

The Fate and Bioavailability of Resuspended Phosphorus in Lake Erie's Western Basin

Connor Gluck

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Thesis Committee:

Dr. Casey Godwin, Primary Advisor

Dr. Allen Burton

Abstract

Lake Erie regularly experiences harmful algal blooms (HABs) that occur as a result of eutrophication from excess phosphorus (P) inputs. Due to this history of eutrophication, there is a large pool of P in the sediment of Lake Erie. Given the lake's shallow western basin, and large fetch, this sediment P is regularly physically mixed into the water column. In other shallow lakes, this resuspended P is a source of bioavailable P (BAP) and contributes to primary production in the water column. However, the fate and bioavailability of this mechanically resuspended sediment P in Lake Erie has not previously been quantified. To investigate this, I took sediment cores harvested from Lake Erie's western basin and increased the shear stress to resuspend sediment into the water column. I then took this resuspended water and diluted it with overlying lake water to simulate in-lake dilution of suspended sediment. The water was mixed for 48 hours in darkness while I took samples for nine functional fractions of P at regular intervals. Additionally, I investigated if small changes in pH affect the release of bioavailable P from the sediment by artificially lowering the pH of the overlying water prior to adding the resuspended water in duplicate units. I found that the majority of resuspended phosphorus is in particulate forms, and that a smaller percentage of these forms is bioavailable than in the Maumee River. Additionally, I found that total concentrations of P forms were stable over 48 hours regardless of the sediment resuspension, suggesting that sorption-desorption processes do not play a large role in changing the net bioavailability of P. I estimated that a mild resuspension event could result in a release of 2.782-8.381 mg/m² of DRP, which would not be removed from the water column by sorption processes. This is larger than the daily release in the western basin from diffusive fluxes and represents an estimated 15.21% of DRP in the water column. These findings are important for determining how sediment resuspension may affect BAP in the water column, and their potential contributions to primary production in the western basin.

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Acronyms

BAP	Bioavailable phosphorus
DAHP	Dissolved acid-hydrolyzable phosphorus
DAPI	4',6-diamidino-2-phenylindole
DRP	Dissolved reactive phosphorus
EPC	Equilibrium phosphorus concentration
EPIP	Exchangeable particulate inorganic phosphorus
ER	Evidence ratio
GLWQA	Great Lakes Water Quality Agreement
HAB	Harmful algal bloom
IJC	International Joint Commission
P	Phosphorus
PAHP	Particulate acid-hydrolyzable phosphorus
SRE	Sediment resuspension event
SRP	Soluble reactive phosphorus
TDP	Total dissolved phosphorus
TP	Total phosphorus
TPP	Total particulate phosphorus
TSI	Trophic State Index
TSS	Total suspended solids
VSS	Volatile suspended solids

Introduction

Globally, eutrophication is one of the primary stressors on water and habitat quality in marine and freshwater systems (Istvanovics 2010; Smith 2003). In phosphorus (P) limited systems excessive input of P can lead to eutrophication, hypoxia, and harmful algal blooms (HABs) (Istvanovics 2010). In the mid-20th century, Lake Erie experienced frequent HABs due to an excessive influx of phosphorus from point and nonpoint sources, severely degrading the water quality of the lake (Depinto et al. 1981). The frequent algal blooms and decline in water quality led to the passage of the Great Lakes Water Quality Agreement (GLWQA), that set targets on the annual total phosphorus load into Lake Erie. However, despite a decrease in algal bloom severity and improved water quality following the passage of the GLWQA and other changes, HABs have increased in severity since the late 1990s and early 2000s (Watson et al. 2016). HABs, including those in Lake Erie, are projected to become even more severe due to global climate change, which will increase temperatures, increase precipitation and runoff, and alter the pH within the Great Lakes (Gobler 2020; Phillips et al. 2015).

Predicting the intensity or distribution of HABs based on environmental conditions such as nutrient availability is a priority for both forecasting and predicting responses to current or changing management scenarios. Models predicting HABs based on bioavailable P (BAP) loads are better predictors of bloom biomass than those based solely on total phosphorus (TP) loads (Stumpf et al. 2016; Bertani et al. 2016). The proportion of BAP is critical in the development of HABs because it is more readily accessible by phytoplankton (Logan et al. 1979). The BAP load is not always correlated with TP loads across space or time (Baker et al. 2014). In Lake Erie, there may be an increased sensitivity to P loads, particularly the bioavailable loads (Bertani et al. 2016). The importance of BAP has been seen in practice in Lake Erie, as lower DRP loads in 2019 due to less agricultural application in a watershed led to a smaller than predicted HAB that year (Guo et al. 2021). Although monitoring watershed inputs of total and bioavailable P is useful for seasonal forecasts and long-term management, there is also a need to understand how P is transformed and processed once in the lake.

In lakes with long histories of P eutrophication, excess P from tributary input of particles or from primary producers will settle and create a large pool of nutrients in the sediment (Sonzogni et al. 1982; Orihe et al. 2017). This sediment pool of P may contribute to HAB formation and reduce the efficacy of external load reductions (Orihe et al. 2017; Welch & Cooke

2005; Ho & Michalak 2017). Once in the sediment, P can either be permanently immobilized, or recycled into the water column through a set of distinct processes collectively known as internal P loading (Søndergaard et al. 2001). Internal P loading consists of all physical, chemical, and biological processes which mobilize and transport P from the benthic environment to the overlying water column (Orihe et al. 2017). Sediment anoxia can lead to release of sorbed SRP to the overlying water (Anderson et al. 2021; Matisoff et al. 2016). There is evidence that sediment P meaningfully contributes to P concentrations in the water column in the western (Elsbury et al. 2009) and especially central basins of Lake Erie (Anderson et al. 2021; Nürnberg et al. 2019). It is unlikely that this internal P loading alone can trigger an algal bloom, but rather has potential to intensify or sustain HABs (Ho & Michalak 2017; Matisoff et al. 2016). Additionally, this diffusive process requires stable stratification of the water column which is not typical of the shallow western basin where HABs typically occur. P can also move from the sediment to the water via mechanical resuspension (Søndergaard et al. 2001) which can involve sorption-desorption processes and other biogeochemical transformations.

Sediment resuspension events (SREs) have been shown to result in much larger increases in BAP than diffusive fluxes in several small systems (Kristensen et al. 1992; Dapeng et al. 2011; Niemisto et al. 2011), but the relative bioavailability of that resuspended P has not been characterized in Lake Erie. Given the substantial differences between Erie and smaller lakes, those published results might not be directly applicable, but demonstrate SRE as a potential source for BAP. In Lake Michigan, a recurrent coastal sediment plume is a key driver of spring primary productivity in the southern nearshore of the lake (Lohrenz et al. 2004; Johengen et al. 2008; Vanderploeg et al. 2007). The western basin of Lake Erie is shallow with a large fetch which allows for the build-up of more energy to create larger waves and resuspend large sediment loads (Kang et al. 1982; Lick et al. 1994). This is substantiated by the estimated proportion of suspended matter in the water column that originates from the benthic layer in Lake Erie, which ranges from 83-94% in the nearshore and 62-75% in the offshore region, indicating a role for resuspended material in the water column (Matisoff and Carson 2014). Still, there is a knowledge gap about the potential contribution of physically resuspended P to BAP in the water column, which may support primary production.

