September 23rd, 2019). During this period, biomass growth occurred in every vessel in all four treatments at

different levels. P spike stock solution was added to each vessel on September 23rd, 2019, and immediately after the spike, the initial point (Day 0) was collected. The study was then conducted in the following four months. During the latter period of the field study, especially as the temperature declined, biomass decay was also observed in every vessel.

Chl-a concentrations showed no significant differences among treatments ($p=0.690$), but a significant overall decrease over time ($p<0.0005$) (Figure 4. 1). Bagged MDR treatment had greater initial algal biomass growth than the other three treatments, probably due to lesser suspended solids in the water column after set-up due to MDR functioning as a coagulant. By the end of study, all four treatments had relatively similar low Chl-a concentrations ($<5 \mu\text{g/L}$), indicating seasonal biomass death and decay over time corresponding to the decreasing temperatures.

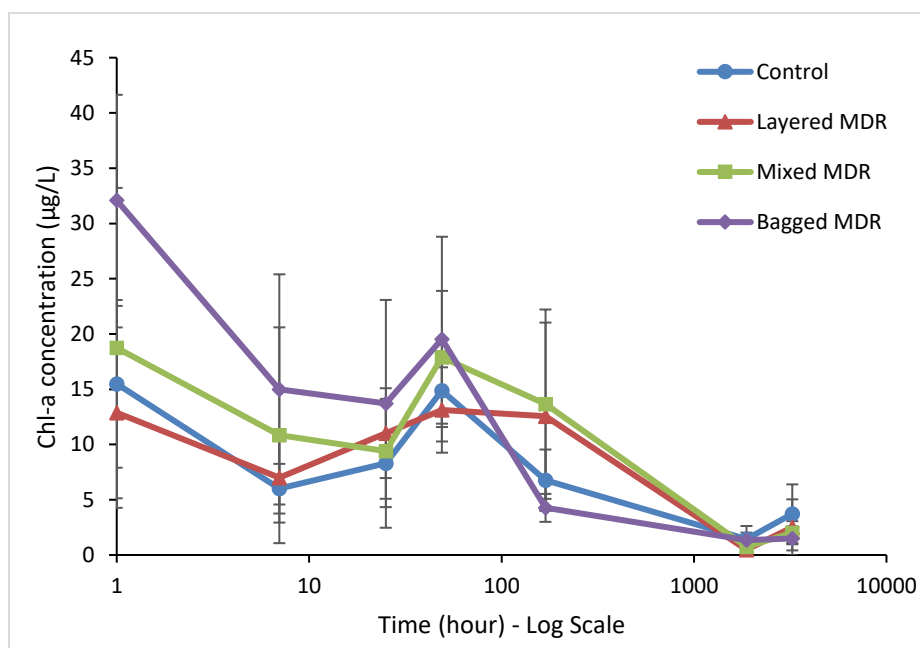


Figure 4. 1. Chlorophyll a (Chl-a) concentrations of four treatments over the study time. Data are mean \pm SD. X-axis is in log-scale.

Nutrient concentrations in the water column and P sorption percentage

For nutrient concentrations in the water column, SRP and NO_2+NO_3 were based on filtered (0.45 mm) water samples, while TP and TN were based on unfiltered water samples. In this study, sometimes $\text{SRP} > \text{TP}$ was observed likely because SRP concentrations were determined using the filtrate from Chl-a examinations and biomass cells may have broken under vacuum pressures, releasing biologically held P into the filtrate. This phenomenon was also noticed by Tarapchek et al. (1982) as they confirmed that higher SRP than TP values from water samples were due to the SRP released from fragile biotic and abiotic particulate materials during filtration processes.

Nutrient concentrations for the four treatments were plotted over time (Figure 4. 2). For SRP, there were no significant differences among four treatments ($p=0.922$), but showed significant decreases over time ($p<0.0005$), dropping from 11.66-13.62 mg/L at Day 0 to 0.01-0.03 mg/L at Day 135. For NO_2+NO_3 , there were also no significant differences among four treatments ($p=0.419$), but significant decreases over time ($p=0.004$), dropping from 0.07-0.33 mg/L at Day 0 to 0.01-0.02 mg/L at Day 135. For TP, again there were no significant differences among four treatments ($p=0.962$), but significant decreases over time ($p<0.0005$) dropping from 11.63-12.54 mg/L at Day 0 to 0.02-0.07 mg/L at Day 135. TN concentrations were not plotted due to the majority of the data below the PQL of 0.02 mg/L.

