

**Results from the Internal Phosphorus Loading Study in
Muskegon Lake: Summer, 2020**

Prepared for:

Kathy Evans

WMSRDC, Muskegon, MI

Prepared by:

Alan D. Steinman, Maggie Oudsema, Michael Hassett, Emily Kindervater,
and Bopaiah A. Biddanda

Annis Water Resources Institute, Grand Valley State University, 740 West Shoreline
Drive, Muskegon, MI 49441

December, 2020

I. Introduction

Muskegon Lake was listed as a Great Lakes Area of Concern (AOC) in 1985 due to a long history of environmental abuse (Steinman et al., 2008). Ultimately, nine beneficial use impairments (BUI) were designated for Muskegon Lake, including eutrophication or undesirable algae. Given the many years of discharge from various industries located on the shoreline directly into the lake, total phosphorus (TP) concentrations became elevated, and were averaging $>60 \mu\text{g/L}$ in 1973 (Freedman et al., 1979), indicative of eutrophic conditions.

In the early 1970s, point source discharges were regulated through the Federal Clean Water Act, and over time the TP concentrations have declined in Muskegon Lake. In the past few decades, TP concentrations have been averaging close to or below $25 \mu\text{g/L}$ (Steinman et al., 2008), which was established as the restoration target to remove the eutrophication BUI for the lake. However, P levels have increased slightly over the past few years (unpubl. data), and recent results obtained from the Muskegon Lake Observatory (<https://www.gvsu.edu/wri/buoy/>) suggest that mid-summer hypoxia in the lake may be inducing phosphorus release from the sediments (Weinke and Biddanda, 2018).

Internal phosphorus loading can be defined as all physical, chemical, and biological processes by which phosphorus is mobilized and translocated from the benthic environment (Steinman and Spears, 2020). IPL can delay the recovery of lakes, even after external loading is managed, as diffusion or wind-wave action can promote P release from the sediment into the water column (Jeppesen et al., 2005, Søndergaard and Jeppesen, 2020). This legacy phosphorus in the sediment may be decades old (Carey and Rydin, 2011), and working its way to the sediment-water interface due to concentration gradients within the sediment profile. If IPL is a

significant source of phosphorus to the lake, then new management strategies may be needed to maintain TP concentrations below the restoration target.

Our study was designed to determine the importance of internal phosphorus loading as a source of P to Muskegon Lake. We collected sediment cores from three locations using established protocols (Ogdahl et al., 2014; Steinman et al., 2004), measured sediment P release rates and sediment P fractions.

II. Methods

Site Description:

Muskegon Lake has a surface area of ~17 km², with mean and maximum depths of 7 and 23 m, respectively. Average hydraulic retention time is ~23 days (Freedman et al., 1979). The major inflow (~95% of discharge) to the lake is the Muskegon River, with a navigation channel connecting to Lake Michigan as the primary outflow (Fig. 1). However, reverse flow can occur depending on prevailing wind direction (Liu et al., 2018), pulling Lake Michigan water inland.

Muskegon Lake has suffered from a long history of environmental abuse. Lumbering activity reached its peak in the mid 1880's, when 47 sawmills surrounded Muskegon Lake. After the crash of the lumber industry, due to the unsustainable harvesting practices of the time, industrial activity was attracted to Muskegon, and the lake's shoreline included foundries, metal finishing plants, a paper mill, and petrochemical storage facilities throughout much of early and mid-1990s. As of 2004, before shoreline restoration began, 64% of the lake's shoreline was hardened in some form (Steinman et al., 2008).

Field Methods:

Three sites were selected for sediment core collections (Fig. 1). Two of the sites were selected to be within the lake's previously established summer hypoxic zone (sites 1 and 2; Biddanda et al., 2018), although water depth limited the locations to depths <8 m. A third site was selected within the littoral zone on the southern shore of Muskegon Lake (site 3; Fig. 1), but physical conditions resulted in coring outside the littoral region. All collections were made on 14 July 2020.

At each site, dissolved oxygen (DO), pH, temperature, and total dissolved solids (TDS) were measured at the surface, middle, and bottom of the water column using a YSI 6600 sonde (only surface and bottom data presented; Table 1). Photosynthetically active radiation (PAR) profiles were measured using a LiCor Li-193SA spherical quantum sensor. Secchi disk depth was measured at each site to estimate water clarity. Water samples for P analysis were collected with a Niskin bottle. Water for soluble reactive phosphorus (SRP) analysis was syringe-filtered immediately through 0.45- μ m membrane filters into scintillation vials. Samples were stored on ice until transported to the laboratory, within 5 h of collection. Total P (TP) and SRP samples were stored at 4°C until analysis.

Sediment core sampling and laboratory incubation followed the procedures of Steinman et al. (2004). A total of 18 cores (6 per site x 3 sites) were collected using a piston corer (Fisher et al., 1992, Steinman et al., 2004). After collection, each core was brought to the surface and the bottom was sealed with a rubber stopper prior to removal from the water, resulting in an intact sediment core that was ~20 cm in length, with a 25 cm overlying water column. One core was lost during sediment length adjustment in the laboratory. Core tubes were placed in a vertical rack and kept on ice during transit. An additional core was collected from each site for sediment chemistry analysis; the top 5 cm was removed for the chemical analysis (see below).

Lab Methods:

The 18 sediment cores (6/site) were placed in an environmental growth chamber with the temperature maintained to match the mean ambient condition in the hypolimnion at the time of collection (Table 1). The water column in three of the cores from each site was bubbled with N₂ (with 330 ppm CO₂) to create buffered hypoxic conditions, while the remaining three were bubbled with filtered air to create oxic conditions.

Internal load estimates were made using the methods outlined in Moore et al. (1998), with minor modifications (Steinman et al., 2004). Briefly, a 40 mL water sample was removed by syringe through the sampling port of each core tube at 0 h, 12 h, and days 1, 2, 4, 8, 12, 16, 20, 24, and 28. Immediately after removal, a 20 mL subsample was refrigerated for analysis of TP, and a 20 mL subsample was filtered through a 0.45 µm membrane filter and stored at 4°C for analysis of SRP. TP and SRP were analyzed on a Seal AQ2 Discrete Analyzer (USEPA, 1993). SRP values below detection were calculated as one-half of the 5 µg/L detection limit. The 40 mL subsample was replaced with 1.0 and 0.2 µm sequentially filtered water collected from the corresponding site in the lake; this maintained the original volume and concentration gradient in the core tubes.

