# ST. ANTHONY FALLS LABORATORY

Project Report No. 601

# *Assessment of Internal Phosphorus Release and Treatment with Iron Filings in five RPBCWD Ponds*

**Final Report** 

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# Summary

Five ponds, Aquila Pond (in Bloomington), Pond BC-P4.10C (in Chanhassen), Bren Pond (in Eden Prairie), Pond 849\_W (in Minnetonka) and Pond 42 (in Shorewood), were evaluated in this two-part study.

- a) In the first part of the study, the potential anoxic sediment phosphorus release was evaluated using laboratory sediment cores. A moderately-high flux of phosphate was measured under anoxic conditions, which was supported by high sediment oxygen demand and high organic matter content in the sediments. A low oxic flux was observed only for Pond BC-P4.10C and Bren Pond sediments, indicating mobilization of organic P by bacteria. Detailed sediment phosphorus characterization revealed low to moderate concentrations of mobile P (redox-P + labile organic P) mass, which is releasable under low oxygen conditions and by microbacterial degradation under both oxic and anoxic conditions. The relative mobile P mass (as % of the total sediment phosphorus mass) was 53% in Aquila Pond, 43% in Pond BC-P4.10 C, 47% in Bren Pond, 41% in Pond 42, and 63% in Pond 849\_W, highlighting the importance of mobile phosphorus in driving internal phosphorus loading during anoxia in the ponds.
- b) In situ monitoring of surface to bottom DO and temperature profiles in the ponds were indicative of a stratified water column that was anoxic from top to bottom during much of the summer period. The observation of pervasive anoxia was common in Pond BC-P4.10C, Bren Pond, Pond 849\_W, and Pond 42 during all three field seasons, as indicated by the relatively high summer anoxic factor (AF) for these ponds. Aquila Pond appeared to partially mix intermittently although bottom DO was still low during certain periods.
- c) All five pond sites had floating vegetation (duckweed and watermeal) that had a dense surface coverage (nearly 100%) from June to September. We have found strong evidence of duckweed cover influencing the DO dynamics in several ponds and have observed a strong pattern between summer anoxic factor and duckweed cover in our pond research projects. It is possible that the effect of duckweed may be exacerbated in dry years (like 2021) when stormwater inputs to provide direct mixing are less frequent.
- d) The application of iron filings was utilized to reduce phosphate release from the pond sediments. Ponds BC-P4.10C and 849\_W were treated with iron filings in February 2020 and Bren Pond was treated in February 2020. Aquila Pond can be used as a control for the RPBCWD region, where surface water TP was seen to increase greatly from 2019 to 2020, and then stayed about the same in 2021. In Pond BC-P4.10C, the average TP went up after treatment with iron filings in February 2020, but not as substantially as the Aquila Pond. In Bren Pond, the average TP had a slight reduction in all three years. In Pond 849\_W, the average TP went up in 2020 but then reduced in 2021. A similar reduction can be seen in comparing average TP for Shoreview Commons Pond (a fourth iron-treated pond located in the Ramsey Washington Metro Watershed District) to the Alameda Pond (located in

Roseville), where Shoreview Commons had a reduced average TP in 2021 after iron filings addition and the Alameda Pond, with no iron filings addition, did not.

- e) The analysis of the iron-treated sediments from Pond BC-P4.10C, Pond 849\_W, and Bren Pond showed an increase in the iron-bound P mass and a concomitant decrease in the mass of labile organic P and loosely-bound P after iron filings application to the sediments, suggesting the partial or full movement of phosphate from the organic P form and looselybound P to iron-phosphate minerals in the sediments. The iron-treated sediment cores from Bren Pond exhibited an anoxic phosphate flux that was significantly lower than the phosphate flux from untreated sediments.
- f) While the column studies confirmed that sediment phosphate flux was controlled after iron addition, the reduction in internal phosphorus loading in the ponds was not directly assessed. The post-treatment water quality data showed reductions in SRP levels (surface and epilimnion) at the three iron-treated ponds but did not conclusively show reductions in TP levels, specifically in ponds BC-P4.10C and 849\_W. The interpretation and assessment of treatment effectiveness is complicated by the year-to-year variation in pond water quality driven by rainfall patterns and runoff inputs among other factors, especially in ponds BC-P4.10C and 849\_W, which have pretreatment data for only one year before iron filings were applied. Treatment of the ponds will likely require a combination of remediation techniques such as sealing the sediments from phosphate flux, aeration to enhance mixing and watershed-based phosphorus control actions to reduce the inflow of TP. Aeration may work well in Pond 849\_W, which has a small amount of inflow or outflow.