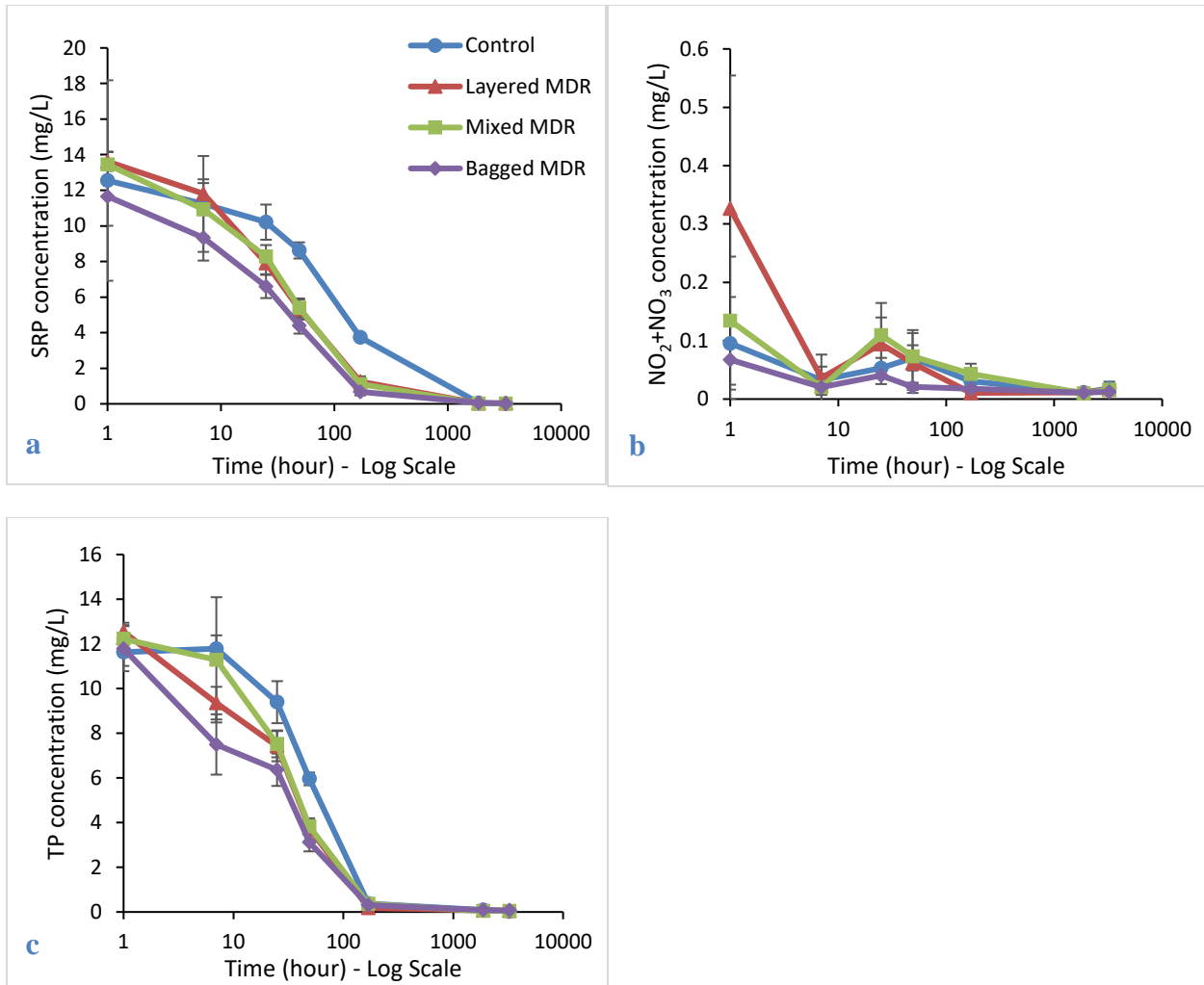


Figure 4. 2. Soluble Reactive Phosphorus (SRP) (a), Nitrite+Nitrate (NO₂+NO₃) (b) and Total Phosphorus (TP) (c) concentrations of four treatments over the study time. Data are mean \pm SD. X-axis are in log-scale.

During the first 7 days, all four treatments had rapid decreases in SRP, NO₂+NO₃ and TP concentrations which then stayed relatively constant and low from Day 78 to Day 135 (2-4 months). The decrease of P and N may have been due to biomass uptake, but for P (both SRP and TP) with a much greater spiked initial concentration (around 12 mg/L), sorption to MDR and sediment also contributed to the significant decrease. SRP and TP sorption percentages were calculated by comparing initial water column values at Day 0 (Table 4. 3) to values throughout the study. For

both SRP and TP, there was a significant trend for sorption percentage changes over time (both $p < 0.0005$), which included continuously increasing from Hour 6 to Day 7 (all $p < 0.05$) and staying relatively constant after Day 7 (for SRP, $p = 0.060$ for Day 7 vs Day 78 and $p = 0.981$ for Day 78 vs Day 135; for TP, $p = 0.774$ for Day 7 vs Day 78 and $p = 0.978$ for Day 78 vs Day 135). Also, during the first seven days of rapid P sorption, there were also significant differences among treatments with all p values < 0.05 for both SRP and TP, while there were no significant differences among treatments on Day 78 and Day 135 (Table 4. 4).

Table 4. 3. Soluble Reactive Phosphorus (SRP) and Total Phosphorus (TP) sorption percentages during study period. Data shown are means.

SRP sorption (%)	Hour 6	Day 1	Day 2	Day 7	Day 78	Day 135
C	10.49	18.63	31.30	70.13	99.56	99.90
L	13.22	41.82	60.86	90.88	99.78	99.75
M	18.77	38.49	59.78	91.78	99.80	99.83
B	19.94	43.44	62.28	94.14	99.51	99.78
TP sorption (%)	Hour 6	Day 1	Day 2	Day 7	Day 78	Day 135
C	-1.29	19.28	48.81	96.83	99.31	99.87
L	25.45	40.80	70.02	98.56	99.46	99.50
M	7.63	38.40	68.72	97.01	99.68	99.63
B	36.38	45.98	73.55	97.39	99.25	99.45

Table 4. 4. ANOVA p-values for Soluble Reactive Phosphorus (SRP) and Total Phosphorus (TP) sorption percentage on each sampling event. $p < 0.05$ considered to be significant.

	Hour 6	Day 1	Day 2	Day 7	Day 78	Day 135
SRP sorption (%)	0.011	0.008	0.001	<0.0005	0.436	0.204
TP sorption (%)	<0.0005	<0.0005	<0.0005	<0.0005	0.776	0.054

Even though at the end of study (Day 135), all four treatments had over 99% P removal for both SRP and TP, the control treatment had only 70.13% SRP removal on Day 7, while all three MDR addition treatments had over 90% P removal, with relative performance showing Bagged (94.14%) > Mixed (91.78%) > Layered (90.88%). This indicates that although the long-term study showed no significant differences in P sorption between the control and three MDR addition treatments, the short-term data show MDR addition treatments achieved greater P removal than the control treatment. These trends agree with P sorption rates of over 20 mg P/g/h removal reported by Zeng et al. (2004) and Moreira et al. (2017), and are much greater than sediment removal rates of around 0.2-0.3 mg P/g/h reported by Appan and Wang (2000) and Xie et al. (2019). Therefore, MDR addition could help to achieve rapid and greater P removal performance than the control treatment with only sediment in the short-term.