Flux (P release rate) calculations were based on the change in water column TP or SRP using the following equation (Steinman et al., 2004):

$$P_{rr} = ((C_t - C_0)/d) * (V/A) \quad [1]$$

where, P_{rr} is the net P release rate (positive values) or retention rate (negative values) per unit surface area of sediments, C_t is the TP or SRP concentration in the water column at time t , C_0 is the TP or SRP concentration in the water column at time 0, d is the number of days of incubation, V is the volume of water in the water column, and A is the planar surface area of the

sediment cores. Both maximum and overall P release rates were calculated. Maximum release is based on P accumulation in the water column over the time period that resulted in the maximum apparent release rate, with the caveat that the initial and final samplings cannot be consecutive dates to avoid potential short-term bias. The overall P release rate is based on P accumulation from days 1 to 28.

Following the incubations, the top 5 cm of sediment was removed from each core. The sediment was homogenized, subsampled, and dried and then ashed (550°C for 1 hr) for AFDM (Steinman and Ogdahl, 2016) and TP. The ashed material was analyzed for TP as described previously. The additional sediment core was dried to a constant mass for metals (Fe, Al, Ca, Mg) and analyzed using EPA method 6010b (USEPA, 1996). Other subsamples (2 g) of wet sediment were sequentially fractionated (Psenner and Pucsko, 1988 modified by Hupfer et al., 2009 and Dieter et al., 2015) to identify the major P compounds in the sediment. The 1.0M NH₄Cl extraction produces the loosely sorbed P; the 0.11M buffered dithionite (BD) extraction produces reductant-soluble P (iron oxides and Mn-bound); the 1.0 M NaOH extraction produces Fe- and Al-bound P, which are mineral associations that can become soluble under hypoxic conditions; and the 0.5 M HCl extraction produces Ca-bound P, which represents a stable mineral association.

Statistical analysis

SRP and TP release rates under oxic and anoxic conditions were separately analyzed for both maximum release rate and overall release rate calculations using 2-way Analysis of Variance (ANOVA) tests, incorporating site (3 levels), oxygen state (2 levels: oxic and anoxic), and the interaction of site and oxygen state as factors. Normality assumptions were tested using Shapiro-Wilk tests; maximum release rates of both SRP and TP required log transformation.

Equal variance assumptions were tested using Brown-Forsythe tests. The presence of outliers was tested using Grubb's test. Significant differences were detected using $\alpha = 0.05$. Data analysis was conducted using SigmaPlot (v14.0; Systat Software, Inc.).

III. RESULTS

Field Conditions

Only one of the three sites conformed to our initial expectations regarding stratification and hypoxia. Site 1, at the eastern end of Muskegon Lake and near the edge of the purported hypoxic zone, showed a clear pattern of stratification with temperatures $\sim 7^{\circ}\text{C}$ lower at bottom than the surface and DO concentrations ~ 1.2 mg/L compared to a surface concentration of 9.6 mg/L (Table 1). In contrast, site 2 was in shallower water and had a temperature difference between surface and bottom of only 2°C with a bottom DO > 5 mg/L (Table 1). Site 3, just outside the littoral zone of the lake's south shore, where the shelf drops off quickly, showed signs of stratification with a 6°C difference in temperature between surface and bottom, and a bottom DO concentration of just above 2 mg/L (Table 1). TDS concentrations were similar between surface and bottom depths at all sites, whereas pH was consistently 0.7 to 0.8 units lower at the bottom than at the surface.

Surface SRP concentrations were below detection at sites 1 and 2 but were 7 and 13 $\mu\text{g/L}$ at the near bottom, respectively. In contrast, SRP was 13 $\mu\text{g/L}$ at the surface but below detection at the near bottom at site 3 (Table 1). TP was detectable at all sites and followed the same trends seen for SRP, with concentrations higher at the bottom than surface at sites 1 and 2, and the reverse at site 3. TP concentrations ranged from 24 to 41 $\mu\text{g/L}$ (Table 1).

The lake was relatively turbid with similar Secchi depths (1 to 1.1 m) and light extinction coefficients (~1.4 to 1.5) at all three sites (Table 1).

Phosphorus Release Rates

Phosphorus release rates were calculated as both a maximum apparent flux (using maximum release dates) and an overall flux using release from day 1 through day 28. The maximum release rate for SRP was constant and relatively low among the 3 sampling sites under oxic conditions, ranging from 0.71 to 0.77 mg/m²/d (Table 2, Fig. 2). Rates were much more variable under anoxic conditions due to episodic releases; at site 1, the spike occurred on day 2, and was modest in magnitude but consistent in all 3 replicates (Fig. 2). However, no spikes were measured at site 2, and only 1 replicate at site 3 showed a spike on day 8 under anoxic conditions (Fig. 2). The overall means ranged from 1.25 to 9.71 mg/m²/d (Fig. 2). Maximum release rates under anoxic conditions were significantly greater than under oxic conditions, but this reversed when measuring overall P release rates (Table 2). Neither site location nor the oxygen × site interaction was statistically significant at the 0.05 level (Table 2).

The maximum release rate for TP also was relatively constant and low among the 3 sites under oxic conditions, ranging from 0.62 to 0.98 mg/m²/d (Table 3, Fig. 3). Consistent with the SRP data, release rates were much more variable under anoxic conditions, and the TP followed the same general pattern as observed for SRP, although the TP spikes lagged the SRP spikes by a few days at sites 1 and 3 (Fig. 3). SRP accounted for ~45 to 65% of the TP being released from the sediment. Maximum TP release rates under anoxic conditions were significantly greater than under oxic conditions, as observed for SRP, but oxygen status had no significant effect when measuring overall P release rates (Table 3). The Site factor had a marginally significant effect on

maximum TP release rates and was highly significant on overall release rate. Interestingly, site 1 had the greatest release rate when assessed with the maximum release rate approach, but the lowest release rate when using the overall release rate approach (Table 3). There was no significant interaction effect, regardless of measurement approach.

Sediment Fractionation

Post-incubation fractionation results were relatively consistent among sites and oxygen content (Table 4, Fig. 4). The greatest percent of SRP in the sediment was measured in the HCl fraction (Ca-bound SRP), ranging from 42-67%, followed by the BD fraction (Fe oxide- and Mn-bound SRP) ranging from 25-42% (Table 4). Lower values were measured in the NaOH fraction (Fe- and Al-bound SRP) at 5-25%, while very low (< 0.5%) amounts of SRP were associated with NH₄Cl fraction (loosely sorbed P; Table 4).