Once sediment phosphorus is resuspended, little is known about its fate or how the relative bioavailability may change in Lake Erie. The release of BAP from the sediment during

SRE is not dependent solely on the shear stress on the sediment, but also on the environmental conditions of the water column (Søndergaard et al. 1992). Variation in sediment composition, water temperature, redox conditions, and pH all influence the equilibrium P concentration (EPC) which influences the release of BAP from sediment during resuspension (Gibbons & Bridgeman 2020; Koski-Vähälä et al. 2000; Katsev et al. 2006, Mayer & Jarrell 2000). BAP concentrations could increase or decrease over time following the initial resuspension depending on the conditions in the lake (Niemisto et al. 2011; Wang et al. 2022). King et al 2022 found that less suspended sediment in the Maumee River led to an increase in BAP transported to Lake Erie, because the lack of sediment provided fewer sorption sites for the BAP. This suggests an increase in suspended sediment could be a sink for suspended phosphorus. The concentrations in BAP also could increase over time as more P may be released with prolonged exposure to a turbulent water column with a different EPC than the sediment. The net effect of these processes could vary seasonally within the lake, with SRE being a source or a sink for BAP with changes in temperature or other environmental conditions (Huang et al. 2018)

Changes in pH can have significant influence on the release of P through diffusive flux and resuspension (Jacoby et al. 1982; Koski-Vähälä et al. 2000). Freshwater that is more basic (>9 pH) and more acidic (<5 pH) both lead to significant increases in the P release from sediment during resuspension (Koski-Vähälä et al. 2000). At high pH conditions (which can occur in later summer months due to CO₂ uptake by algal blooms) the intensified P release is believed to be due to an increase in competition between hydroxide and phosphate ions for sorption sites (Koski-Vähälä et al. 2000; Niemisto et al. 2011). Under more acidic conditions, aluminum and iron bound P, and authigenic calcium P may dissolve and form a more bioavailable weakly adsorbed P (Ge et al. 2017). Koski-Vähälä et al investigated how large changes in pH affected P release, while Ge et al. 2017 demonstrated that smaller changes in pH, such as those from climate change induced acidification, can also lead to increases in BAP release. It is unclear if the expected drop in pH from acidification for the Great Lakes (0.3-0.4 pH units, Rowe et al. 2020) is significant enough to impact sorption of P in relation to SRE loads in Lake Erie given the differences in sediment characteristics. However, natural and anthropogenic drivers other than climate change influence the pH in the lakes, so the relationship between BAP flux during SRE and small changes in pH requires study (Geller and Schultze 2009).

In this study I investigate the effects of site, season, and pH on the fractionation and fate of physically resuspended BAP. The four primary questions driving this research are: 1) What is the release of P from the sediment during sediment resuspension events in the western basin? 2) What is the relative bioavailability of P that is resuspended during SRE? 3) Does relative bioavailability of resuspended P change over time while in the water column? and 4) how do environmental conditions affect the bioavailability and fate of the resuspended P? I hypothesized that relative bioavailability of P decreases following resuspension due to sorption of DRP to suspended material. Additionally, I hypothesized that decreases in pH will lead to a relative increase in DRP concentrations over time. Results from my experiment provide an insight on the relative bioavailability of P resuspended in Lake Erie's western basin and the potential for SRE to contribute to HABs in the shallow eutrophic basin.

Methods

Core Collection

Lake Erie's western basin is the shallowest of the three basins with a mean depth of 7.4 meters. I collected sediment cores at sites WE2 and WE12 (figure 1) that correspond to long-term routine monitoring by NOAA GLERL and CIGLR (NCEI, www.ncei.noaa.gov). Two cores were harvested and used for each site. Multiple sites were chosen to evaluate variation in resuspension from different substrate characteristics and sediment deposition environments. Each site had a depth of 6 meters. WE2 is nearer the mouth of the Maumee River and has a soft, muddy sediment substrate. WE12 is closer to the shore and has a coarse substrate texture and a larger population of Dreissenid mussels on the substrate. Coring was performed on May 31 at WE2 and on July 7 at WE2 and WE12. Multiple coring dates were used to account for seasonal variation in the P fractionation of the sediment. Coring on May 31 occurred prior to the formation of an algal bloom and coring on July 7 occurred while a bloom was already occurring.

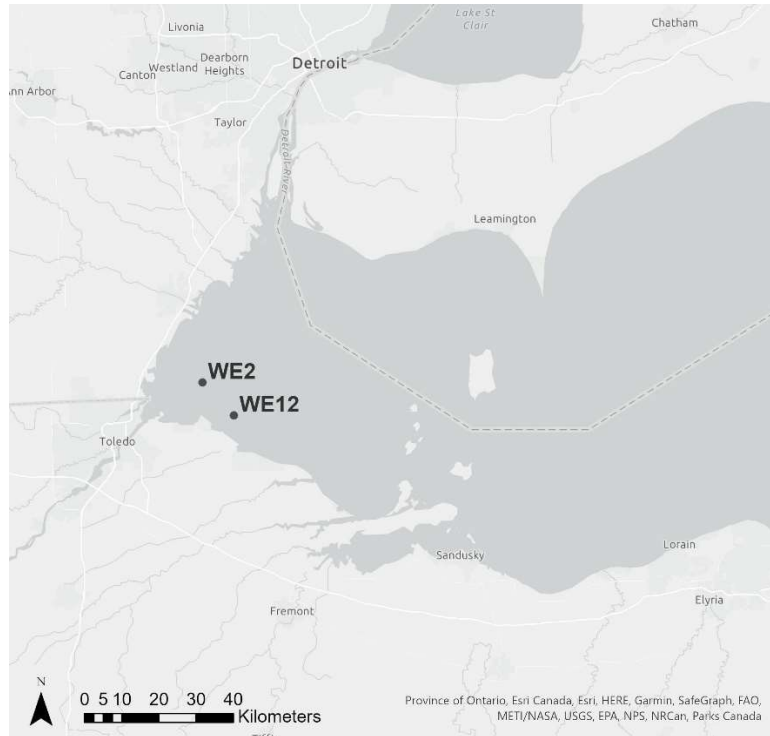


Figure 1: Map of coring sites for study.

Cores from WE2 were harvested using a gravity box corer to obtain an undisturbed benthic sediment and overlying water from the sites. To acquire a sample from locations (WE12) that could not be penetrated with the box corer, I used a Ponar grab to collect sediments. The Ponar jaws were opened slowly with the bottom of the grab resting on a petri dish with an outside diameter equal to the inside diameter of the core barrel (dish height 3 cm). The core barrel was then immediately pressed down onto the contents of the Ponar and the dish, then sealed as for the regular coring procedure. Given that the sites requiring the Ponar approach had more consolidated sediments with larger gravel and mussel shells, this approach satisfactorily retained the soft surface sediments and vertical layering of the material. Experimental cores were collected using polycarbonate cylindrical cores (length 30.5 cm, internal diameter 14.6 cm). One experimental core was collected from each box core. At least two cores were harvested from each site during each trip. I also collected overlying water from each site for use as a control and for dilution in the experiment. Cores and water were stored in coolers for transport and incubated in a darkened controlled climate room at lake temperature for at least 12 hours to allow for resettling of any disturbed particles before beginning the experiment.