# **1** Introduction and purpose

Stormwater ponds are common stormwater runoff quantity and quality control measures in suburban and urban areas. Solids and associated pollutants such as phosphorus (P) in the inflow runoff typically settle to the bottom of the pond, and the settled phosphorus is expected to be permanently buried the pond. However, there are recent indications that ponds may not provide the expected phosphorus treatment, especially for dissolved phosphorus. Export of dissolved phosphorus in the pond outflows (Song et al. 2015) and high total phosphorus (TP) concentrations in the pond water (Forster et al. 2012, RPBCWD 2014) suggest that many ponds are performing below their potential in terms of phosphorus retention, and may be a source of phosphorus to receiving water bodies (Taguchi et al. 2020). The analysis of water quality in 98 stormwater ponds in the Riley Purgatory Bluff Creek Watershed District (RPBCWD) indicated that 32% of those ponds contained median TP greater than 0.38 mg/L (Taguchi et al. 2020), the upper 95% confidence interval (CI) of expected TP in the Twin Cities Metro Area runoff (Janke et al. 2017). Studies on phosphorus release from pond sediments and monitoring of runoff inflows and outflows at ponds have shown that internal phosphorus loading is contributing to the phosphorus loads in those ponds (Olsen 2017, Taguchi et al. 2020, Janke et al. 2021). Significant internal phosphorus release from pond sediments affects not only the pond water quality but also the downstream lakes and streams that receive the pond outflows, thereby increasing risks of harmful algal bloom occurrence in all water bodies.

The primary purpose of this project was to assess internal phosphorus release in five stormwater ponds in the RPBCWD and the treatment of sediments to reduce internal phosphorus release in three of those ponds. The project consisted of two phases- (i) a pretreatment study to evaluate the sediment phosphorus release potential through a laboratory column study and concurrent field monitoring, and (ii) a post-treatment study consisting of iron filings treatment to chemicallyinactivate the sediment phosphorus in select ponds and impact evaluation of treatment on the phosphorus water quality and pond sediments. For the pretreatment study, a column study with pond sediment cores was performed, along with in situ water quality monitoring at the five ponds for one field season (2019). Based on the results of the first-year study, iron filings application was implemented in three out of the five ponds and all ponds were monitored for two more field seasons (2020 and 2021). The results from the three-year study were used to interpret the risks of internal phosphorus loading in the ponds studied and to evaluate the effects of iron filings treatment on internal phosphorus loading and pond phosphorus concentration. Additionally, the data collected were combined with information from our other pond research projects to develop recommendations on pond maintenance measures to reduce phosphorus loading in ponds and improve their water quality.

# 2 Methods

# 2.1 Site description

Five stormwater ponds were selected for this study after consultation with the RPBCWD and the cities of Bloomington (Aquila Pond), Chanhassen (BC-P4.10C Pond), Eden Prairie (Bren Pond), Minnetonka (849\_W Pond), and Shorewood (Pond 42) as provided in Table 1 (map provided in the Appendix). The selected ponds have historic data of high surface TP concentrations during the warmer months (RPBCWD 2014). All five ponds have a dense cover of the floating vegetation *Lemna* and *Wolffia* (duckweed and watermeal) during the growing season, along with filametateous algae at some of the ponds (sample site photographs provided in the Appendix). BC-P4.10C, Bren, 849\_W, and Pond 42 are open water ponds without any emergent vegetation, although submerged vegetation is present in most of these ponds. Aquila Pond has emergent vegetation that covers nearly 50% of the total pond area. All ponds are located in primarily residential settings and sheltering by tree cover is heavy at all sites.

Table 1. Characteristics of the five ponds monitored in this study. The listed pond age is relative to 2019. Bren Pond was dredged in 2003, hence the age is not specified. Maps of the ponds are shown in the Appendix.

City	Pond	Pond area (SA, ac)	Mean depth (ft)	Max depth (ft)	Drainage area (DA, ac)	DA/ SA	Pond age	Surrounding land use
Bloomington	Aquila Pond	2.9		1.6	13.9	4.9	41	residential
Chanhassen	BC-P4.10C	1.1	2.9	8.5	79.3	48	13	park and residential
Eden Prairie	Bren Pond	2.2	4.0	4.6	71.2	33		residential
Minnetonka	849_W	1.6	2.3	8.2	6.9	4.1	59	residential
Shorewood	Pond 42	0.30	1.9	3.6	4.4	16	31	residential

# 2.2 Laboratory phosphorus release study

The purpose of the phosphorus release column study was to determine the phosphorus flux from the pond sediments under high and low dissolved oxygen (DO) conditions and to analyze the sediments for phosphorus fractions that control the release of phosphorus.

The Aquila Pond, Pond BC-P4.10C, Bren Pond, and Pond 42 were cored in February and March 2019 (Figure 1). Using a piston corer attached to drive rods, five sediment cores containing ~0.2 m sediment with ~0.8 m overlying pond water were extracted into polycarbonate tubes (70 mm I.D.) by coring through holes drilled in ice. Sediment coring in Pond 849\_W was completed as part of a previous study in 2016 (Olsen 2017).



Figure 1. Sediment core collection from BC-P4.10C pond in February 2019.

# 2.2.1 Sediment-water column studies

The pond sediment cores were set up for a phosphorus release column study at room temperature  $(19.4 \pm 0.454 \text{ °C})$ . First, the water columns above the sediments were drained from the cores, filtered to remove particulates (using a 1.2-µm glass fiber filter) and then carefully refilled into the columns without disturbing the sediments. Porous air stones attached to vinyl tubing were placed ~8 cm (~3 inches) above the sediment surface to gently mix the water column without agitating the sediments.