Sediment Metals and Content

Sediment content exhibited several trends (Table 5). First, Ca concentrations were elevated relative to the other measured metals, possibly a result of the lake's prior industrial history, which included concrete disposal in the lake and limestone aggregate stored along the lakeshore (Steinman et al., 2008). Second, the Al, Fe, and Mg concentrations, as well as sediment organic matter and TP content, all were noticeably greater at site 1 than at the other two sites (Table 5). Site 1 is closest to the now decommissioned and demolished coal-fired power plant located at the lake's eastern end, which may account for the elevated metals. Finally, the sediment Fe:P ratio ranged from ~10 to 21, with no clear pattern in oxic vs. anoxic conditions among sites (Table 5).

IV. Discussion:

One of the key stressors facing aquatic ecosystems is excess nutrients, leading to cultural eutrophication (Smith, 2003). This is a global phenomenon (Birk et al., 2020), with a growing recognition that the nutrient sources to lakes can be external, coming from the watershed and atmosphere (cf. Carpenter et al., 1998; Sharpley et al., 2013), as well as internal from the sediment (Olihel et al., 2017; Søndergaard et al., 2012).

Eutrophication or Undesirable Algae is a common BUI impairment for AOCs in the Laurentian Great Lakes (Hartig et al., 2018). The federal Clean Water Act regulated point source discharges, which significantly reduced nutrient loads to many water bodies in the US, but did not address nonpoint source loads. These diffuse inputs are now considered the major cause of harmful algal blooms, with specific regions of the Great Lakes (Green Bay, Saginaw Bay, western Lake Erie) being targeted for remediation through the federally-administered Great Lakes Restoration Initiative.

Muskegon Lake, another designated AOC, has exhibited significant reductions in TP since wastewater was diverted from direct discharge into the lake to the Muskegon County Waste Management System in the early 1970s. TP concentrations have declined from ca. 60 $\mu\text{g/L}$ in 1972 to more recent concentrations of ca. 25 $\mu\text{g/L}$ (Steinman et al., 2008). Weinke and Biddanda (2018) identified a DO threshold for TP concentration in Muskegon Lake; at DO levels <3 mg/L, TP concentrations averaged about 48 $\mu\text{g/L}$ and >3 mg/L, TP concentrations declined to an average of 24 $\mu\text{g/L}$, providing further support to the putative role of internal loading.

Our laboratory incubations suggest that internal loading can be an important source of P to Muskegon Lake, but the process appears episodic and spatially heterogenous. Spatial heterogeneity of Muskegon Lake sediments is well-established, with both natural features (morphometry, hydrologic regime) and anthropogenic forces (prior lumber and industry on the

shoreline) accounting for variation in sediment toxicity, chemistry, and biology (Carter et al., 2006; Liu et al., 2018; Nelson and Steinman, 2013; Rediske et al., 2002, Steinman et al., 2008). In the current study, there was considerable variation in sediment %OM and TP concentrations among the three collection sites. The greater maximum release rates at site 1 are consistent with the higher sediment OM and TP concentration at this site. One replicate sediment core at site 3 released TP up to ~800 $\mu\text{g/L}$ under anoxic conditions, but the other two sediment cores, with similar sediment OM and TP concentrations to the high-release core, released virtually no TP during the same time period. It is plausible that mineralization of organic matter (e.g., phytoplankton) in the high-release core accounted for this spike of TP (cf. Palmer-Felgate et al., 2011). Episodic changes in SRP concentration in Muskegon Lake hypolimnion have been documented previously (Fig. 5; Mancuso, 2020), and have been attributed to changes in DO concentrations (Weinke and Biddanda, 2018).

Post-incubation fractionation data indicated that most of the sediment SRP was associated with the calcium and Fe oxide- and Mn-bound fractions. The relatively high Ca sediment concentrations at all our sampling sites in Muskegon Lake provide stable binding sites for P, but the Fe concentrations were spatially variable. Unfortunately, we did not fractionate sediments prior to incubation, precluding a comparison of how P fractions changed under oxic vs. anoxic conditions, although it make sense that the more mobile fractions would decline following incubations, especially in the anoxic treatments. The Fe:P ratio under oxic conditions at sites 2 and 3 slightly exceeded 15, above which P release is limited (Jensen et al., 1992). Although this ratio's applicability will depend on the dominant fraction to which P is associated, the relatively important role of Fe in Muskegon Lake suggests the ratio has relevance here, and is

consistent with the higher maximum release rates measured under anoxic conditions at Site 1, which had a Fe:P ratio <15.

The sediment P flux varied considerably with the measurement approach. Hupfer et al. (2020) provide a comprehensive review of different approaches to measure internal P loading, acknowledging that both theoretical and methodological issues contribute to the complexity of these approaches. While it is recognized that laboratory-based sediment core incubations are not representative of whole lake or annual loads, given the spatial and temporal variation in lakes, the difference in internal loading estimates that derive from how the rate is calculated when employing sediment core incubations has received much less attention. Our study reveals that very dramatic differences in flux can be estimated from the same set of experiments, depending on the approach used.

The problem is compounded if these data are then extrapolated beyond the individual sampling dates to a longer time period, or beyond the sediment core surface area to a larger lake sediment surface area. To demonstrate the influence of different assumptions in assessing the importance of internal phosphorus loading in Muskegon Lake, we provide a set of estimates under various scenarios (Table 6). The main factors that are varied include the length of time of oxic vs. anoxic conditions; the amount of sediment surface area that is experiencing oxic vs. anoxic conditions; and whether the P release rate is based on maximum rate or entire incubation period.

Under the base scenario (1 and 2), we assume: 1) oxic conditions apply for 4 months of the year, anoxic conditions apply for 2 months of the year (Weinke and Biddanda et al., 2018), and there is no discernible release for 6 months of the year (Steinman et al., 2009); and 2) the percent surface area of Muskegon Lake that goes anoxic during those two months is 50% (Fig.