Resuspension and Mixing Experiment

The resuspension experiment was modified from the technique used by Kalnejais et al 2007. For each core, a 76.2 mm diameter stainless steel impeller controlled by a stepper motor was suspended 5 cm above the surface water interface. The impeller was mounted at the end of a stainless-steel shaft coupled to a stepper motor. An acrylic baffle (**figure 2**) with an internal diameter of 13.2 cm and height of 10.0 cm was slowly lowered into the core, which prevented the formation of a vortex during the impeller rotation. The inside of the baffle has size strips of 15.5mm by 3.35 mm affixed in a radial pattern at 60° increments with respect to the center. The rotation rate of the impeller was increased at increments of 25 rpm every 8 minutes until bulk sediment resuspension was observed (by 150 rpm), where it was held for 8 minutes prior to sampling (equivalent to 0.104488 Pa shear stress). A separate calibration was performed to convert the rotation rate of the impeller to shear stress using the Shields curve or parameterization (Soulsby and Whitehouse 1997; Kalnejais et al. 2007). The water containing the resuspended sediment was removed by siphon and immediately sampled or mixed with lake water to mimic resuspension in the water column. Water from two experimental cores for each site was used for further treatment and sampling. I took samples of the resuspended water for total phosphorus (TP), total particulate phosphorus (TPP), and soluble reactive phosphorus (SRP). These samples were taken for each individual core and from the combined resuspended water from both cores.

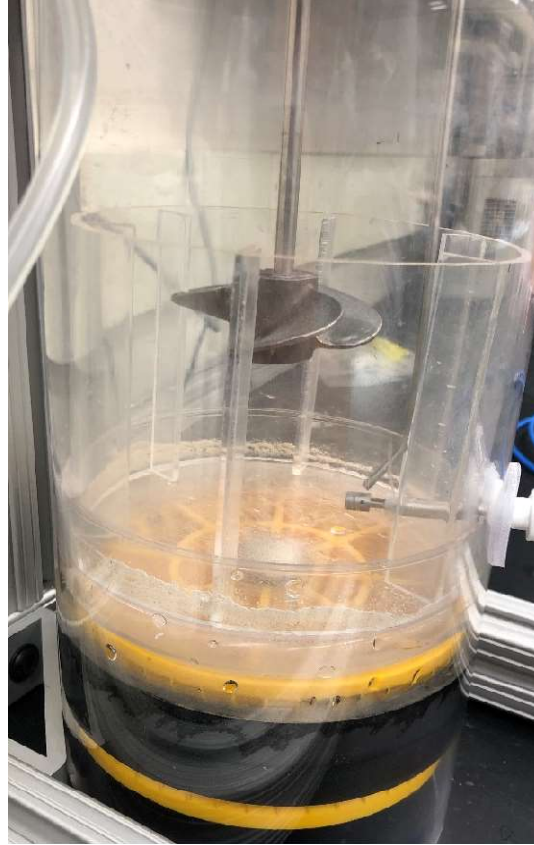


Figure 2: Example set up of experimental core with baffle and impeller in place.

Resuspended water (500 mL) was added to 7.5 L of overlying water to simulate mixing of the resuspended sediment across the entire 6 m deep water column. I then sampled this water for all 9 functional P fractions (described below in *Phosphorus Analysis*). This water was then divided into two clear round 4 L Nalgene® bottles used as duplicate experimental units. Additionally, 4 L of overlying water from the site containing no resuspended sediment was added to a separate 4 L bottle for use as a control. This process was repeated using overlying water with the pH artificially lowered by 0.3 pH units. The pH of the site water was measured using a pH meter, and then hydrochloric acid was added incrementally to 12 L of site water until the desired drop in pH was achieved. This artificially acidified overlying water was then split and used for control and experimental units as described above. A breakdown of the experimental units and experimental design is shown in **figure 3**. This process was repeated using two cores from each site for each sampling date.

Each bottle was inverted 4 times to ensure complete mixing and placed horizontally on roller racks rotating the bottles at 4 rpm for a period of 48 hours. The roller racks were kept in darkness in a climate-controlled room to minimize the effects of photosynthesis and phytoplankton uptake on changes in P bioavailability. Temperature was maintained at 18.5 °C for the May experiment and 24.0 °C for the July experiments, corresponding with the temperature of the bottom waters at the time of coring. Samples were taken from each experimental unit prior to being placed on the roller racks, and then 1, 6, 12, 24, and 48 hours after the start of the experiment. Bottles were inverted 4 times at each sampling period to ensure complete mixing. Samples were taken from one experimental unit at a time, with the order of experimental unit sampling and the order of P fraction sampled for randomized. I collected samples using a 50 mL syringe and a syringe filter holder. Samples were processed immediately after collection using 0.7 um Whatman glass fiber filters. Particulate fractions were collected on the filters, which were frozen at -20 °C until analysis. Samples were analyzed within 6 months of collection. Dissolved fractions are defined as those that passed through the 0.7 um glass fiber filter. I collected these fractions in polypropylene centrifuge tubes which were then also frozen at -20 °C until analysis. Following sampling, water in the 4 L experimental unit bottles was not replaced. All materials, including the 4 L bottles, syringes, filter holders, and carboys were acid-washed to remove trace amounts of P prior to use in the experiment. A new acid-washed syringe was used for each experimental unit at each timepoint.