The phosphorus release experiment consisted of three phases. First, the water columns over the sediments was kept oxic by aeration (DO > 9 mg/L). Then, air bubbling was turned off and the DO in the unmixed water column was allowed to decrease due to the sediment oxygen demand (SOD). In the third phase, the water columns were mixed by ultrapure nitrogen gas bubbling to maintain anoxic conditions (DO < 1 mg/L). The water column concentrations of orthophosphate (soluble reactive phosphorus or SRP; Standard Methods 4500-P, APHA 1995) were determined at regular intervals throughout the experiment. Total phosphorus (TP) concentrations were also measured to determine if particulate phosphorus had accumulated (due to bacteria growth), but at a lower frequency than SRP measurements. One water sample was drawn from the approximate center of the mixed water columns during the air bubbling and nitrogen bubbling phases. During the air off phase, water sampling was done at multiple points distributed across the water column depth to account for the concentration gradient that can develop under an unmixed state; the

average phosphorus concentration in the entire water column was estimated assuming an exponential distribution with height.

The sediment phosphorus flux  $(mg/m^2/day)$  was calculated as the linear change in phosphorus mass in the overlying water (where, mass = concentration × water column volume; mg) divided by the phase duration (days) and the sediment area (same as the column area, m<sup>2</sup>). The flux was calculated over 24 days to 30 days, depending on the phase duration. The water column volume was adjusted for the volume withdrawn during each sampling exercise.

For the 849\_W pond sediments, Olsen (2017) applied a slightly modified method in the third phase under N<sub>2</sub> bubbling. Following the air off phase, the water columns in the cores were replaced with synthetic stormwater to simulate the input and mixing of pond water with runoff following a rainfall event. Two flushing events were performed, first with synthetic stormwater containing 138  $\mu$ g/L phosphate and then 57  $\mu$ g/L phosphate. The anoxic phosphate flux for the 849\_W sediments was, therefore, calculated for the air off phase instead of the N<sub>2</sub> bubbling phase.

The DO concentrations in the water columns of all sediment cores were measured (~8 cm above the sediment surface) during the unmixed phase of the experiment and the Michaelis-Menten kinetic model (Michaelis and Menton 1913) was fit to the DO data to obtain a measure of the sediment oxygen demand (SOD):

$$S = \frac{S_{max}[C_{02}]}{K_{M} + [C_{02}]}$$
(1)

where S is the substrate consumption rate,  $S_{max}$  is the maximum DO consumption rate or SOD,  $C_{O2}$  is the substrate (oxygen) concentration, and  $K_M$  is the half-consumption concentration. A constant  $K_M$  of 1.4 mg/L was used for all cores based upon a regression of 60 sediment types in Walker and Snodgrass (1986). It is assumed that all DO reduction comes from the microbial oxygen demand of the sediments, so  $K_M$  represents the characteristics of the microbial community in the surface of the sediments.

#### 2.2.2 Sediment phosphorus analysis

After the completion of the phosphorus (P) release study, the upper 10 cm depth of sediments were analyzed for the different types of P fractions contained in the total sedimentary phosphorus pool. The sediment cores were sectioned at depth intervals of 0-1, 1-2, 2-3, 3-4, 4-5, 5-7, and 7-10 cm (0 cm is the sediment surface). Using the sequential phosphorus extraction procedure (method adapted from Psenner and Puckso 1988, SCWRS 2010), the concentrations of loosely-bound and iron-bound P (together termed redox-P and releasable under low DO conditions) and labile organic P (organic P available for microbial degradation) were determined as a measure of the biologically-available phosphorus that contribute to internal phosphorus loading. The P forms that are insensitive to changes in DO conditions and are relatively unavailable, i.e., the aluminum-bound P (P attached to aluminum minerals), mineral-bound P (P attached to primarily

calcite and apatite), and residual organic P (P considered recalcitrant or not available for microbial degradation) were also determined. The labile organic P fraction was determined by subtracting the aluminum-bound P from the nonreactive NaOH-extractable P (Al-P + labile organic P determined by persulfate digestion of NaOH extract). The extracts from each step were centrifuged at 3000 RPM for 10 minutes and analyzed for SRP concentrations. The extracts from iron-bound P step were bubbled with oxygen for 20 minutes before SRP analysis.

Water content analysis (oven drying at 105 °C) and organic matter content analysis (loss on ignition at 550 °C) were also performed on the sediment samples.

# 2.3 Field monitoring

The purpose of the field sampling and monitoring efforts in the ponds was to collect measurements of phosphorus (total, dissolved, and soluble reactive P) and physio-chemical parameters, including dissolved oxygen, temperature and specific conductivity, which influence the pond stratification dynamics and phosphorus cycling in ponds.

The ponds were sampled from May to November in 2019, 2020, and 2021. The ponds were visited every two weeks for the collection of water samples and profiles of water quality (DO, temperature, conductivity) using a Hach multi-parameter water quality meter (HQ40D, Hach, Loveland, CO). The profile was collected near the pond's deepest point. Surface (epilimnion) water samples were collected just below the water surface, avoiding as much floating vegetation (duckweed and *Wolffia*) as possible. Samples were collected from five locations in the pond and composited into a single sample in the field. One water sample was collected from near the pond bottom (hypolimnion; ~ 25 cm above the bottom sediments) using a Kemmerer-type sampler. The maps showing the sampling locations in the ponds are provided in the Appendix. All water samples were processed, stored, and analyzed at the St. Anthony Falls Laboratory for concentrations of total phosphorus (TP), total dissolved phosphorus (TDP), and soluble reactive phosphorus (SRP; Standard Methods 4500-P, APHA 1995; detection limit = 10  $\mu$ g/L P).