1). After correcting for area, the estimated combined internal load under oxic and anoxic conditions when applying the maximum release rate approach is 6.65 MT per year and when applying the overall incubation time (28 d) approach is 0.57 MT per year (Table 6). The external load entering Muskegon Lake from the Muskegon River (which accounts for 95% of the discharge; Freedman et al., 1979) is estimated at 24 MT (Marko et al., 2013). Hence the estimated internal P loads, based on the maximum and overall release rate calculations, are estimated to be 21.7% and 2.3% of the total load, respectively (Table 6). In scenarios 3 and 4, the duration of oxic, anoxic, and no P release periods in Muskegon Lake is changed to 8 mo, 2 mo, and 2 mo, respectively, while the surface area of oxic vs. anoxic is the same as in scenarios 1 and 2; in this case, the estimated combined internal load is 8.34 MT per year (25.8% of total P load) when applying the maximum release rate approach and 1.01 MT per year (4.1% of total load) when applying the overall incubation time approach (Table 6). Finally, altering the oxic vs. anoxic portions of lake surface area from 50:50 to 75:25 oxic:anoxic (scenarios 5 and 6) result in an estimated combined internal load of 4.59 MT per year (16.1% of total P load) with the maximum release rate approach and 0.62 MT per year (2.5% of total load) with the overall incubation time approach (Table 6).

These percent estimates of internal P loading in Muskegon Lake clearly have huge uncertainties associated with them. First, they don't account for other external sources, such as other inflows (including eutrophic Bear Lake; Steinman and Ogdahl, 2015) and atmospheric deposition; second, it is unlikely that the anoxic portion of the lake remains entirely anoxic for those two summer months; third, while it is well documented that internal loading is significantly reduced in winter months due to reduction in mineralization and enzymatic reactions, it is unclear whether it drops to zero in Muskegon Lake; and fourth, P release rates are almost

certainly not uniform across the entire lake bottom due to differences in bioturbation and sediment geochemistry (cf. Nogaro and Steinman, 2014; Hupfer et al., 2019). However, the data reveal two important points: 1) Only under the most extreme assumptions does internal P loading account for a sizeable (~26%) portion of total P load in Muskegon Lake; and 2) the role of internal loading, at least based on sediment core incubations, can be biased in different directions depending on assumptions.

Our results suggest that under certain conditions, such as low DO, sufficient sediment OM, and low Fe and Ca sediment concentrations, internal loading can contribute to elevated P concentrations in Muskegon Lake. However, this impact will be localized spatially and limited temporally. It is unclear if these pulses of P result in increased algal production and biomass, and if so, how widespread is the effect. Prior laboratory studies showed that algae grown in overlying water from P-release experiments did not significantly stimulate algal production (Cymbola et al., 2008) but there has been no attempt to evaluate this in the field. At this point, it doesn't appear that mitigation measures are needed to address internal P loading in Muskegon Lake.

Finally, one last unresolved question is whether this seasonal low DO state in Muskegon Lake is a natural phenomenon, given the morphometry and hydrodynamics of drowned river mouth lakes (Larson et al., 2013; Liu et al. 2018), or is it due to past water quality impairments. If it is the former, then it is questionable whether restoration efforts are appropriate under the AOC program; if it is the latter, then intervention may be required to achieve the restoration target for TP. A monitoring program that measures both DO and P levels in drowned river mouth lakes would provide the necessary information to determine if seasonal hypoxia/anoxia is a natural or anthropogenic-induced phenomenon and help quantify its ecosystem level impact.

V. Acknowledgments:

Funding for this project was provided by NOAA. We gratefully acknowledge the support of Kathy Evans (West Michigan Shoreline Regional Development Commission), as well as the technical assistance of Rick Rediske and Brian Scull (GVSU). Anthony Weinke and Jasmine Mancuso (GVSU) kindly shared their Muskegon Lake data with us.

VI. References:

- Biddanda, B.A., Weinke, A.D., Kendall, S.T., Gereaux, L.C., Holcomb, T.M., Snider, M.J., Dila, D.K., Long, S.A., VandenBerg, C., Knapp, K., Koopmans, D.J., et al., 2018. Chronicles of hypoxia: Time-series buoy observations reveal annually recurring seasonal basin-wide hypoxia in Muskegon Lake—A Great Lakes estuary. *J. Great Lakes Res.* 44, 219-229.
- Birk, S., Chapman, D., Carvalho, L., Spears, B.M., Andersen, H.E., Argillier, C., Auer, S., Baattrup-Pedersen, A., Banin, L., Beklioğlu, M. et al., 2020. Impacts of multiple stressors on freshwater biota across spatial scales and ecosystems. *Nature Ecol. Evol.* 4, 1060-1068.
- Carey, C.C., Rydin, E., 2011. Lake trophic status can be determined by the depth distribution of sediment phosphorus. *Limnol. Oceanogr.* 56, 2051-2063.
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.* 8, 559-568.
- Carter, G.S., Nalepa, T.F., Rediske, R.R., 2006. Status and trends of benthic populations in a coastal drowned river mouth lake of Lake Michigan. *J. Great Lakes Res.* 32: 578-595.
- Cymbala, J., Ogdahl, M., Steinman, A.D., 2008. Phytoplankton response to light and internal phosphorus loading from sediment release. *Freshw. Biol.* 53, 2530-2542.
- Dieter, D., Herzo, C., Hupfer, M., 2015. Effects of drying on phosphorus uptake in re-flooded lake sediments. *Environ. Sci. Poll. Res.* 22: 17065-17081.
- Fisher, M.M., Brenner, M., Reddy, K.R., 1992. A simple, inexpensive piston corer for collecting undisturbed sediment/water inter-face profiles. *J. Paleolimnol.* 7, 157–161.

- Freedman P., Canale R., Auer, M., 1979. The impact of wastewater diversion spray irrigation on water quality in Muskegon County lakes. U.S. Environmental Protection Agency, Washington, D.C. EPA 905/9-79-006-A.
- Hartig, J.H., Krantzberg, G., Munawar, M., Doss, M., Child, M., Kalinauskas, R., Richman, L. Blair, C., 2018. Achievements and lessons learned from the 32-year old Canada-US effort to restore Impaired Beneficial Uses in Great Lakes Areas of Concern. *Aquat. Ecosys. Health Managem.* 21, 506-520.
- Hupfer, M., Zak, D., Roßberg, R., Herzog, C., Pöthig, R., 2009. Evaluation of a well-established sequential phosphorus fractionation technique for use in calcite-rich lake sediments: identification and prevention of artifacts due to apatite formation. *Limnol. Oceanogr.: Methods* 7, 399-410.
- Hupfer, M., Jordan, S., Herzog, C., Ebeling, C., Ladwig, R., Rothe, M., Lewandowski, J., 2019. Chironomid larvae enhance phosphorus burial in lake sediments: Insights from long-term and short-term experiments. *Sci. Total Environ.* 663, 254-264.
- Hupfer, M., Reitzel, K., Grüneberg, B., 2020. Methods for measuring internal phosphorus loading. In: A.D. Steinman and B. M. Spears (Eds.), *Internal Phosphorus Loading: Causes, Case Studies, and Management* (pp. 1543). Plantation, FL: J. Ross Publishing.
- Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, A., 1992. Iron: phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiologia* 235, 731-743.
- Jeppesen, E., Søndergaard, M., Jensen, J.P., Havens, K.E., Anneville, O., Carvalho, L., Coveney, M.F., Deneke, R., Dokulil, M.T., Foy, B.O.B., Gerdeaux, D., et al., 2005. Lake responses