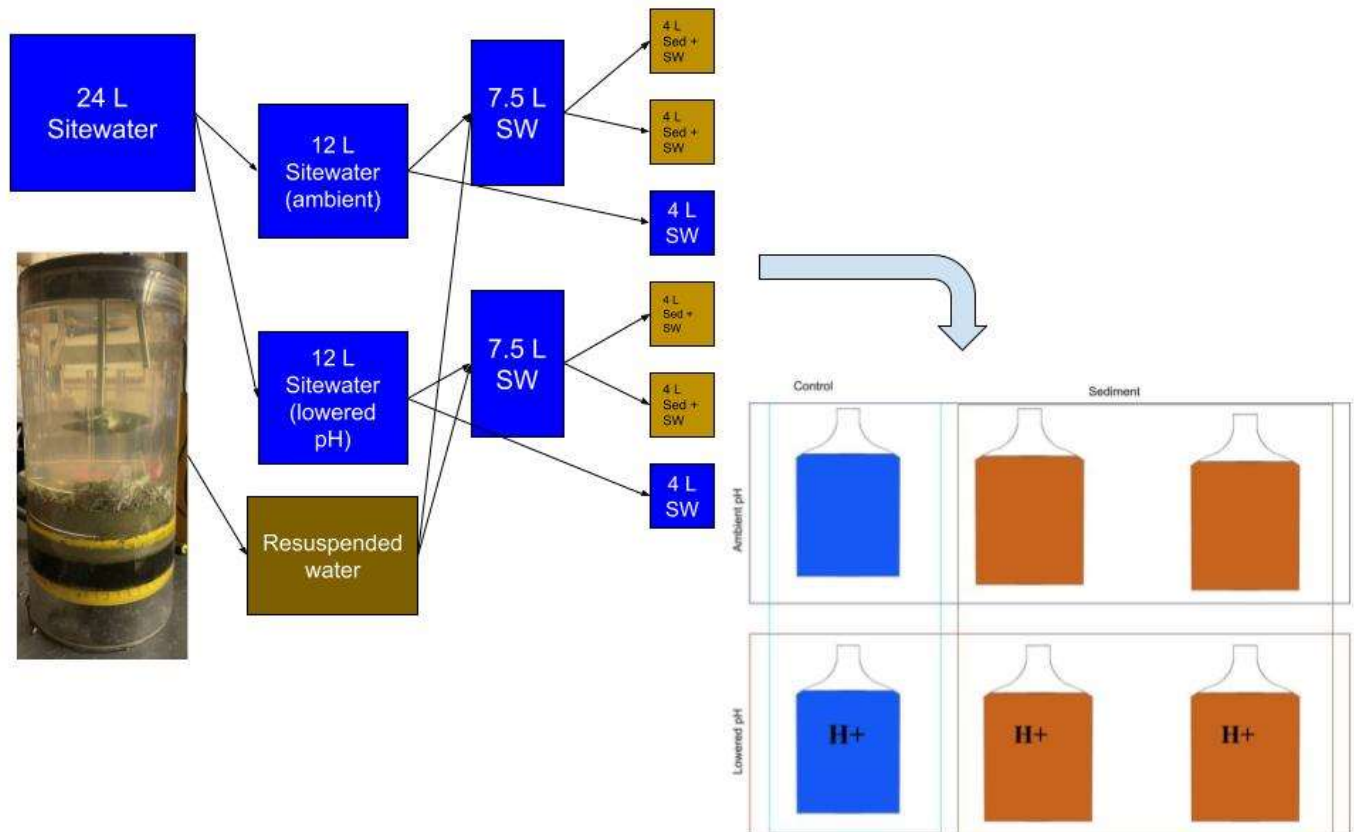


Figure 3: Experimental design and treatment breakdown. Resuspended water from each core (1 L from each) was mixed together before 500 mL of it was mixed with 7.5 L of sitewater that was then split into the experimental unit bottles. Each experiment had 6 bottles, 2 controls (one for each pH) and 4 which received sediment (2 at each pH). The treatments were the same across all experiments for each site and season.

Phosphorus Analysis

Particulate P fractions measured included total particulate phosphorus (TPP), exchangeable particulate inorganic phosphorus (EPIP), and particulate acid-hydrolyzable phosphorus (PAHP) (Baker et al. 2014). Dissolved P fractions measured include total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP), and dissolved acid-hydrolyzable phosphorus (DAHP). DRP and EPIP are considered the most bioavailable fractions, while PAHP and DAHP are less bioavailable, labile forms of P measured (Baker et al. 2014). The remaining measured P is considered recalcitrant and not bioavailable. DAHP measured includes DRP within the measurement and PAHP measured likely includes much of the EPIP. Measurements were also made from particulate filter samples of total suspended solids (TSS), volatile

suspended solids (VSS), and two biomolecule fractions of P: polyphosphate and phosphorus from RNA and DNA.

All non-biomolecule fractions of P were measured using the ascorbic acid molybdenum method (Hansen and Koroleff 1999) following the digestion steps described in Baker et al and Laramie et al (in review). Absorbance was measured at 880 nm using a SEAL® AQ400 discrete analyzer. Briefly, TP, TDP, and TPP were measured after digestion with 0.025 M potassium persulfate with 0.045 M sulfuric acid at 121 °C for 30 minutes in an autoclave. PAHP and DAHP samples were autoclaved at the same temperature and duration with just 0.045 M sulfuric acid and no persulfate. For EPIP samples, 0.1 M sodium hydroxide was added to each sample and allowed to extract for 16 hours with shaking prior to being neutralized with HCl and centrifuged prior to analysis (modified from Cowen and Lee 1976; Williams et al. 1967). DRP samples received no digestion treatment prior to the ascorbic acid molybdenum treatment. I made primary standards from a NIST-traceable phosphate solution (Hach Company) and each analytical run included method blanks, a QA/QC standard, and two different recovery standards: Trace Elements in Spinach (NIST 1570a), and Inorganics in Marine Sediments (NIST 2702). Filter blank samples were used where appropriate as well for a blank correction of fluorescence caused by filter particles. Measurements below detection limit were reported as 0 for statistical analyses.

I measured RNA and DNA of the seston using an extraction and quantification method described in Gorokhova and Kyle 2002 and Phillips et al. 2017. The method uses Ribogreen, a fluorophore, which fluoresces when bound to RNA and DNA. In half of the samples, RNA is hydrolyzed with RNase while the other half receives no RNase. The fluorescence in the RNase-treated samples is considered to be exclusively from DNA while the difference between the raw and RNase treated samples provides the measure of RNA. Fluorescence was measured in 96-well microtiter plates with triplicate technical samples using a Synergy Biotek H2 plate reader with excitation at 485 nm and emission at 528 nm. Commercial standards for RNA and DNA were obtained from Fisher Scientific.

I measured polyphosphate using a method modified from Aschar-Sobbi et al. 2008 where polyphosphate forms a fluorescent complex with DAPI (4',6-diamidino-2-phenylindole). A nuclease is added to each sample to hydrolyze the nucleic acids and prevent their fluorescence with DAPI from interfering in the measurement of polyphosphate. Additional interference can

occur from the fluorescence of DAPI with the buffer compounds. To account for this, in half of the samples the fluorescence from polyphosphate is quenched by the addition of magnesium chloride. The difference between the quenched and unquenched fluorescence is considered to be solely from polyphosphate. Fluorescence of extracted samples was measured in 96-well microtiter plates with 4 technical samples using a Synergy Biotek H2 plate reader with excitation at 415 nm and emission at 550 nm. Polyphosphate standards were prepared from sodium phosphate glass (Sigma S4379).

Statistical Analysis

I fitted separate hierarchical models for each phosphorus fraction as a linear relationship with time and evaluated the effects of pH treatment and sediment treatment. I additionally fitted an intercept based on sediment treatment to estimate the increase in phosphorus concentration for those units which received resuspended sediment. Initially, a nested grouping effect of experimental unit was included to acknowledge the non-independence of these samples, but this did not improve model fit based on a LOO comparison. The final model included fixed effects of time, pH treatment, and sediment treatment and a grouping term of combined site and season acting on those fixed effects. All models were built using the ‘brms’ package in the statistical software R, which compiles code that is then run in stan (Bürkner, 2018). Bayesian Regression models were fitted with a Markov Chain Monte Carlo with four chains. Each chain was allowed to warmup for 5000 iterations before sampling from 5000 iterations. I used weakly informative priors for each model, setting the mean to zero and variance to seven for each slope. I assessed convergence of the chains using the r-hat statistic (Gelman et al. 2018), which was found to be less than 1.01 for all parameters. I used evidence ratios (ER) to quantify support for select hypotheses. Briefly, the evidence ratio is the quotient of the number of posterior draws consistent with the hypothesis over the number of posterior draws inconsistent with the hypothesis (Johnson 2013).

The initial concentrations of measured fractions were extracted from the modeled intercepts. This incorporates the uncertainty of measurements at the start and throughout the experiment into the estimates of the values. I estimated the release of DRP from a sediment resuspension event based on the measured DRP values from the pre-dilution resuspended water from each sediment core, the overlying water volume for each core, and the area of sediment

within the core. The contribution of an SRE to background DRP concentrations was calculated assuming it was completely mixed in a 6 m deep water column.