Within seven days, bagged MDR showed the greatest removal performance for SRP, while Layered MDR showed the greatest removal performance for TP. In the long term, both the control and MDR treatments reached similar P removal percentages for SRP and TP based on water quality changes, because sediments provided some P sorption capacity. These results are also similar to

those found in studies on internal P loadings from lake sediments (Chen et al. 2018, Jin et al. 2006, Nikolai and Dzialowski 2014), where under certain conditions, the sediment served as a short-term or long-term storage for P in lake and reservoir systems. Bagged MDR addition treatment was considered the best treatment method due to its faster and greater P sorption during the first seven days for both SRP and TP.

P concentrations in the sediment/MDR and P adsorption capacity

In order to evaluate the viability of using MDR as an amendment to control P in lakes and reservoir systems, P concentrations in the sediment and MDR (Table 4. 5) as well as maximum PAC (Figure 4. 3) were examined and compared. P concentrations in lake sediments showed a significant difference among the five groups (Set-up Sediment (SS), final Control sediment (CS), final Layered MDR addition sediment (LS), final Mixed MDR addition mixture of sediment and MDR (M), final Bagged MDR addition sediment (BS)) ($p < 0.0005$). The LSD post-hoc tests also showed that each treatment was significantly different from the others ($p < 0.05$), except between CS and BS ($p = 0.178$) and LS and BS ($p = 0.121$). P concentrations in MDRs showed significant differences among the three groups (Set-up MDR (SMDR), final Layered MDR addition MDR (LMDR), final Bagged MDR addition MDR (BMDR)) ($p < 0.0005$), while the LSD post-hoc tests also showed each treatment was significantly different from the other ($p < 0.0005$), except between LMDR and BMDR ($p = 0.091$). The similarity between LMDR and BMDR might due to the fact that both Layered and Bagged treatments had a MDR layer on top of sediment layer with no mixing, and the only difference between them was that BMDR had a screen mesh bag between it and the sediment. With such similar contacting surfaces and a clear separation from the sediment layer, LMDR and BMDR should had similar performances.

Table 4. 5. Initial and final phosphorus concentrations in sediments and MDRs and percentage changes for different treatments. Data shown are means.

		Sediment P (mg/kg)	Change (%)
Initial	Set-up Sediment (SS)	3.97	NA
	Set-up MDR (SMDR)	15.77	NA
Final	Control sediment (CS)	6.55	65.13
	Layered MDR addition sediment (LS)	9.73	145.38
	Mixed MDR addition sediment (M) (compared to SS)	37.61	848.11
	Mixed MDR addition sediment (M) (compared to SMDR)	37.61	138.53
	Bagged MDR addition sediment (BS)	8.03	102.31
	Layered MDR addition MDR (LMDR)	34.68	119.98
	Bagged MDR addition MDR (BMDR)	32.58	106.66

Increased final P concentrations showed that P sorbed to both sediment and MDR in the mesocosms. The changes of P concentrations in MDRs (an increase of 18.91 mg/kg for Layered MDR addition; an increase of 16.81 mg/kg for Bagged MDR addition) were all greater than the changes of P concentrations in sediments (an increase of 2.58 mg/kg for Control; an increase of 5.76 mg/kg for Layered MDR addition; an increase of 4.06 mg/kg for Bagged MDR addition). Note that analysis of the Mixed MDR addition was challenging as P concentrations were measured

from a mixture of both sediment and MDR, therefore, a comparison was made separately between initial sediment and initial MDR P values, which showed a P concentration increase of 33.64 mg/kg for SS and 21.84 mg/kg for SMDR. These greater concentration changes in MDR than in sediment indicate MDR has a stronger P sorption ability than sediment. Also, the greater sediment P percentage changes with MDR addition showed that MDR amendments to the sediment created larger P sinks.

To evaluate sediment and MDR P retention capabilities, laboratory Phosphorus Adsorption Capacity (PAC) tests were performed and used to develop sorption isotherms (Figure 4. 3). They were fitted to Langmuir model based on the assumption that sorption of the phosphorus occurs as a single layer on the MDR/sediment, with a general form of the Langmuir model shown in Equation 1 and a linearized form of the Langmuir equation is shown in Equation 2.

$$C_s = \frac{x}{m} = \frac{abC_e}{1+bC_e} \quad (1)$$

$$\frac{C_e}{C_s} = \frac{1}{ab} + \frac{C_e}{a} \quad (2)$$

Where, C_s and C_e were metal concentration on the solid surface (mg/g) and in the solution at equilibrium (g/L), a was the maximum adsorption capacity (mg/g), b was the saturation coefficient (L/g), and x and m were the mass of P sorbed on the material (g) and mass of the material (g). The empirical coefficients “ a ” and “ b ” may be obtained by plotting the ratio of C_e/C_s as a function of C_e . Using linear regression on the raw data provides the equation of a line with the slope = $1/a$ and the y-intercept = $1/(ab)$.