Visual observations of floating plant coverage (extent, density, type) in the pond surface were made during each visit. We also collected samples of the floating plants in 2020 and 2021 for biomass analysis as part of our other pond research projects. *Lemna* and *Wolffia* was pulled out from five locations using a 12-inch diameter mesh skimmer, dried, and weighed in the lab. The biomass analysis is ongoing and are not discussed in this report.

At Pond 849\_W, a continuous monitoring station, equipped with a water level sensor, an anemometer to measure wind speed and a thermistor chain to record water temperature, was installed to collect data during the 2020 monitoring season. The continuous data collection allowed the assessment of pond mixing dynamics throughout the growing season.

# 2.4 Iron filings treatment and post-treatment study

After the completion of the first-year field sampling (2019) and laboratory studies, three ponds were selected for treatment with iron filings with the goal of sequestering phosphorus in the sediments and reducing re-release of phosphorus to the pond water column. Iron filings ( $D_{50} = ~0.60 \text{ mm}$ ) were applied to ponds BC-P4.10C and 849\_W in February 2020, and to Bren Pond in February 2021. At each pond, the city maintenance crew used a fertilizer spreader to spread iron filings over ice to allow the iron particles to deposit to the pond sediments after ice melt (Figure 2). The total mass of iron applied was approximately 4773 lbs at Pond BC-P4.10C, 7584 lbs at Pond 849\_W, and 9680 lbs at Bren Pond, which corresponds to a dosing rate of 500 g iron/m<sup>2</sup> sediment area (4461 lb/ac) based on a previous experimental iron-dosing study (Natarajan et al. 2021). However, a uniform application of iron filings over the entire pond surface was difficult to achieve.



*Figure 2. Photographs showing iron filings application in (a) Pond BC-P4.10 C (on 2/19/2020), (b)Pond 849\_W (on 2/21/2020), and (c) Bren Pond (on 2/24/2021).* 

# 2.4.1 Field monitoring

The 2020 and 2021 field sampling provided the post-iron treatment water quality data for ponds BC-P4.10C and 849\_W. For Bren Pond, the 2021 field season served as the post-treatment assessment year. Aquila Pond and Pond 42 were not treated with iron filings and served as

control ponds. Sampling at Pond 42 was suspended after the 2020 field season due to issues with pond access.

# 2.4.2 Sediment analysis

Sediments from the iron-treated ponds were collected approximately eight months after the iron filings application to examine changes in the sediment phosphorus composition due to iron addition. At ponds BC-P4.10C and 849\_W, five sediment cores were collected per pond in November 2020 and the top 15 cm of sediments were analyzed for the various P fractions by the sequential phosphorus extraction method (as described in Section 2.2.2). Five sediment cores with overlying water column were collected from Bren Pond in October 2021. The cores were set up for phosphorus release experiment (as detailed in Section 2.2.2) and then analyzed for the sediment phosphorus fractions.

The total concentrations of iron and other metals in the sediments were also determined. The five sediment cores from each pond were composited (0-2, 2-4, 4-6, 6-8, 8-10 cm depth intervals) and analyzed for metal concentrations by the ICP method (EPA Method 3051) at the University of Minnesota Research Analytical Laboratory (RAL). The sediment metal analysis results for Bren were not completed at the time of writing the draft report.

# 2.5 Data processing

The DO profile data collected in the ponds were used to calculate Anoxic Factor (AF) as a measure of the persistence of anoxia and exposure of sediment to anoxic conditions. Anoxic factor is defined by Nurnberg (1995) as "the number of days that a sediment area, equal to the whole-lake surface area, is overlain by anoxic water" and the equation for AF is as follows:

$$AF = \left(\frac{\text{duration of anoxia}}{\text{duration of monitoring period}}\right) \times \left(\frac{\text{anoxic sediment area}}{\text{pond surface area}}\right)$$
(2)

where we used 2.0 mg/L as the threshold for anoxia and anoxic sediment area was determined from hypsographic curves derived from bathymetry for each of the ponds.

Using the temperature time series data obtained from the monitoring station at Pond 849\_W, the mixing dynamics in the pond was characterized using the Relative Thermal Resistance to Mixing (RTRM), which is a measure of stratification strength and is defined as:

$$RTRM = \frac{\rho_i - \rho_j}{\rho_{4^\circ C} - \rho_{5^\circ C}} \tag{3}$$

where  $\rho$  is the density of water at layers *i* and *j* (two points in the vertical profile), relative to the difference in water density at 4°C and at 5°C. The more positive the RTRM, the more stable the water column, while a RTRM less than zero indicates an unstable water column that will mix. Decreases in RTRM can be interpreted as mixing events, and may result from stormwater inflows, physical mixing by wind, or thermal (convective) mixing from high rates of heating

(sun) or cooling (clear, cool night) at the pond surface. The RTRM for the entire water column (top vs. bottom of the profile) was calculated for the 2020 data.