Results and Discussion

Magnitude and Proportion of Resuspended Phosphorus

My first question for this study was regarding the potential release of sedimentary P during SRE. **Figure 4** shows that for TPP, there was an average increase in concentration of 31.56% with the inclusion of resuspended sediment. There was strong support for this increase for WE2 for both May (ER = 4999) and July (ER = 952) and some support for this increase for July WE12 (ER = 50). Additionally, there was strong support that TPP was higher at WE2 than at WE12 (ER = 4999) and weaker support for higher concentrations of TPP in July than May (ER = 129). For PAHP, the change was an average of an 21.39% increase, but there was only weak support for this increase (ER = 15). For DAHP, there was support for an increase of 20.89% in concentration for July WE2 (ER = 144), but only weak and inconsistent support for increases for July WE12 or June WE2 (ER = 19). For the rest of the measured fractions, TDP, DRP, and EPIP, the changes between control and sediment treatments were smaller and inconsistent and had no support or weak support (ER = 18). There was strong support that DRP concentrations were higher at site WE2 than WE12 (ER = 4999) and higher in July than in May at WE2 (ER = 4999). There was also strong support that TDP concentrations were greater in July than in May (ER = 4999) but only weak support for a difference across sites (ER = 78). For EPIP, there was no support for a difference in concentrations between sites (ER = 2) or seasons (ER = 14). Given the lack of statistical difference between sediment treated units and control units for TDP, DRP, and EPIP, these differences between site and season are not necessarily indicative of any spatial or temporal variation in the resuspended sediment fractionation.

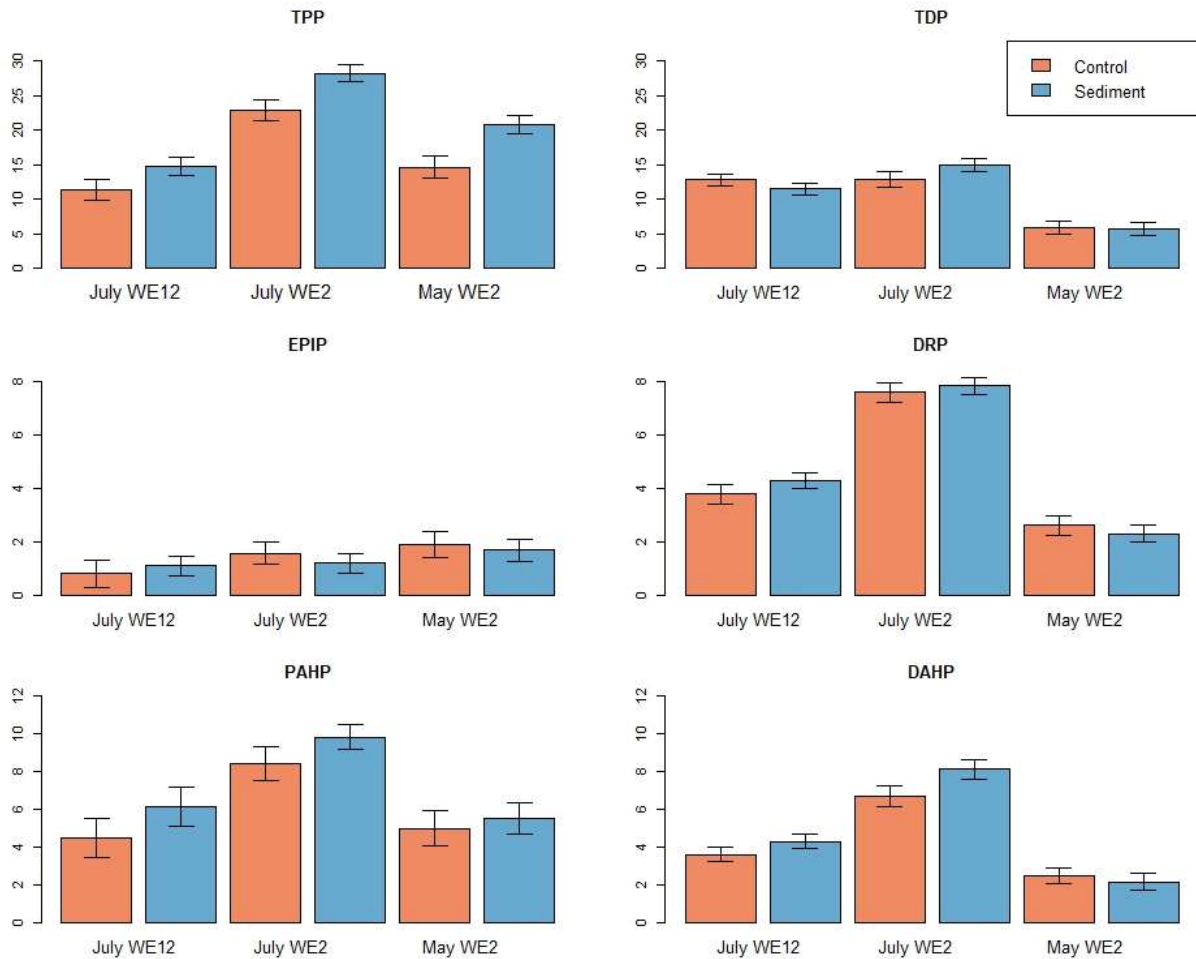


Figure 4: Comparison of magnitude of each phosphorus fraction. Experimental units which were pH-treated are not included. All measurements are in ug/L from the beginning of the experiment prior to any mixing. Values are the extracted intercepts from the hierarchical models for each fraction and the error bars are the measures of uncertainty for those intercept estimates.

My second question was regarding the relative bioavailability of P that is resuspended. **Figure 5** shows that the majority of phosphorus in water with resuspended sediment was in particulate forms. The highest proportion of TP that was particulate occurred at WE2 in May (78.51%) while the lowest proportion was particulate at WE12 in July (56.25%). Following the resuspension, the proportion of TP that was particulate increased by an average of 6.01%. The largest increase in proportion for TPP was at WE12 in July, where the proportion of TP that was particulate increased by 9.12% with the addition of the suspended sediment, while the smallest increase was at WE2 in May (1.53%). The change in proportion of TPP with the suspended sediment was the largest of any of the fractions. Only a small portion of this TPP is bioavailable. On average, 6.71% of the resuspended TPP was comprised of EPIP. The highest portion of TPP

was EPIP at WE2 in May and the lowest portion was EPIP in July at WE2. This is a smaller proportion of TPP than in the Maumee River which ranged from 20.1-28.0% (Baker et al. 2014). This suggests a shift in fraction once sediments reach the lake and settle to the benthos. This shift could be due to differences in sorption dynamics in the benthic lake sediment and uptake of the desorbed DRP by algae. It is also notable that only a very small portion of the measured TPP was found in biomolecules. Less than 1% of the measured TPP was from RNA and DNA and no polyphosphate measurements were above the minimum detection level. This is in contrast to pelagic areas where a higher percentage of TPP is in the form of biomolecules (Labry et al. 2013; Hu et al. 2022). This suggests that not only is most of the resuspended sediment TPP not bioavailable, much of it is associated with minerals and not organic matter.

The proportion of TP that is bioavailable did not change with the addition of suspended sediment. Compared to TPP, a higher portion of the TDP was bioavailable. On average, 43.56% of the measured TDP was comprised of DRP. This is again lower than in the Maumee River where DRP made up approximately 86.9% of TDP. The highest proportion occurred in May at WE2, and the lowest proportion occurred in July at WE12. It is notable that the highest proportion of bioavailable P in the sediment in both particulate and dissolved forms occurred in May, prior to the formation of the large algal bloom. However, DRP still only comprises a smaller portion of the TP in the water column, 14.43% on average. This contrasts with other work that has shown or attributed a large increase in DRP following SRE (Søndergaard et al. 1992; Koski-Vähälä & Hartikainen 2001; Kalnejais et al. 2010; Matisoff et al. 2017; Niemisto et al. 2011) One possible explanation for this is that my study methodology was meant to resuspend only the topmost layer of sediment, simulating a mild resuspension that occurs more frequently. Deeper scouring and erosion from a higher shear stress would expose anoxic layers of the sediment which should lead to a large increase in DRP. The small increase in BAP concentrations across the water column increases the importance of any transformation of BAP following the resuspension for the potential contribution of SRE to water column BAP.