- to reduced nutrient loading—an analysis of contemporary long-term data from 35 case studies. *Freshw. Biol.* 50, 1747-1771.
- Larson, J.H., Trebitz, A.S., Steinman, A.D., Wiley, M.J., Mazur, M.C., Pebbles, V., Braun, H.A., Seelbach, P.W., 2013. Great Lakes rivermouth ecosystems: scientific synthesis and management implications. *J. Great Lakes Res.* 39, 513-524.
- Liu, Q., Anderson, E.J., Zhang, Y., Weinke, A.D., Knapp, K.L., Biddanda, B.A., 2018. Modeling reveals the role of coastal upwelling and hydrologic inputs on biologically distinct water exchanges in a Great Lakes estuary. *Estuarine, Coastal and Shelf Science* 209, 41-55.
- Mancuso, J., 2020. Bloom or bust: Search for phytoplankton community drivers using long-term time-series observations and field measurements in a model Great Lakes estuary. MS Thesis, Grand Valley State University, Allendale, MI.
- Marko, K.M., Rutherford, E.S., Eadie, B.J., Johengen, T.H., Lansing, M.B. 2013., Delivery of nutrients and seston from the Muskegon River Watershed to near shore Lake Michigan. *J. Great Lakes Res.* 39, 672-681.
- Moore Jr, P.A., Reddy, K.R., Fisher, M.M., 1998. Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variations. *J. Environ. Qual.* 27, 1428-1439.
- Nelson, W.A., Steinman, A.D., 2013. Changes in the benthic communities of Muskegon Lake, a Great Lakes Area of Concern. *J. Great Lakes Res.* 39, 7-18.
- Nogaro, G., Steinman, A.D., 2014. Influence of ecosystem engineers on ecosystem processes is mediated by lake sediment properties. *Oikos* 123, 500-512.

- Ogdahl, M.E., Steinman, A.D., Weinert, M., 2014. Laboratory-determined phosphorus flux from lake sediments as a measure of internal phosphorus loading. *J. Vis. Exp.-Environ.*
<http://www.jove.com/video/51617>.
- Orihel D.M., Baulch H.M., Casson N.J., North R.L., Parsons C.T., Seckar D.C., Venkiteswaran J.J., 2017. Internal phosphorus loading in Canadian fresh waters: a critical review and data analysis. *Can. J. Fish. Aquat. Sci.* 74, 2005-2029.
- Palmer-Felgate, E.J., Mortimer, R.J., Krom, M.D., Jarvie, H.P., Williams, R.J., Spraggs, R.E., Stratford, C.J., 2011. Internal loading of phosphorus in a sedimentation pond of a treatment wetland: Effect of a phytoplankton crash. *Sci. Total Environ.* 409, 2222-2232.
- Psenner, R., Pucsko, R. 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. *Arch. Hydrobiol. Beih.* 30, 43-59.
- Rediske, R., Thompson, C. Schelske, C., Gabrosek, J., Nalepa, T.F., Peaslee, G., 2002. Preliminary investigation of the extent of sediment contamination in Muskegon Lake, MI. GL-97520701-01. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL.
- Sharpley, A., Jarvie, H.P., Buda, A., May, L., Spears, B., Kleinman, P., 2013. Phosphorus legacy: Overcoming the effects of past management practices to mitigate future water quality impairment. *J. Environ. Qual.* 42, 1308-1326.
- Smith, V.H., 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environ. Sci. Poll. Res.* 10, 126-139.
- Søndergaard, M., Bjerring, R., Jeppesen, E., 2012. Persistent internal phosphorus loading during summer in shallow eutrophic lakes. *Hydrobiologia* 710, 95-107.

- Søndergaard, M., Jeppesen, E., 2020. Lake Søbygaard, Denmark: phosphorus dynamics during the first 35 years after an external loading reduction. In: A.D. Steinman and B. M. Spears (Eds.), *Internal Phosphorus Loading: Causes, Case Studies, and Management* (pp. 285-299). Plantation, FL: J. Ross Publishing.
- Steinman, A.D., Chu, X., Ogdahl, M., 2009. Spatial and temporal variability of internal and external phosphorus loads in Mona Lake, Michigan. *Aquat. Ecol.* 43, 1-18.
- Steinman, A.D., Ogdahl, M.E., 2015. TMDL reevaluation: reconciling internal phosphorus load reductions in a eutrophic lake. *Lake Reserv. Managem.* 31, 115-126.
- Steinman, A.D., Ogdahl, M., 2016. From wetland to farm and back again: phosphorus dynamics of a proposed restoration project. *Environ. Sci Poll. Res.* 23, 22596-22605.
- Steinman, A.D., Ogdahl, M., Rediske, R., Ruetz III, C.R., Biddanda, B.A., Nemeth, L., 2008. Current status and trends in Muskegon Lake, Michigan. *J. Great Lakes Res.* 34, 169-188.
- Steinman, A.D., Rediske, R., Reddy, K.R., 2004. The reduction of internal phosphorus loading using alum in Spring Lake, Michigan. *J. Environ. Qual.* 33, 2040-2048.
- Steinman, A.D., Spears, B., 2020. What is internal loading and why does it occur? In A.D. Steinman and B. M. Spears (Eds.), *Internal Phosphorus Loading: Causes, Case Studies, and Management* (pp. 3-13). Plantation, FL: J. Ross Publishing.
- USEPA, United States Environmental Protection Agency, 1993. *US Environmental Protection Agency. 1993 Methods for Chemical Analysis of Inorganic Substances in Environmental Samples (EPA600/4-79R-93-020/100)*. Washington, D.C.
- USEPA, United States Environmental Protection Agency, 1996. *Method 6010B. Inductively coupled plasma-atomic emission spectrometry*. Washington, D.C.
- <https://www.epa.gov/sites/production/files/documents/6010b.pdf>

Weinke, A.D., Biddanda, B.A., 2018. From bacteria to fish: ecological consequences of seasonal hypoxia in a Great Lakes estuary. *Ecosystems* 21, 426-442.