# 2.6 Data collection quality issues

With this type of field measurement program, there are always issues with collection quality and data processing. Those that developed for this report will be discussed in this section.

At Aquila Pond (max depth = 0.5 m), it was difficult to collect hypolimnion water samples without entraining the bottom sediments. Although such water samples containing sediments were chemically analyzed, those data points were excluded from the mean concentration calculation.

It was often difficult to collect water samples without entraining duckweed and/or *Wolffia* in the surface water samples, especially in the presence of a dense vegetation mat during the peak growing season. Additional effort was made to scoop out most of the floating vegetation at the time of water sample processing in the laboratory. Still, a few water samples contained some duckweed or *Wolffia*, which was noted during chemical analysis. On the other hand, it must be noted that the reported surface TP concentrations do not include the phosphorus trapped in the floating vegetation, as plant biomass analysis was not part of this project.

Since the bathymetric information was unavailable for Aquila Pond, hypsography measured in an old pond in St. Paul (located near Adolphus St. and Larpenteur Ave) with a similar depth as the pond with emergent vegetation and assumed to have a similar bathymetric profile was used. Anoxic factor was calculated for the entire season (May to November) and for the summer period (June to August) for each of the three field seasons.

# **3** Results

# 3.1 Pretreatment column study

#### 3.1.1 Sediment phosphorus release

The phosphorus release study results for the five ponds are shown in Figure 3, where the rate of change of phosphate concentration in the water column indicates phosphate release rate. Under oxic (aerated) conditions, sediment phosphate release was not observed in the sediment cores from Aquila Pond, Pond 849\_W, and Pond 42. The sediment cores from Pond BC-P4.10C and Bren Pond released a small amount of phosphate, resulting in the associated slope over time of water column phosphate concentrations. Phosphate release under oxic conditions can be attributed to the mineralization of labile organic phosphorus in the sediments and mobilization into phosphate (Jensen and Andersen 1992).

Once the air supply was switched off, the water column DO concentrations decreased over time due to the sediment oxygen demand (Figure 4). The rate of water column DO consumption was rapid in Pond 849\_W cores, with DO reaching <0.2 mg/L within 4 days in all cores (Olsen 2017). In the other pond cores, the water columns approached the anoxic state (DO <1 mg/L) over a period of 6 days (Aquila Pond, Pond 42) to up to 15 days (Pond BC-P4.10C, Bren Pond). Smax, the maximum oxygen consumption by the biologically active sediments, ranged between an average of 1.29 and 4.23 mg/m<sup>2</sup>/day in the five ponds (Table 2). High sediment oxygen demand is indicative of opportunistic aerobic respiration by microbes and is roughly proportional to the microbe population. Further, the sediment microbial activity is related to the phosphorus release from the sediments (Taguchi et al. 2018). This is supported by the concomitant increase in phosphate concentrations under reduced DO conditions after 6 to 15 days (after 4 days for Pond 849\_W) during the air off phase of the study (Figure 3).

In the last phase with an anoxic water column maintained by  $N_2$  bubbling, water column phosphate continued to increase due to sediment phosphate release in all cores from Aquila Pond, Pond BC-P4.10C, Bren Pond, and Pond 42. Some variability in phosphate release was observed within the replicate cores collected from a pond (for example, see Aquila Pond and Pond BC-P4.10C).

In the Pond 849\_W cores, after the water column was flushed with synthetic stormwater, a decrease in water column phosphate concentrations (or negative release) was observed. It is possible that the available sediment phosphate was depleted during the previous 150 days because the cores were not flushed with new organic material that would be eventually supply phosphate to the water column (Olsen 2017). In other words, most of the phosphate that was ready to be released had already been released because the columns were not resupplied with organic material.

Under the anoxic phase, the TP mass accumulation in the pond water columns generally followed the same trend as phosphate in all pond cores, although TP concentrations higher than SRP were sampled in some pond columns (plots not shown). Biofilm growth was noted in several columns and it is possible that some increase in TP occurred due to particulate phosphorus mass from bacterial growth in the water columns. Therefore, we calculated TP release from the sediments with the available TP data.



Figure 3. Phosphate (SRP) release measured from the pond sediment cores at 20 °C. The three phases of the phosphorus release study (air on, air off,  $N_2$  on) are separated by dashed lines. Data for 849 W are from Olsen (2017). Note differences in Y-axis scale.



Figure 4. Water column dissolved oxygen (DO) concentrations after air supply was switched off in the sediment cores from the five ponds. The DO measurements were taken ~8 cm above the sediment surface. The 1 mg/L DO (dashed line) represents anoxic state. Pond 849\_W data are from Olsen (2017).

The mean sediment phosphate (SRP) and TP release rates for the five ponds are summarized in Table 2. The TP fluxes are less reliable because they are not based upon as many measurements as the phosphate fluxes. For the anoxic conditions, the phosphate fluxes are close to the TP flux measurements, which indicates that the phosphorus absorbed by bacteria and not counted as phosphate flux was not substantial. Some of the oxic fluxes were different, but this could be due to the lack of TP data.