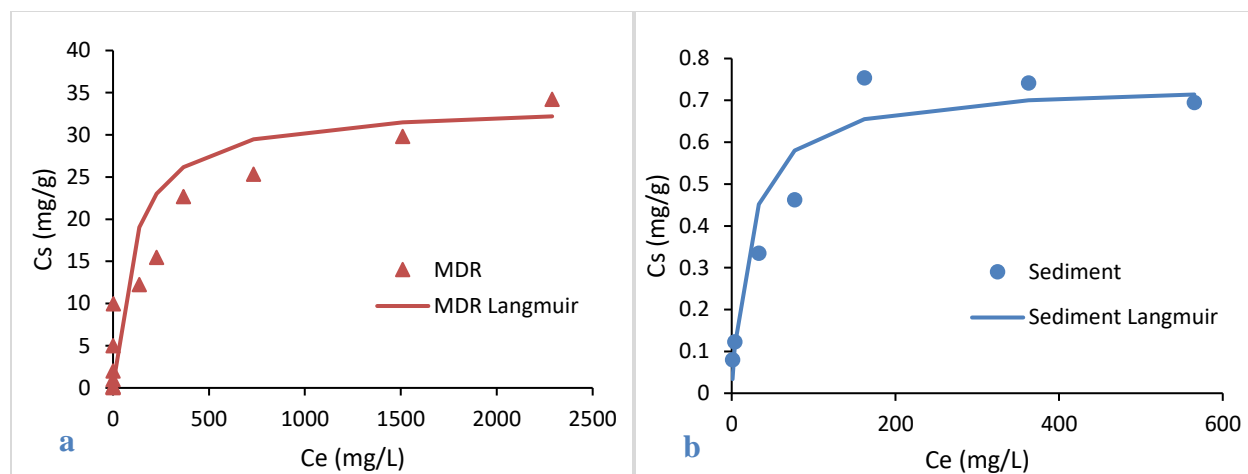


Figure 4. 3. Phosphorus sorption isotherms with Langmuir model fits for initial set-up MDR (a) and sediment (b). Data are means.

The parameters for Langmuir isotherm models were listed in Table 4. 6. Both MDR and sediment have good fittings with R^2 values of 0.97 and 0.99, respectively; and MDR had much greater PACs than sediment, which were estimated to be 33.7 mg/g for MDR and 0.74 mg/g for sediment. This supported the previous results of both control and MDR addition treatments decreasing water column P concentrations and increasing in sediment/MDR concentrations. The greater PAC value for MDR compared to sediment showed MDR to be more effective P sink for internal P loadings.

Table 4. 6. Parameters for Langmuir isotherm models for MDR and sediment.

Material	MDR	Sediment
Slope	0.0297	1.3497
Y intercept	3.1139	28.706
R^2	0.9748	0.9911
a	33.7	0.74
b	0.0095	0.047

To evaluate sediment and MDR P retention capabilities, laboratory Phosphorus Adsorption Capacity (PAC) tests were performed by developing sorption isotherms (Figure 4. 3). Both MDR and sediment have good fittings with R^2 values of 0.87 and 0.92, respectively; and MDR had greater PACs than sediment. At greater range of initial P solutions (up to 800 mg/L for sediment and 8000 mg/L for MDR), observed PACs were greater than 30 mg/g for MDR and around 0.6 mg/g for sediment, which supported the previous results of both control and MDR addition treatments having decreases in water column P concentrations and increases in sediment/MDR concentrations. The greater PAC value for MDR compared to sediment made it a more effective P sink for internal P loadings.

Metal concentrations in water and sediment

For both dissolved metal (DM) and total metal (TM) concentrations (Table 4. 7), Pb, As, Ni and Cd concentrations for all samples were below the practical quantitation limits (PQLs), which were 0.0195 mg/L, 0.02 mg/L, 0.004 mg/L and 0.0006 mg/L, respectively. Compared to hardness adjusted National Recommended Water Quality Criteria (U.S. EPA 2014), dissolved Zn concentrations over the entire study period were below both the acute Criterion Maximum Concentration (CMC) and chronic Criterion Continuous Concentration (CCC). Compared to control treatments, all MDR addition treatments did not indicate trace metal release to the water column over the four-month study period.

Table 4. 7. Dissolved and total iron, zinc and manganese concentrations over the entire study period. Data shown are means. Final dissolved and total zinc concentrations were data from Day 7, since samples from Day 78 and Day 135 were all below PQL.

Conc. (mg/L)	DM [Fe]	DM [Zn]	DM [Mn]
C	0.015±0.015 -	0.009±0.005 -	0.003±0.001 -
	0.205±0.227	0.026±0.029	0.008±0.006
L	0.009±0.004 -	0.007±0.002 -	0.001±0.001 -
	0.031±0.029	0.015±0.005	0.003±0.002
M	0.009±0.003 -	0.008±0.002 -	0.002±0.002 -
	0.049±0.051	0.019±0.005	0.004±0.002
B	0.007±0.006 -	0.010±0.003 -	0.001±0.001 -
	0.090±0.176	0.022±0.015	0.003±0.002
Conc. (mg/L)	TM [Fe]	TM [Zn]	TM [Mn]
C	0.043±0.042 -	0.016±0.004 -	0.013±0.007 -
	0.674±0.463	0.037±0.003	0.037±0.017
L	0.049±0.036 -	0.011±0.007 -	0.003±0.002 -
	1.147±1.476	0.024±0.004	0.015±0.004
M	0.050±0.071 -	0.009±0.003-	0.006±0.011 -
	0.444±0.254	0.026±0.003	0.019±0.011
B	0.025±0.018 -	0.011±0.002 -	0.004±0.006 -
	0.430±0.340	0.021±0.007	0.013±0.004

The metal concentrations in sediments and MDRs were compared between the initial and final stages (Table 4. 8). For sediment (SS/CS/LS/M/BS), there was a significant difference among the

five groups for As, Mn, Ni, Cd, Fe, Pb and Zn ($p < 0.0005$) and the LSD post-hoc test also showed that the Mixed MDR addition treatment was always significantly different from the other three treatments ($p < 0.0005$) for all metals, except for M vs LS ($p = 0.149$) and M vs BS ($p = 0.834$) for Mn. For MDR (SMDR/LMDR/BMDR), there was a significant difference among the three groups for As, Mn, Ni, Cd, Fe, Pb and Zn ($p < 0.0005$) and the LSD post-hoc test also showed each treatment was significant different from the others except for SMDR vs BMDR for As ($p = 0.213$), BMDR vs LMDR for Fe ($p = 0.855$), SMDR vs BMDR for Pb ($p = 0.717$) and SMDR vs BMDR for Zn ($p = 0.301$).