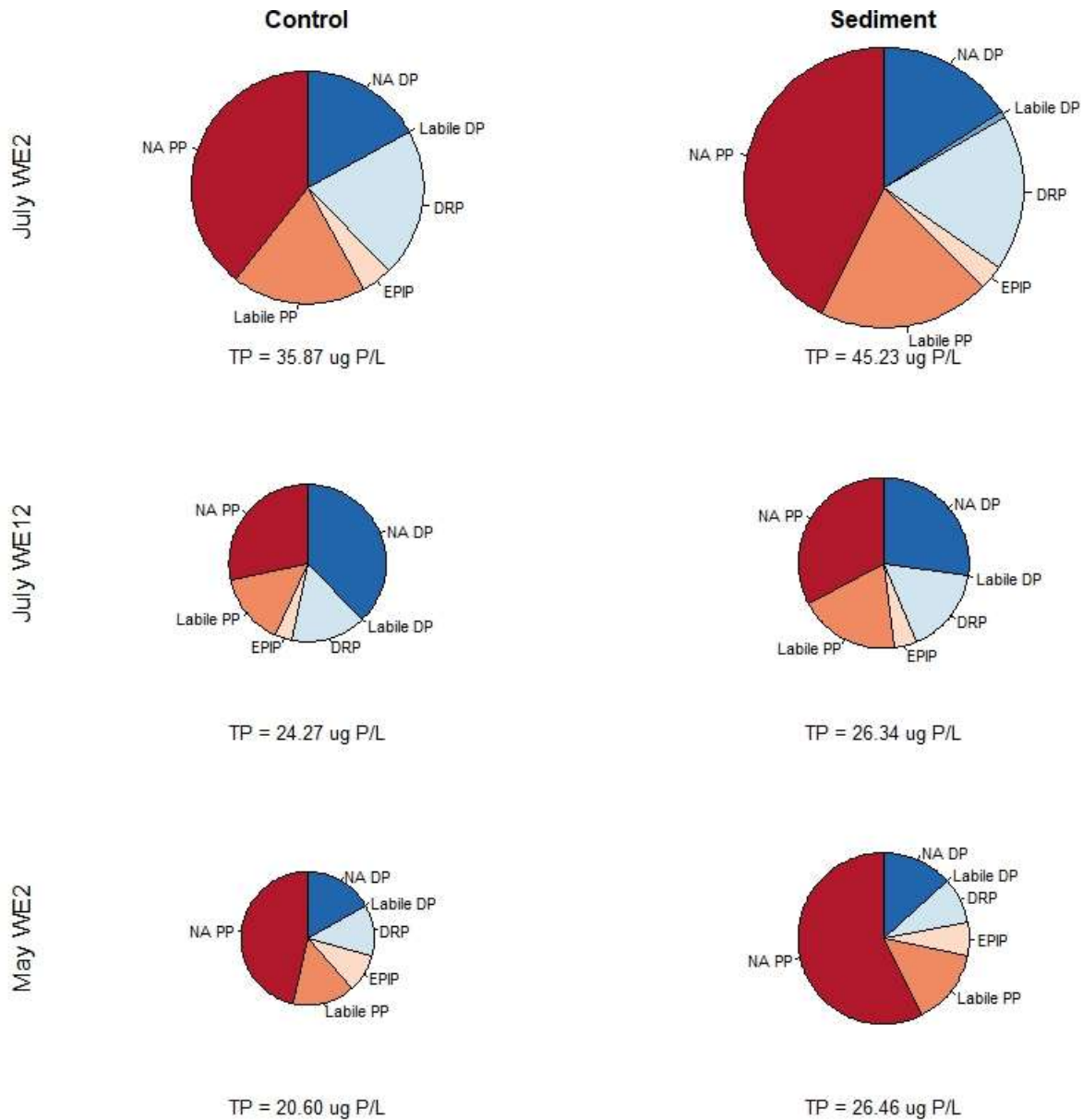


Figure 5: Relative proportion of each fraction measured at the starting point prior to any mixing. The radius of each chart is proportional to the calculated total phosphorus for that treatment (sum of TDP and TPP). Labile PP is the fraction of PAHP that does not include EPIP while labile DP is the fraction of DAHP that does not include DRP. NA PP is the non-bioavailable portion of TPP that does not include PAHP while NA DP is the portion of TDP that does not include DAHP.

Transformation of Resuspended Phosphorus

My third question was regarding how the relative bioavailability of P changed following resuspension. I hypothesized that bioavailable P forms would decrease over time following resuspension due to sorption to suspended material. DRP concentrations did not decrease over time and there was no increase in TPP or EPIP that would be expected if sorption was occurring. When considering for all experiments, concentrations of DRP did not increase or decrease over time (population level ER = 2). The same held true for individual experiments for July WE12 or May WE2 (ER = 5). For the July WE2 experiment there was support for a DRP concentration increase by 1.44 $\mu\text{g/L}$ each day (ER = 1818). There is no evidence to support that the inclusion of resuspended sediment had any effect on changes in DRP concentration considering all experiments (population level ER = 2) or for any individual experiment (ER = 4). This suggests that the change in DRP for July WE2 was not related to the sediment resuspension. Further, there is also no support for a change in TPP or EPIP concentrations time for July WE2 (ER = 9) with or without sediment (ER = 3) that would be expected with desorption processes related to resuspension. TPP and EPIP concentrations did not change with time when considering for all experiments (population level ER = 3) or within any experiment individually (ER = 17). The inclusion of suspended sediment did not have any impact on the slope for TPP and EPIP concentrations over time when considered for all experiments (ER = 3) or within any individual experiment (ER = 7). There is no support for any sorption or desorption of P following the resuspension and mixing of sediment across the water column. Therefore, there is no support for my hypothesis that BAP would decrease over time following resuspension.