The oxic phosphate flux was negative for the Aquila Pond, Pond 849\_W, and Pond 42 sediments, which means the sediments do not release phosphate under oxic water column conditions. The positive oxic phosphate flux observed for Pond BC-P4.10C and Bren Pond sediments are low but are indicative of mobilization of phosphate by aerobic bacteria. It is possible that, in these two ponds, mixing of the pond (by aeration, for example) would not be as helpful without sediment phosphorus remediation. Both of these ponds are therefore well suited

to iron filings addition or alum addition to remediate phosphate release from the sediments. The anoxic phosphate fluxes for the five ponds are in the moderate range and suggest the possibility for significant phosphorus mass contribution from internal loading, especially during summertime anoxia in the ponds.

It was thought that the sediment oxygen demand  $(S_{max})$  would be a prospective indicator of sediment phosphate flux, but the Smax data change by a factor of three without a substantial change in anoxic SRP or TP flux. Sediment oxygen demand is a time-consuming measurement anyway, but this indicates that the relationship between sediment phosphate flux and organic matter content of the sediment (a less time-consuming measurement) will not be good.

Table 2. Mean sediment phosphorus (SRP and TP) release rates and sediment oxygen demand ( $S_{max}$ ) determined from the laboratory phosphorus release study. Values listed are mean  $\pm$  67% confidence interval for five sediment cores from each pond. n/a indicates no data. Data for 849\_W is from Olsen (2017).

Pond	Oxic SRP flux (mg/m²/day)	Anoxic SRP flux (mg/m²/day)	Oxic TP flux (mg/m <sup>2</sup> /day)	Anoxic TP flux (mg/m²/day)	S <sub>max</sub> (g/m <sup>2</sup> /day)
Aquila Pond	$-4.09 \pm 1.57$	$3.54\pm0.888$	$-3.81 \pm 1.42$	$4.36\pm0.615$	$2.79\pm0.519$
BC-P4.10C	$0.538\pm0.534$	$4.64\pm0.652$	$2.22\pm0.612$	$3.09\pm0.406$	$1.29\pm0.119$
Bren Pond	$0.897\pm0.290$	$4.41\pm0.286$	$-3.45 \pm 0.583$	$4.55\pm0.393$	$2.05\pm0.212$
Pond 42	$-0.708 \pm 0.576$	$3.97\pm0.696$	$\textbf{-2.97} \pm 1.98$	$4.70\pm0.882$	$1.89\pm0.147$
849_W	$-0.612 \pm 0.426$	$4.45\pm0.725$	n/a	$4.16\pm1.06$	$4.23\pm0.844$

#### 3.1.2 Sediment phosphorus composition

The physical characteristics of the pond sediments are presented in Table 3. The sediment moisture content decreased with depth from the surface (0 cm). A low moisture content (< 80%) indicating sediment consolidation was detected beyond the 7 cm depth in the Aquila Pond and BC-P4.10C pond sediments, while Pond 42 sediments appeared to be consolidated beyond the 2 cm depth. The mean sediment organic matter content (% of dry sediment by weight) in the top 10 cm depth was moderate at 18% in Aquila, 27% in BC-P4.10C, 27% in Bren, and 19% in Pond 42. The 849\_W sediments contained a high moisture content (94%) and a high organic content (78%) throughout the upper 10 cm depth of sediments. This could be due to the small drainage area, which would carry inorganic sediment, and large leaf loading from trees around Pond 849\_W.

Table 3. Sediment moisture content and sediment organic matter content in the five ponds. The mean concentration (% of dry sediment weight) for five sediment cores from each pond are shown. Data for 849\_W is from Olsen (2017).

	Aquila Pond	BC-P4. 10C	<b>Bren Pond</b>	Pond 42	849_W
Sediment depth	Avera	ge sediment m	oisture contei	nt (% dry we	ight)
0-1 cm	93.6%	95.0%	94.4%	94.5%	97.2%
1-2 cm	88.3%	90.8%	91.0%	81.0%	96.1%
2-3 cm	85.6%	89.3%	89.8%	73.9%	95.6%
3-4 cm	84.4%	87.4%	88.4%	70.9%	94.9%
4-5 cm	83.0%	86.9%	88.6%	67.0%	94.1%
5-7 cm	82.1%	83.9%	87.4%	65.1%	92.1%
7-10 cm	78.3%	75.2%	85.8%	61.2%	91.1%
	Average	sediment orga	nic matter cor	ntent (% dry	weight)
0-1 cm	29.6%	22.5%	28.5%	31.0%	81.7%
1-2 cm	28.7%	20.7%	28.3%	21.1%	79.0%
2-3 cm	28.5%	19.5%	26.9%	17.9%	79.0%
3-4 cm	26.0%	18.2%	26.9%	16.1%	78.0%
4-5 cm	26.0%	18.4%	26.9%	16.1%	77.3%
5-7 cm	24.3%	16.0%	26.0%	15.0%	75.3%
7-10 cm	22.6%	12.1%	24.1%	13.6%	78.7%

The concentrations of the various bioavailable and unavailable forms of phosphorus in the top 10 cm depth of sediments from the five ponds are plotted in Figure 5. Loosely-bound P was measured only in 849\_W sediments. Aquila Pond sediments contained high iron-bound P (0.45 mg P/g mean), where the peak concentration was observed 4-5 cm below the sediment surface. In the other ponds, lower concentrations of iron-bound P were measured (< 0.22 mg P/g mean) with vertical variation between the surficial and deeper sediments (for example, see Pond 42 in Figure 5). High concentrations of labile organic P were measured in Pond 849\_W (0.46 mg/g mean) and Bren Pond (0.33 mg/g mean), when compared to other ponds (< 0.20 mg/g mean), which corresponds to their high sediment organic content. The unavailable P forms were found to be significant in some pond sediments; for example, aluminum-bound P and mineral-bound P in Pond 42, and mineral-bound P and residual organic P in Pond BC-P4.10C were present at more substantial concentrations than either the iron-bound P or labile organic P fraction.