The significant differences for many metal concentrations for Mixed MDR addition compared to other treatments were likely due to the mixing of sediment and MDR. Based on the fact that the MDR had greater initial trace metal concentrations (especially for Fe, Cd, Pb and Zn), the presence of MDR in this mixture brought the final average concentrations of such mixtures to be much higher than initial sediments. For Layered MDR addition and Bagged MDR addition treatments which had a clear separation between MDR and sediment, the final sediment showed lesser impacts from the contact to MDRs. As for the previously identified greatest P-removal performance option, Bagged MDR addition, decreased concentrations of As, Mn, Ni, Cd, Fe and Pb in sediment as well as the smallest increase in sediment Zn concentrations indicate that this addition method resulted in minimal impacts to sediment quality for trace metal contamination.

Table 4. 8. Initial and final metal concentrations in sediments and MDRs and percentage changes for different treatments. Data shown are means.

Treatment		As	Mn	Ni	Cd	Fe	Pb	Zn
		mg/kg						
Initial	SS	9.2	1281.6	11.2	2.4	22090	58.9	26.3
	SMDR	495.7	288.9	167.8	57.0	449568	800.9	6797
Final	CS	6.5	1036.5	8.2	1.9	15043	43.3	31.5
	LS	10.1	571.4	8.9	2.5	21040	50.6	82.9
	M	68.9	727.8	30.7	10.5	83898	165.9	883.9
	BS	8.1	750.1	8.9	2.1	17502	46.6	51.1
	LMDR	256.2	679.8	89.7	33.4	288395	474.2	3325
	BMDR	463.7	507.2	155.4	61.5	448749	812.1	6585
		As	Mn	Ni	Cd	Fe	Pb	Zn
		% change						
	CS	-28.99	-19.12	-26.77	-19.48	-31.90	-26.47	19.55
	LS	10.60	-55.41	-20.95	5.06	-4.75	-14.04	214.9
	M (compared to SS)	651.90	-43.21	173.57	344.94	279.80	181.92	3259
	M (compared to SMDR)	-86.11	151.94	-81.71	-81.64	-99.81	-79.28	-87.00
	BS	-11.85	-41.47	-20.35	-9.16	-20.77	-20.80	94.22
	LMDR	-48.31	135.33	-46.52	-41.32	-99.36	-40.79	-51.08
	BMDR	-6.46	75.58	-7.36	7.92	-99.00	1.40	-3.12

Table 4. 9 compares these metal concentrations to the Tri-State Mining District (TSMD) specific Sediment Quality Guidelines (SQGs), which include a Probable Effect Concentrations (PECs) above which harmful effects on sediment-dwelling organisms were expected to occur frequently (MacDonald et al. 2000; Ingersoll et al. 2009).

Table 4. 9. Sediment and MDR metal concentration ranges compared to TSMD-SQGs.

Conc. (mg/kg)	Zn	Cd	Pb
TSMD PEC	2083	11.1	150
Range of conc. for SS	22.7-32.7	1.94-3.19	48.5-75.0
Range of conc. for C	25.8-36.9	1.78-2.04	39.6-48.9
Range of conc. for L	38.7-139.1	2.00-3.27	43.4-63.7
Range of conc. for M	739.7-1072.4	9.20-10.94	146.9-201.3
Range of conc. for B	31.5-87.8	1.93-2.41	44.9-48.7
Range of conc. for SMDR	6686-6957	55.7-58.6	715-870
Range of conc. for LMDR	3009-4252	29.90-43.28	434.4-584.5
Range of conc. for BMDR	6136-7190	56.25-67.32	763.5-887.8

For sediment (SS/CS/LS/M/BS), results showed none of the treatments exceeded the TSMD PECs, except for Cd and Pb of final Mixed MDR treatment sediment with 16.7% 16.7% exceedance rates for both. For MDR (SMDR/LMDR/BMDR), results showed all of the treatments exceeded the TSMD PECs because they were highly concentrated mine drainage residuals. For Zn, concentrations are 3.3 times, 1.6 times and 3.2 times of TSMD PEC for SMDR, LMDR, BMDR,

respectively. For Cd, concentrations are 5.1 times, 3.0 times and 5.5 times of TSMD PEC for SMDR, LMDR, BMDR, respectively. For Pb, concentrations are 5.3 times, 3.2 times and 5.4 times of TSMD PEC for SMDR, LMDR, BMDR, respectively.

It should be noted that Zn, Cd and Pb concentrations for LMDR were lower than SMDR and BMDR due to difficulty of perfectly separating MDR layers from sediment layer and therefore inevitably mixing sediment and MDR in the samples, which diluted metal concentrations. Similar values between SMDR and BMDR again supported the idea that using the mesh bag helps to prevent MDR leaking out into sediments to cause trace metal contamination. Bagged MDR additions were also identified as the most effective method for P retention due to its lowest potential to contaminate the sediment layer contacting it.

Conclusions

Overall, in this study, MDR addition was shown to accelerate P removal from the water column and enhance the P sink in the sediment. Compared to control sediment, which had its original P adsorption capacity, MDR addition amendments increased the maximum P adsorption potential due to greater PAC of MDR materials. There was no detectable trace metal contamination in the water column throughout the four-month study time for all three different MDR addition treatments, and only limited sediment trace metal contamination in the mixed MDR treatment. The Bagged MDR addition treatment seemed to be the most effective option for future practice, due to its P-removal performance from the water column, lack of exceedances of the NRWQCs and TSMD-SQGs, and its clear separation from the sediment layer which allowed easy extraction from the system and least leakage potential to cause further contamination. Future studies are needed to

examine performance of engineering designs for large-scale MDR amendments to eutrophic reservoirs, which could identify the most appropriate MDR to sediment ratio and amendment time to achieve greatest P removal. Other examinations could target the recycle and reuse of the P sorbed to the MDR as fertilizers for local pastures and farms to help establish a closed and renewable P cycling process between pasture and farm/run-off to reservoir water/P sink. In this way, best management practices suggestions could be provided for local authorities to improve the water quality of reservoirs and achieve the most efficient use of P in the watersheds.