Table 1. Selected limnological characteristics of sampling sites in Muskegon Lake. BD = below detection (5 µg/L).

Parameter	Site 1		Site 2		Site 3	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Depth (m)	7.15		4.29		7.10	
Temp (°C)	26.31	19.61	26.23	24.52	26.10	19.92
DO (mg/L)	9.63	1.16	9.51	5.38	9.54	2.1
TDS (g/L)	0.226	0.220	0.222	0.235	0.220	0.214
pH	8.47	7.70	8.52	7.86	8.46	7.66
SRP (µg/L)	BD	13	BD	7	13	BD
TP (µg/L)	30	41	25	34	35	24
Light Extinction K_d	1.42		1.45		1.51	
Secchi depth (m)	1.0		1.0		1.1	

Table 2. Two-way analysis of variance of SRP release rates (mg P/m²/d), with oxygen status and site location as the two factors. Separate analyses were run for the two different release rate calculation approaches. Maximum release rate values were log-transformed for analysis. Bold values indicate P < 0.05.

Site	Oxic	Anoxic	Redox P	Site P	Site × Redox
Maximum Release Rate					
1	0.76±0.30	9.71±5.35	0.009	0.206	0.282
2	0.71±0.39	1.25±0.37			
3	0.77±0.21	5.98±8.82			
Overall Release Rate					
1	0.27±0.11	-0.23±0.24	<0.001	0.061	0.744
2	0.44±0.22	0.08±0.06			
3	0.49±0.16	0.01±0.06			

Table 3. Two-way analysis of variance of TP release rates (mg P/m²/d), with oxygen status and site location as the two factors. Separate analyses were run for the two different release rate calculation approaches. Maximum release rate values were log-transformed for analysis. Bold values indicate P < 0.05.

Site	Oxic	Anoxic	Redox P	Site P	Site × Redox
Maximum Release Rate					
1	0.88±0.55	14.90±7.41	<0.001	0.066	0.234
2	0.62±0.30	2.76±0.66			
3	0.98±0.13	9.01±10.48			
Overall Release Rate					
1	-0.08±0.10	-0.80±0.43	0.332	0.004	0.183
2	0.23±0.38	0.29±0.04			
3	0.50±0.38	0.61±0.54			

Table 4. Sediment fractionation SRP, TP, and organic matter (OM) mean concentrations from post-incubation Muskegon Lake cores, on a dry weight basis.

Site	Oxygen	SRP-bound Fraction								TP	OM
		NH ₄ Cl		BD		NaOH		HCl			
		μg/g	%	μg/g	%	μg/g	%	μg/g	%	mg/kg	%
1	Oxic	0.16	<0.1	223.4	33.3	165.8	24.7	280.7	41.9	1127	13.9
	Anoxic	0.16	<0.1	189.6	33.5	117.7	20.8	258.9	45.7	980	
2	Oxic	0.25	0.3	27.9	28.6	4.4	4.5	64.8	66.6	120	1.0
	Anoxic	0.16	0.2	45.5	42.0	6.5	6.0	56.2	51.9	198	
3	Oxic	0.05	<0.1	33.6	24.6	26.1	19.1	76.9	56.3	221	3.2
	Anoxic	0.70	0.5	43.2	30.0	16.1	11.2	84.1	58.4	195	

Table 5. Mean (\pm SD) metal concentrations (g/kg) from Muskegon Lake sediments (dry weight).

Site	Oxygen	Al	Ca	Fe	Mg	Fe:TP (by weight)
1	Oxic	6 \pm 5	39 \pm 34	14 \pm 12	15 \pm 13	12.4
	Anoxic	14 \pm 3	56 \pm 6	21 \pm 1	22 \pm 2	21.4
2	Oxic	1 \pm 0	71 \pm 44	2 \pm 0	1 \pm 0	16.7
	Anoxic	ND	68 \pm 18	2 \pm 0	1 \pm 0	10.1
3	Oxic	1 \pm 0	27 \pm 12	4 \pm 2	1 \pm 0	18.1
	Anoxic	1 \pm 0	30 \pm 13	4 \pm 2	1 \pm 0	20.5

Table 6. Muskegon Lake total internal P load and % of total P load accounted for by internal P loading release rates for 6 scenarios. See text for further description of scenarios. External load (24 MT/yr) is based on data from Marko et al. (2013) and does not account for all possible external sources, indicating the % internal load values are likely overestimates.

Scenario	Oxygen Status Duration (mo)			Surface Area (%)		P release rate approach		Total Internal Load (MT/yr)	Internal Load (%)
	Oxic	Anoxic	No release	Oxic	Anoxic	Maximum	Overall		
1	4	2	6	50	50	+		6.65	21.7
2	4	2	6	50	50		+	0.57	2.3
3	8	2	2	50	50	+		8.34	25.8
4	8	2	2	50	50		+	1.01	4.1
5	4	2	6	75	25	+		4.59	16.1
6	4	2	6	75	25		+	0.62	2.5

Figure 1. Map of sampling sites (circled numbers) in Muskegon Lake. Star denotes location of Muskegon Lake Observatory (buoy). Dashed contour line represents the 7.5/8.0 m isobath. Inset: Muskegon County outlined within the state of Michigan.