Figure 5. Vertical profiles of the phosphorus fractions in the upper 10 cm of sediments in the ponds. The average concentration (dry sediment weight basis) in three sediment cores is plotted for each pond. The 0 cm depth represents the surface of the sediment core. Concentration is plotted at the mid-point of the depth interval (for example, concentration for 0-1 cm depth is plotted at 0.5 cm). Pond 849 W data are from Olsen (2017).

The average composition of the P fractions as % of the total sediment phosphorus illustrates the relative importance of the bioavailable (mobile) phosphorus in the pond sediments (Figure 6). The redox-P forms (loosely- and iron-bound P) constituted between 12 and 30% of the total sediment P in the pond sediments. The mass of mobile P (loosely-bound P + iron-bound P + labile organic P) relative to TP in the upper 4 cm depth of sediments was 53% in Aquila Pond, 43% in Pond BC-P4.10 C, 47% in Bren Pond, 41% in Pond 42, and 63% in Pond 849\_W. The levels of mobile P in the surficial sediments in the ponds studied indicate that, under conducive conditions in the water column, phosphorus release from the sediments would be substantial. This is supported by our previous (Janke et al. 2021) and ongoing work that has shown strong correlations between anoxic phosphate flux and mass of redox-P and mobile P, between labile

organic P mass and sediment organic content, and between sediment organic matter content and sediment oxygen demand, highlighting the importance of these sediment variables in controlling phosphorus dynamics in ponds.



■ Res Org-P ■ Mineral-P ■ AI-P ■ Labile Org-P ■ Fe-P ■ Loosley-bound P

Figure 6. Sediment total phosphorus composition in the five ponds. The average composition in the upper 4 cm of sediments in three cores from each pond is shown. The sum of loosely-bound *P*, iron-bound *P* and labile organic *P* represents the mobile *P* in the sediments, where this *P* is released by redox changes and bacterial mineralization. The other *P* forms (aluminum-bound, mineral-bound and residual organic *P*) are generally not available for sediment *P* release.

#### 3.1.3 Selection of ponds for iron filings treatment

The risks for internal loading will be significant in ponds that have a high bioavailable phosphorus mass in sediments and experience extended periods of anoxia that can trigger the release of phosphorus in the sediments. As will be discussed later (Section 3.2.1 on field observations), Pond BC-P4.10C, Bren Pond, Pond 849\_W, and Pond 42 exhibited strong thermal stratification and persistent anoxic conditions during much of the summer period in 2019. In the laboratory, a moderately-high release of phosphorus was observed from BC-P4.10C, Bren, and 849\_W pond sediments under anoxic conditions and a low oxic release was measured from BC-P4.10C and Bren Pond sediments. The higher proportion of releasable phosphorus mass in the pond sediments suggests that a sediment remediation measure (such as alum or iron addition) will help control the release of phosphorus. Thus, based on the field and lab observations in 2019 and considering the ease of access to the ponds, the BC-P4.10C, Bren, and 849\_W ponds were the recommended candidates for iron filings treatment of the sediments.

# 3.2 In situ monitoring results

The field data collection efforts at the five ponds are summarized in Table 3. The pond sites were routinely sampled from May to November, with a total of 10 to 13 site visits per pond, during 2019, 2020 and 2021. Based on the rainfall recorded in the Twin Cities during the growing season<sup>1</sup>, 2021 was dry not only compared to 2020 and 2019, but also drier than normal for the Twin Cities<sup>2</sup>. In 2021, low water level at Pond 849\_W made access impossible during June and July and hence the fewer number of visits at Pond 849\_W than the other ponds.

Table 4. Summary of field data collection at the five pond sites from 2019 to 2021. For Turnover, general pattern is given (intermittent or frequent), but if the pond was stratified through most of season then date of fall turnover is given. Average duckweed cover during the entire field season (May to October) is provided. Anoxic factor (AF) for the entire field season (May to October) and the summer period (June to August) are provided.