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Chapter Five: Conclusions

The world has been facing eutrophication problems and harmful algal blooms more frequently and widely. Management of phosphorus (P) loadings, especially internal P loadings in lakes and reservoirs, is critical for aqueous P concentration reductions and to prevent future algal blooms. For reservoirs that are also impacted by trace metal contamination, the interaction between nutrients and metals at the water column and sediment layer interface should also be investigated. P-sorbing materials, such as iron oxyhydroxide-based Mine Drainage Residuals (MDRs), must be evaluated based on both P removal efficiency and potential risk of trace metal release. The goal of this dissertation was to manipulate the phosphorous, iron and trace metal relationships to provide feasible solutions to decrease eutrophication by utilizing MDRs as a reservoir internal P-loading management tool.

The purposes of this research were to understand the metal-nutrient interaction mechanisms at the water column and sediment layer interface; investigate major parameters (such as biomass and mixing) impacts on such nutrients and metals cycling processes; analyze MDR performance as P-sorption materials and provide suggestions for future engineering design with MDRs.

P utilized by biomass growth resulted in decreases of P masses in both the water column and sediment layer in a 30-day study (Chapter One). During the study, a variety of biological processes occurred including different algal taxa growth and decay, increased algal species richness and shifts in dominant algal species. All of these mechanisms led to additional changes in water quality, such as increased pH and decreased ORP, which further impacted internal P loading in this system. Based on the monitoring of metal concentrations in the water column over the study, Pb concentrations were constantly below CMC and above CCC, while Zn concentrations were

constantly below both CMC and CCC. Sediment metal concentrations were all below TSMD-specific PEC-SQGs. Therefore, it was concluded that algal blooms in the reservoir could change the P distribution between water and sediment, but no trace metal release would be introduced in the short-term. That is to say, for reservoir management, it is necessary to monitor nutrient concentrations over the algal bloom, while there should be limited concerns about the trace metal concentrations changes.

Sediment resuspension caused by mixing events is another major potential impact on metal and nutrient cycling processes (Chapter Two). Results from this study showed that during mixing periods, increased total suspended solids, total P, total Fe, Ni and Zn concentrations indicated a release from the sediment layer into the water column. During the subsequent settling period, corresponding decreased concentrations indicated sediment redeposition, metal precipitation and nutrient sorption. The presence of unplanned algal growth in all three treatments allowed a biomass interference to break down metal-P coupling during resuspension and later transformed bioavailable P into non-bioavailable P, resulting in decreases of measurable P in final sediments. Also, any released trace metals eventually precipitated to sediment surface, resulting in increased final sediment metal concentrations. Compared to NRWQC and TSMD-SQGs, all metal concentrations were below respective guidelines over the entire seven-day study, showing no trace metal release caused by mixing. This result indicates that for reservoir management, after substantial mixing events (such as heavy precipitation, flushing events and dredging), it is necessary to monitor immediate internal P releases from the sediment sink, which can lead to algal blooms. However, trace metal concentrations should not cause additional risks.

An MDR addition study with three dosages (Chapter Three) showed decreasing P levels in all treatments and no significant differences in the short-term, due again to unplanned biomass growth

and P uptake. However, in the long-term (after Day 75), significant differences occurred among treatments with P released from biomass death and decay. As control treatments showed a P increase, the MDR addition treatments showed no changes due to P uptake by MDR. For metal concentrations, compared to the relevant guidelines, both water column and sediment layer concentrations were all considered acceptable with no significant toxicity was introduced from added MDR. It is learned from this study that for reservoir management, MDR additions can at least serve as a long-term internal P loading control method to prevent labile P release back into water column, after algae bloom decay which could enhance potential future blooms.

In the final field mesocosm study (Chapter Four), MDRs proved to show capacity for P-sorption due to its elevated P removal performance and no detectable trace metal release to sediment and water. Although both MDR-addition treatments and control treatments with only sediment achieved over 99% P removal after four months, within the first seven days, MDR-addition treatments showed better P removal due to rapid P sorption rate and large P sorption capacity. The addition of MDR accelerated P removal from the water column and enhanced the P sink in the sediment. Bagged MDR-addition treatments were recommended as the most effective option for future practice in reservoir management, due to its P-removal performance from the water column, lack of exceeding NRWQCs and TSMD-SQGs, and clear separation from the sediment layer which allowed easy extraction from the system and least leakage potential to cause further contamination.

Recommendation for future research

Based on the observation of three greenhouse studies in this research (only one of which was designed with biomass addition as a treatment) all studies demonstrated biomass growth (and death

and decay) during the studies, likely due to residual algae in lake sediments used in these studies. Even in the first GHM study, growth of the initial added algal species was exceeded by algal species grown from sediments. Therefore, in the future, if studies are to focus on one impact at a time and avoid unexpected biomass growth, it would be recommended to pre-treat the sediment by autoclaving to kill all live algal cells.

Another area of focus for future work is the amendment of MDR to secure all toxic trace metals (such as Pb) in an inactive state by mixing with other waste materials or modifying MDRs through chemical/physical treatments in a cost-efficient way. The goal would be to further decrease the potential of trace metal release and make MDRs a safer P-sorption material for wide applications.