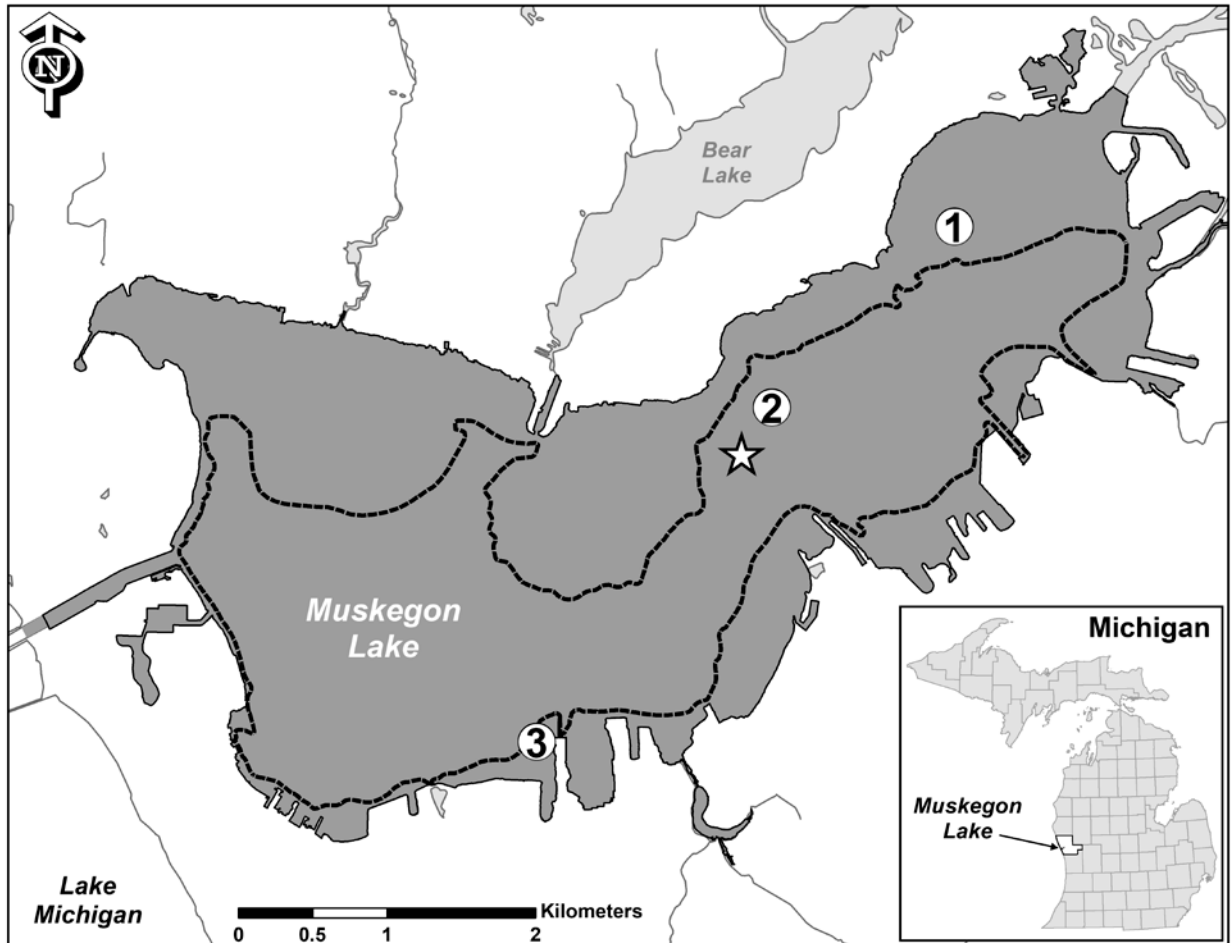


Figure 2. TP release rates from the 3 sampling sites in Muskegon Lake. Legend designations are site number (1-3), aeration treatment (O=oxic; N=anoxic), replicate (1-3).

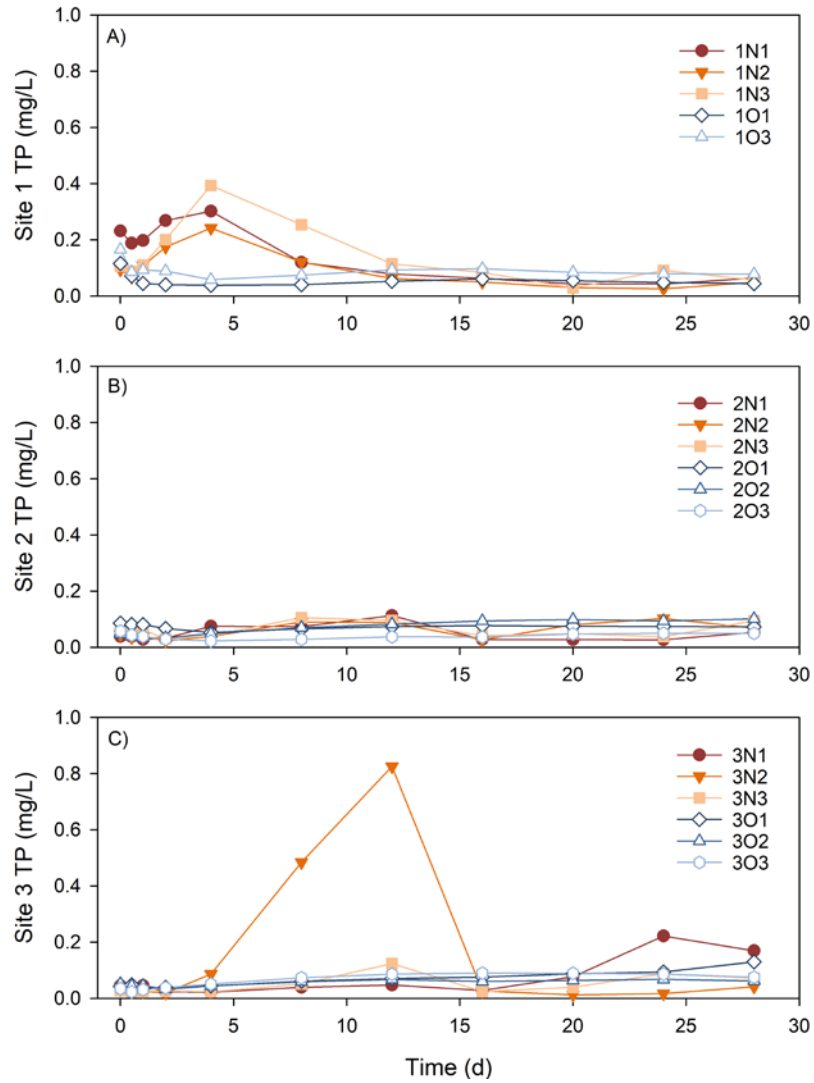


Fig. 3. SRP release rates from the 3 sampling sites in Muskegon Lake. Legend designations are site number (1-3), aeration treatment (O=oxic; N=anoxic), replicate (1-3).