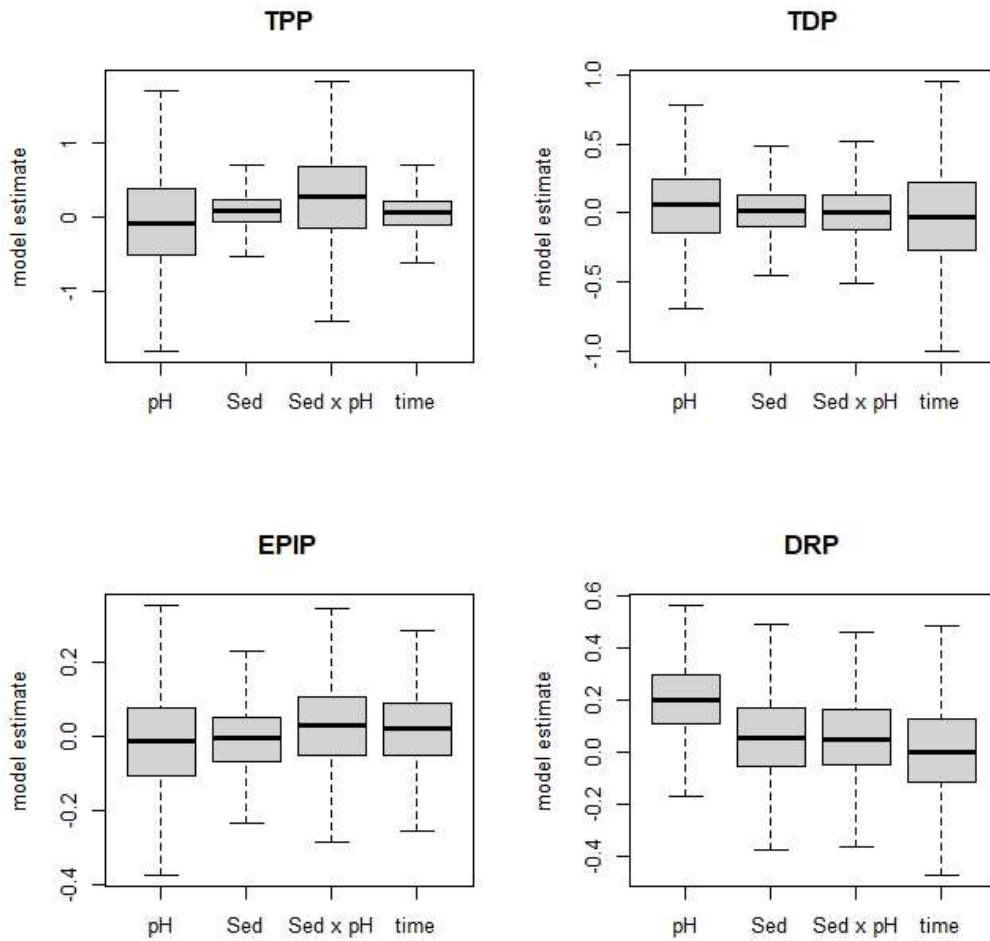


Figure 6: Population-level model estimates for slope of concentration over time and deviation from that slope based on pH treatment, sediment treatment, and the interaction between pH and sediment treatments. Values shown are distributions based on the mean and standard deviation of the posterior model draws.

These findings are different from those in King et al 2022, which found that P sorption dynamics play an important role in reducing BAP concentrations when suspended sediment concentrations in the Maumee River increased. King et al 2022 found that sorption increased with increasing riverbed sediment and with increases in DRP. The difference in my findings from King et al 2022 could be due to several reasons. First, the suspended sediment from runoff in the Maumee River during the high flow events may have spent less time in the water than the sediments from offshore Lake Erie and may not have been exposed to high phosphate concentrations long enough to equilibrate. Therefore, the suspended material has more available

sorption sites for phosphate. The benthic sediment in the western basin, especially the uppermost layer, is regularly exposed to DRP concentrations typical in the lake, so that any available sorption sites are quickly used up, preventing any further sorption during resuspension. Secondly, King et al found that most of the sediment in the Maumee River likely reached a quasi-equilibrium with P sorption P before it reached Lake Erie. If the sediment is saturated with P before it settles in Lake Erie, there may be a smaller exchange during subsequent SRE. As discussed earlier, the proportion of TPP that is EPIP in resuspended lake sediment is lower than that in the Maumee (Baker et al. 2014). Finally, the dilution of sediment particles in the water column could reduce their practical capacity to buffer P. A lower sediment-to-water ratio after the dilution lowers the EPC so that sorption and removal of BAP from the water column is less likely (Cyr et al. 2009). This is important when considering the dilution of resuspended BAP across the entire water column. The lack of change in concentrations indicates that sorption-desorption processes do not play an important role in altering the bioavailability of resuspended P from the sediment. Alternatively, that result could mean that the sorption-desorption processes were already at equilibrium between the surface sediment and the overlying water. Additionally, this relationship did not change in the spatial or seasonal variation investigated which suggests that this equilibrium is consistent across the basin spatially and temporally.

Effects of Environmental Conditions on P Transformation

My final question was regarding how environmental conditions would affect any P fraction transformation, specifically relating to seasonality and acidity. I hypothesized decreases in pH will lead to a relative increase in DRP over time. At the population level for each model, there was no support for an increase or decrease in slope based on pH treatment for TPP, DRP or EPIP (ER = 4). Additionally, the inclusion of suspended sediment did not have an effect on the change of slope with pH for any fraction when considering all experiments (ER = 3) or for any individual experiment (ER = 6). For TPP, there is support that a decrease in pH led to an increase in TPP concentration over time for May WE2 by 0.26 $\mu\text{g/L/hr}$ (ER = 229), but not for either site in July (ER = 2). Similarly, for EPIP there is some support for an increase in EPIP concentrations over time by 0.06 $\mu\text{g/L/hr}$ with a decrease in pH for May WE2 (ER = 79), but no support for this effect for either site in July (ER = 2). There is additionally weak support for a decrease in DRP concentrations over time at the lower pH by 0.05 $\mu\text{g/L/hr}$ for May (ER = 91), but not for either

site in July (ER = 9). This difference in pH effect by season may be due to a difference in P concentrations, temperature, or initial pH. The inclusion of suspended sediment did not impact the effect of pH, indicating that these effects are not specifically related to SRE. There is no support for my hypothesis that DRP concentrations would relatively increase at lower pH, but some to support a decrease in DRP over time for May WE2. This indicates that the 0.3 drop in pH did not have much impact on the sorption desorption dynamics for the resuspended P. While pH is an important factor in sedimentary P sorption based on other studies (Koski-Vähälä et al. 2000; Niemisto et al. 2011), small scale variations in pH that may occur due to SRE or HABs were not enough to significantly alter P forms in my samples. This also indicates that any change in lake pH due to climate change will likely not be large enough to influence the sorption dynamics of resuspended P. Seasonal shifts in pH are larger than the 0.3 pH unit shift investigated in this paper. These shifts have been shown to influence P sorption dynamics in other systems (Niemisto et al. 2011) but their potential impact in Lake Erie remains uncertain and would require further investigation.