Finally, for pilot and full-scale field applications, a more detailed engineering design is required to provide more detailed specifications on amendment ratios, effective contact surface areas, contact times, and other design parameters to achieve the greatest P removal. Also, there is a possibility to reuse P-saturated MDR as fertilizers for local farms and pastures for P recycling. In order to close the P cycling loop between farm and pasture/run-off to reservoir water/P sink with MDR, studies should be conducted to evaluate the feasibility of using MDR as P transport media. Monitoring plans should be implemented for field studies to assess the long-term P cycling efficiency.

Appendix A. Supplemental Information for Chapter One

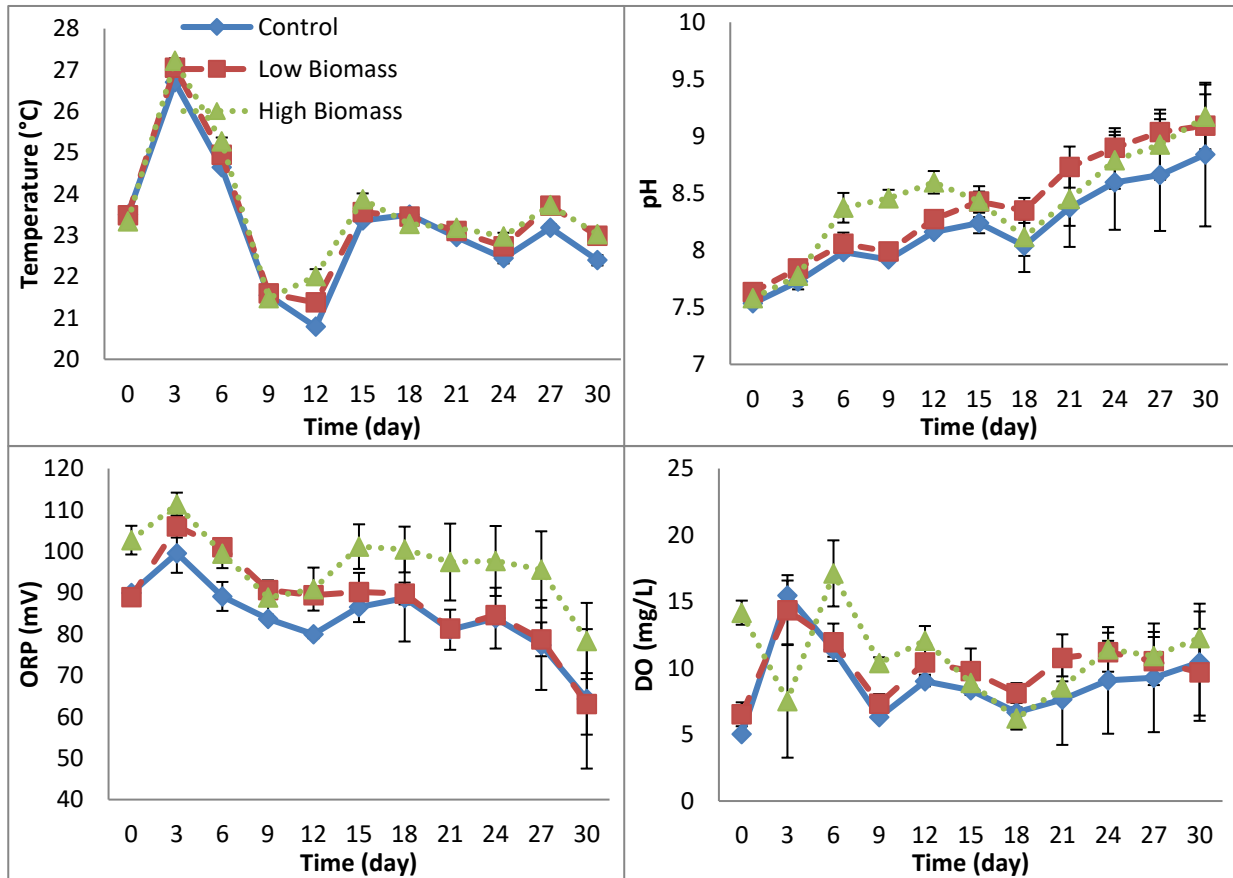


Figure A 1. Changes of water temperature, pH, DO and ORP in the water column of three treatments over the 30-day study period. Data are mean \pm SD.

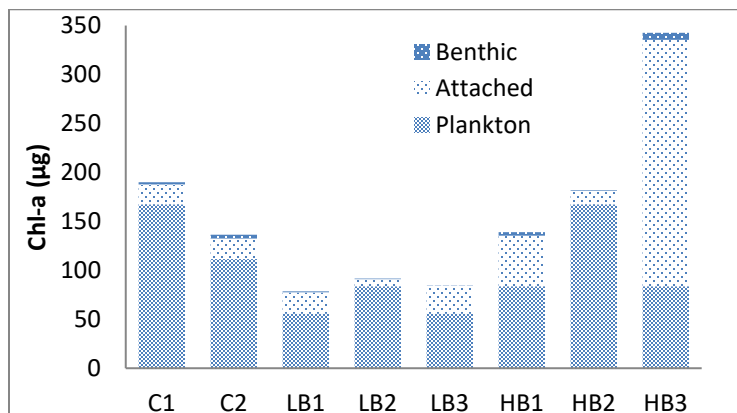


Figure A 2. Final Chl-a mass in each vessel after 30 days

Table A 1. P masses in each vessel before and after the 30-day study period

	Water				Sediment			
	Initial P (mg)	Final P (mg)	P loss (mg)	Mean P loss (%)	Initial P (mg)	Final P (mg)	P loss (mg)	Mean P loss (%)
C1	15.65	0.51	15.15	92.7	52.22	45.24	6.98	10.4
C2	15.65	1.78	13.88		52.24	48.38	3.85	
LB1	15.45	1.20	14.25		52.26	46.34	5.92	
LB2	15.45	0.39	15.06	93.7	52.24	49.33	2.91	7.0
LB3	15.45	1.37	14.08		52.22	50.14	2.07	
HB1	15.17	0.57	14.61		52.28	45.96	6.32	
HB2	15.17	1.31	13.86	90.7	52.26	47.05	5.21	7.6
HB3	15.17	2.35	12.82		52.26	51.83	0.43	

Appendix B. Supplemental Information for Chapter Two

Table B 1. Basic water quality parameters of C treatment (C), LM treatment (LM) and HM treatment (HM) over study period. Data shown are means.