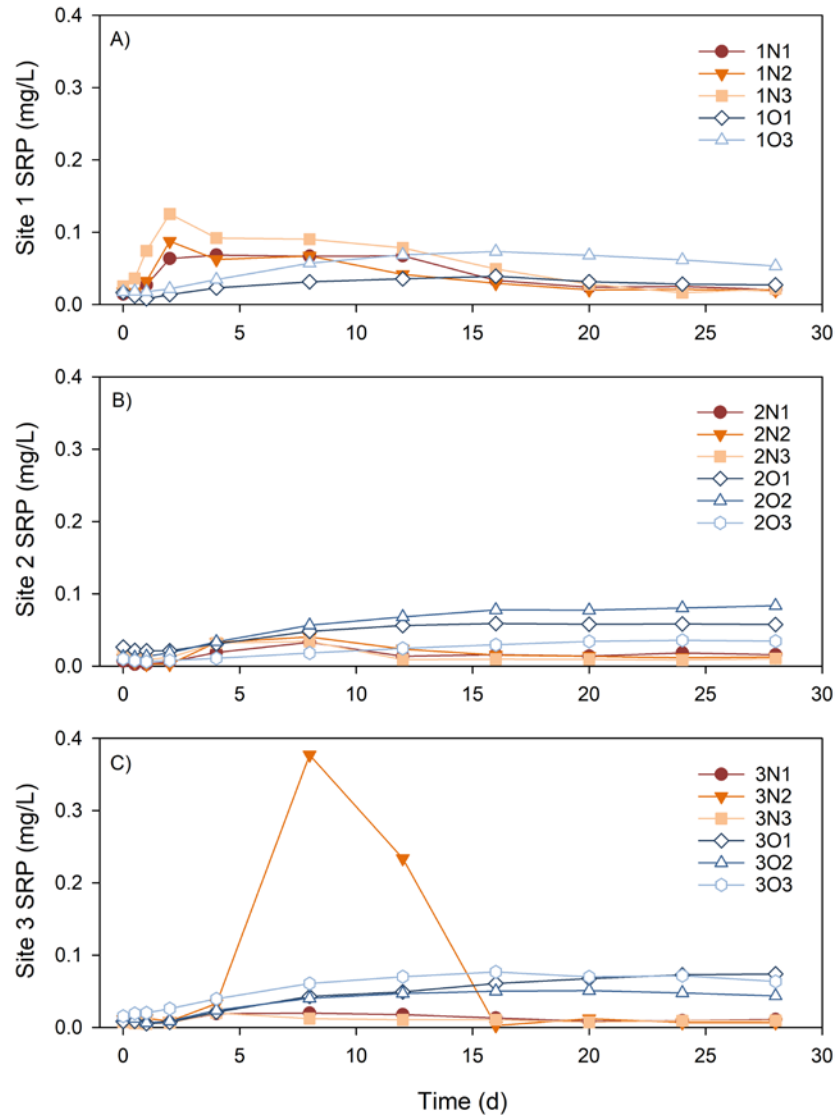


Fig. 4. Mean %SRP from Muskegon Lake sediment fractions. NH_4Cl fractions were less than 0.5% and difficult to see at the top of bars. O = oxic treatment; N = anoxic treatment.

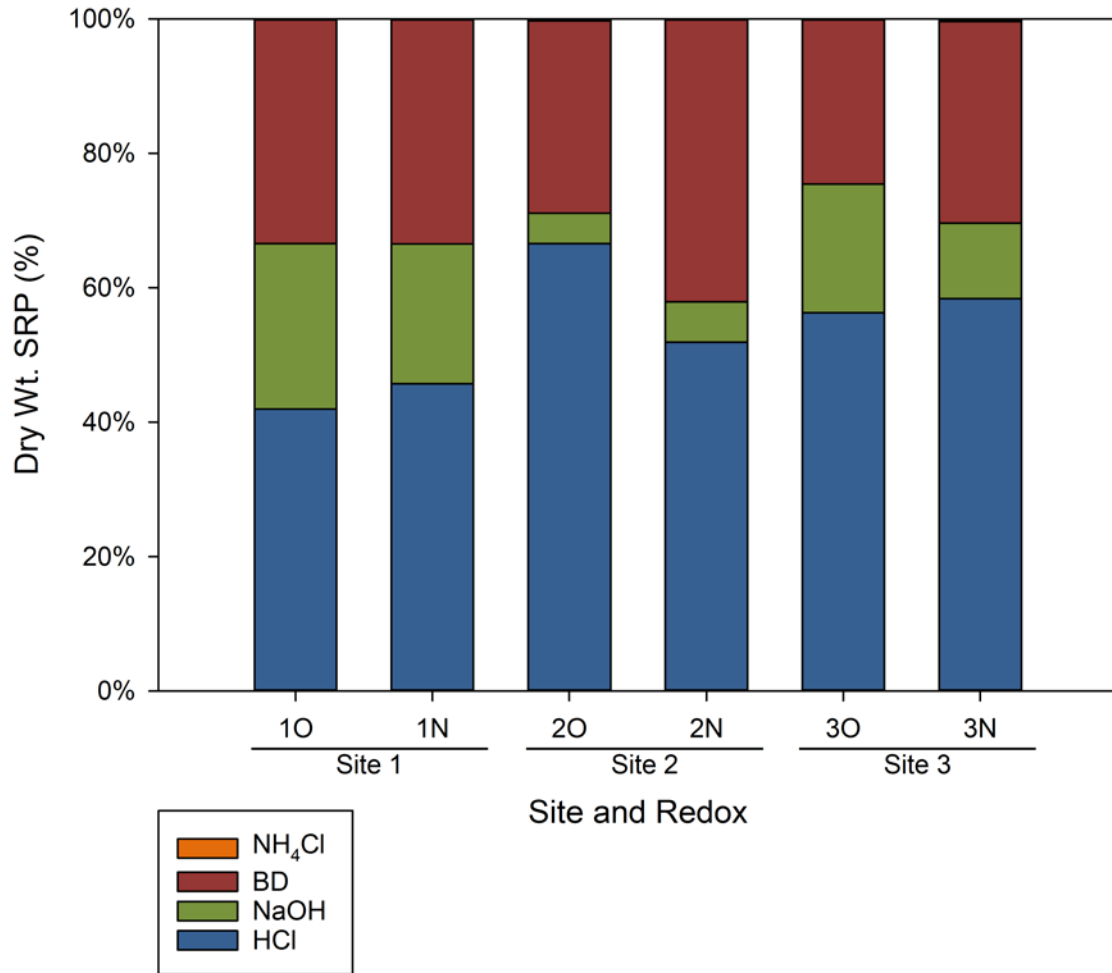


Figure 5. Soluble reactive phosphorus (SRP) concentrations (mg/L) from the Muskegon River inflow (River), near surface and near bottom at the buoy location in Muskegon Lake (MLO Top and MLO Bottom, respectively), and the channel connecting Muskegon Lake and Lake Michigan (Channel). Data from Jasmine Mancuso, M.S. thesis, GVSU.