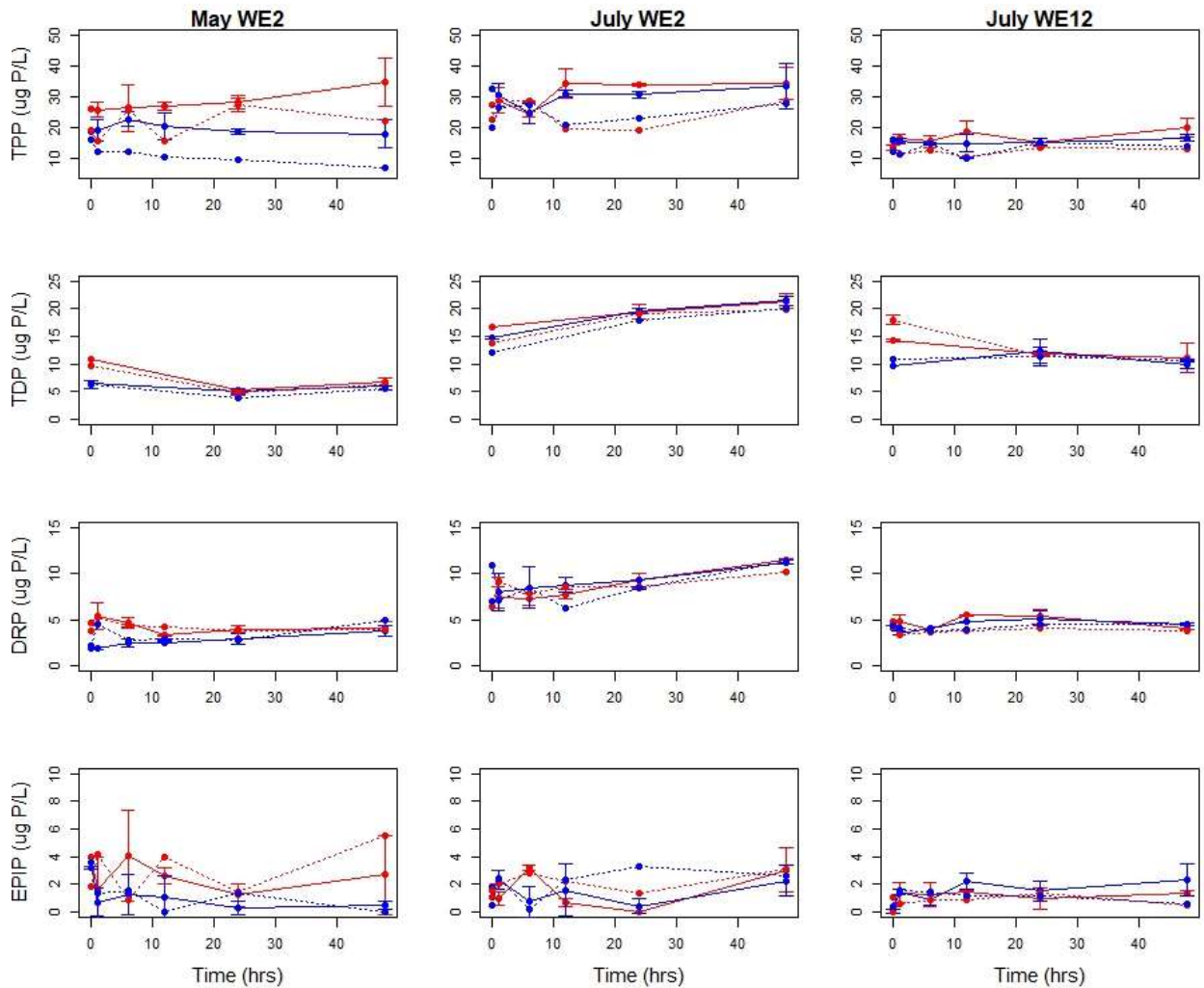


Figure 7: Change in concentration over time for each represented fraction broken down by experiment. The solid lines represent those which received sediment treatment while dashed lines are the control units which received no sediment. The blue lines represent the units which did not receive the HCl pH modification while red lines are those with the artificially lowered pH.

It is also important to discuss the lack of change in P sorption equilibrium across seasons. Huang et al. 2018 found that lake sediment could change from sources to sinks for P based on seasonal changes in temperature and relating to the lake's trophic status. They found that for the moderately eutrophic Gonghu Bay of Lake Taihu (Trophic state index: 64.8) sediments acted as a source for P for summer through desorption and a sink during spring, winter, and fall. While for the lightly eutrophic East Dongting Lake (Trophic state index: 52.6) sediment acted as a source in spring and winter and a sink in fall and summer. Based on a calculation of Carlson's trophic state index (TSI) from TP the investigated sites each had a TSI score between the scores of Gonghu Bay and East Dongting (Carlson 1977). However, there was no sorption or desorption

for either season in this study. One explanation for the lack of a similar seasonal trend is the variation in environmental conditions between the lakes. Huang et al. primarily investigated the influence of temperature on seasonal sorption kinetics, while other factors discussed earlier such as sediment composition and pH will also influence these sorption kinetics for sedimentary P and could vary significantly between the lakes (Cyr et al. 2009; Huang et al. 2018). Secondly, there was little temperature variation between the two sampling dates in this study. While the P concentrations in the water column meaningfully varied between sampling dates, the temperature did not vary by more than 5 °C. Temperature can play a key role in potential P transformation processes and a more robust analysis of variation in temperature and how it affects sorption kinetics for resuspended sediments could reveal different seasonal trends for Lake Erie’s western basin.

Table 1: *DRP release and contribution to background concentrations calculated from the concentrations of resuspended material prior to dilution for the experiment. Mean and standard deviation of fluxes from Matisoff et al. 2016 are based on mean of all cores within 10 km of experiment sites.*

Site/Season	DRP Release (mg/m²)	Contribution to Background DRP Concentration from Release (µg/L)	Water Column DRP from Experiment (µg/L)	Oxic Flux (mg/m²/day) (Matisoff et al. 2016)	Anoxic Flux (mg/m²/day) (Matisoff et al. 2016)
May WE2	2.782 ± 0.892	0.464 ± 0.149	4.627 ± 0.30052	0.426 ± 0.305	8.285 ± 7.282
July WE2	8.381 ± 2.198	1.397 ± 0.366	7.209 ± 0.360	0.426 ± 0.305	8.285 ± 7.282
July WE12	4.106 ± 0.020	0.684 ± 0.003	4.215 ± 0.364	0.71	11.757 ± 13.463

Estimated DRP Release and Water Column Contribution

Table 1 shows a complete breakdown of the release and contribution to water column estimated for a single SRE event. The estimated summertime oxic flux of DRP from the sediment for the western basin ranged from 0.95-1.79 mg/m²/day (Matisoff et al. 2016).

Assuming a single SRE event occurs within a single day, the release of DRP is larger than the oxic flux for both sites and seasons. This is consistent with other published findings where the flux of DRP is greater from resuspension than diffusive mechanisms (Søndergaard et al. 1992). Once diluted across the water column a mild or minor SRE can contribute a background concentration of DRP that is 3.09-9.31% of the IJC target concentration of 15 µg/L for the western basin and an average of 15.21% of average DRP concentration based on the experiment. This is lower than the year-round background contribution of oxic diffusive fluxes from the sediment (Matisoff et al. 2016), but only represents a single, minor SRE. Multiple SREs over short timescales could lead to larger contributions of DRP depending on their timing and frequency. The pool of DRP in the sediment may need to be replenished in between resuspensions (Søndergaard et al. 1992). A replenishment period between May and August was necessary for a similar flux during SRE in Lake Arresø, though this period would likely vary between systems based on the intensity of nutrient loading and of the resuspension.

Implications and Further Investigation

Generally, internal loading in the western basin is not considered a major source of BAP due to its well mixed nature preventing the larger anaerobic fluxes of DRP from the sediment, while not considering mechanical loading mechanisms (Matisoff et al. 2016; Wang et al. 2021). However, my findings suggest that internal loading via mechanical resuspension from wind and waves represents an additional source for BAP in western Lake Erie. The lack of sorption to suspended sediment indicates that dissolved resuspended BAP will likely remain in the water column and be available for uptake by phytoplankton. Multiple SREs per year or larger more intense resuspensions could provide a frequent source of BAP to contribute to HABs. The invasion of the Great Lakes by the Dreissenid mussels has generally increased the importance of benthic-sourced P on the environment (Hecky et al. 2014; Caraco 2009; Li et al. 2021). This only further contributes to the importance of internal sources of P in Lake Erie, including both diffusive and mechanical fluxes. A more robust analysis of the frequency and intensity of sediment resuspension would provide more detail on their overall contributions to BAP in the water column. A more intensive investigation into the EPC at the sediment water interface would reveal more on the sorption dynamics of DRP and EPIP in the topmost layer of the sediment, and how this could vary in the future with continued eutrophication.

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