	Initial				Final				Range			
	C	LM	C	HM	C	LM	C	HM	C	LM	C	HM
Temp (°C)	27.4	27.6	24.5	24.6	24.5	24.5	27.8	28.0	24.5 to 33.6	24.5 to 34.0	23.5 to 32.7	23.7 to 32.1
pH	7.4	8.7	8.6	9.2	8.6	9.3	9.4	9.4	7.4 to 8.6	8.1 to 9.3	8.0 to 9.4	7.1 to 9.4
DO (mg/L)	14.2	18.4	13.1	11.7	13.1	12.3	12.6	10.2	11.0 to 16.2	12.3 to 18.4	12.6 to 17.3	0.9 to 13.9
ORP (mV)	216	200	205	193	205	183	62	78	156 to 234	150 to 211	62 to 215	-85 to 210

Appendix C. Supplemental Information for Chapter Three

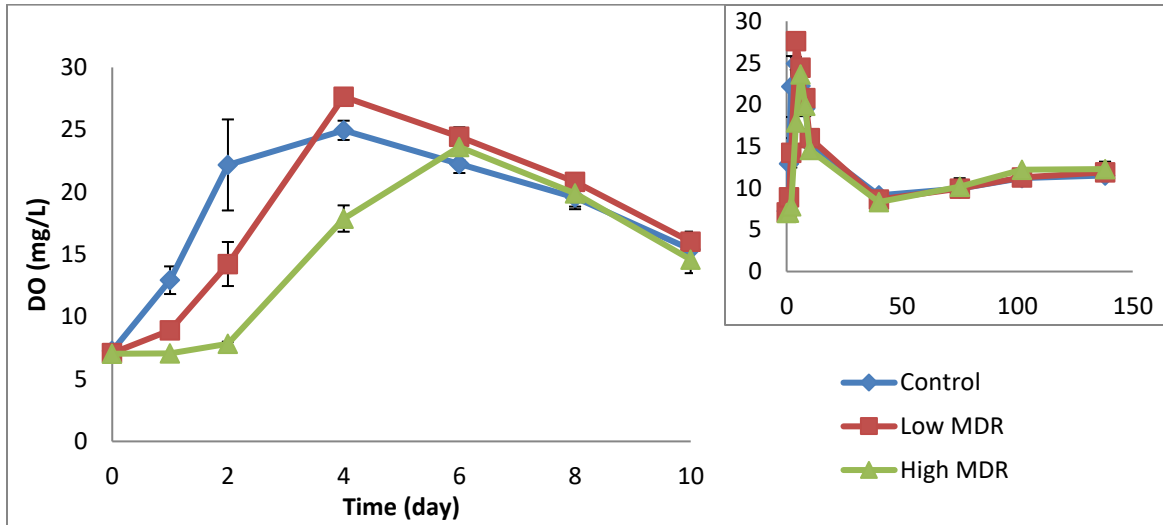


Figure C 1. Dissolved Oxygen (DO) concentrations of three treatments over the study time. Data are mean \pm SD. Original figure shows details of the first 10 days of the study while insert figure shows entire 138-day study period.

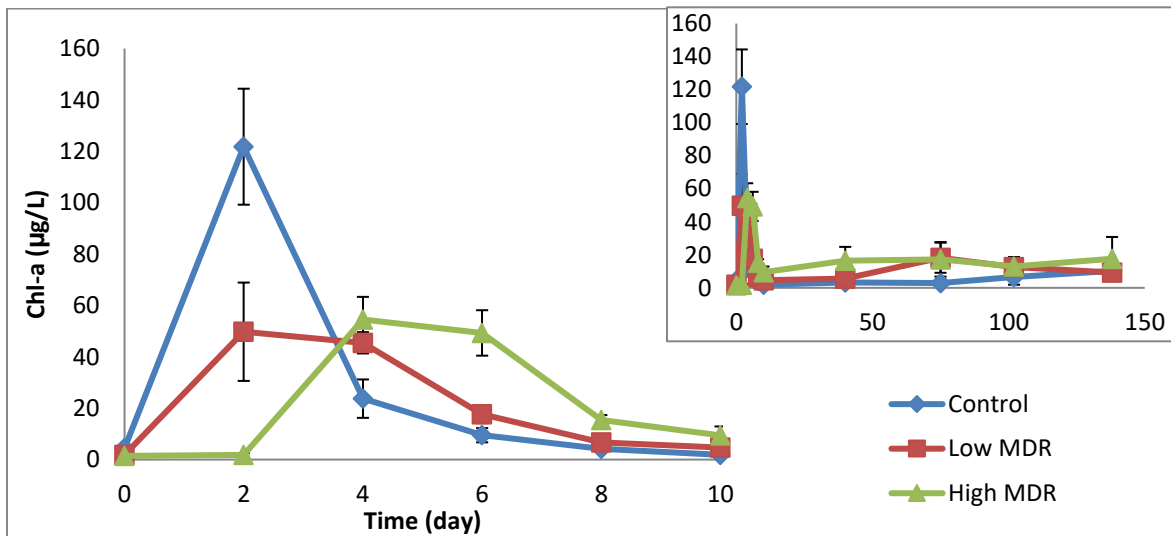


Figure C 2. Chlorophyll a (Chl-a) concentrations of three treatments over the study time. Data are mean \pm SD. Original figure shows details of the first 10 days of the study while insert figure shows entire 138-day study period.