Field Season		Aquila Pond	BC-P4.10C	Bren Pond	849_W	Pond 42
2019	Site visits	10 5/31/19 – 10/29/19	10 5/31/19 – 10/28/19	10 5/29/19 – 10/25/19	10 5/29/19 – 10/28/19	10 5/29/19 – 10/28/19
May – Nov rainfall = 32.4 inches	Turnover	Intermittent	10/14/19	Intermittent	10/14/19	Intermittent
June – Aug rainfall = 15.5 inches	Duckweed cover (mean)	High (66%)	High (72%)	High (85%)	High (80%)	High (94%)
	AF (Summer AF)	0.658 (0.806)	0.718 (0.956)	0.849 (0.878)	0.799 (0.998)	0.944 (0.950)
2020	Site visits	13 5/20/20 – 10/29/20	13 5/19/20 – 10/19/20	11 6/18/20 – 10/19/20	13 5/19/20 – 10/19/20	9 6/18/20 - 10/5/20
May – Nov rainfall = 23.3 inches	Turnover	Frequent	10/19/20	Intermittent	10/19/20	Frequent
June – Aug rainfall = 13.9 inches	Duckweed cover (mean)	High (77%)	High (72%)	High (87%)	High (76%)	High (94%)
	AF (Summer AF)	0.773 (0.886)	0.724 (0.986)	0.868 (0.890)	0.764 (0.885)	0.939 (0.945)
2021	Site visits	11 5/26/21 – 11/10/21	12 5/28/21 – 11/15/21	12 5/28/21 – 11/15/21	10 5/28/21 – 11/4/21	n/a
May – Nov rainfall = 17.3 inches	Turnover	8/31/2021	11/4/21	11/4/21	11/4/21	n/a
June – Aug rainfall = 9.81 inches	Duckweed cover (mean)	High (57%)	High (77%)	High (74%)	High (84%)	n/a
	AF (Summer AF)	0.568 (0.750)	0.767 (1.00)	0.740 (0.930)	0.844 (0.988)	n/a

<sup>&</sup>lt;sup>1</sup> https://www.dnr.state.mn.us/climate/twin\_cities/listings.html

<sup>&</sup>lt;sup>2</sup> https://www.mprnews.org/story/2021/09/22/happy-autumn-summer-was-warmest-on-record-for-twin-cities

The field observations in 2019 (i.e., pretreatment study period) are discussed along with the 2020 and 2021 data in the following sections on pond mixing status and phosphorus water quality. Time series plots, showing the variation in pond phosphorus concentrations (TP and SRP) in the epilimnion and hypolimnion and the extent of duckweed coverage on pond surface during each growing season, are shown in the Appendix, along with sample photographs of duckweed coverage in the ponds and daily precipitation in the study area during the three monitoring seasons.

# 3.2.1 Stratification and dissolved oxygen dynamics

Contour plots (spatially- and temporally-interpolated vertical profiles) of the DO and temperature data are shown for selected ponds in this section. The remaining contour plots are shown in the Appendix.

# Aquila Pond

Aquila Pond is a shallow pond. The pond was weakly stratified with low DO only near the pond bottom during much of the wetter 2019 season (Figure 7). Low surface DO was observed in June and July when duckweed cover was dense. The water column destratified by mid-August, although low bottom DO was measured again in October 2019. During the 2020 season, the pond was weakly stratified with relatively high DO throughout the water column, although the duckweed coverage was >80% from June to September 2020. In 2021 summer, the pond experienced dense duckweed cover in July and August, and during this period, the pond's entire water column was anoxic and stratified despite being only 40 - 50 cm deep at this time. Inputs of stormwater runoff during August rains also appeared to oxygenate the water column all the way to the sediments, and duckweed cover generally decreased from this point onward. Stratification for the rest of the season was weak. Aquila Pond was subject to frequent mixing but the oxygen dynamics appear to be impacted by variable duckweed cover.

#### Pond BC-P4.10C

Pond BC-P4.10C was strongly stratified ponds and experienced persistent anoxia from June to September in 2019, 2020, and 2021 (Figure 8), as indicated by the high summer anoxic factor (AF) values (Table 3). Water column DO was extremely low in the entire pond water column, with bottom DO of nearly 0 mg/L from June through September during the three field seasons. Low surface DO (<1 mg/L) was measured within a few cm below the duckweed cover, which was dense and pervasive from June through August. Runoff inputs appeared to oxygenate the upper water column on some occasions (September 2020) but did not cause complete mixing. One of the reasons for the lack of frequent mixing during stormflow periods is hypothesized to be due to wind sheltering by the banks of the pond and trees, where the poor mixing facilitated a sustained stratification leading to anoxia. Thermal stratification appeared to weaken and the water column was partially mixed toward the end of the season, typically by mid-October (2019 and 2020) or early November (2021).



Figure 7. Dissolved oxygen (DO) and temperature contour plots for Aquila Pond. Color indicates values per the scale at right, with water depth relative to the pond bottom on the y-axis, and time along the x-axis. Vertical dashed lines are dates of site visits when profiles were collected; linear interpolation used to fill in the gaps between profile dates. A contour for 1.0 mg/L DO indicates levels below which the pond is considered anoxic.



Figure 8. Dissolved oxygen (DO) and temperature contour plots for Pond BC-P4.10C. Color indicates values per the scale at right, with water depth relative to the pond bottom on the y-axis, and time along the x-axis. Vertical dashed lines are dates of site visits when profiles were collected; linear interpolation used to fill in the gaps between profile dates. A contour for 1.0 mg/L DO indicates levels below which the pond is considered anoxic.

#### Bren Pond

Bren Pond was also thermally stratified and anoxic during much of summer in 2019, 2020 and 2021. Low bottom DO (< 1 mg/L) was a common observation at this pond and anoxia was extensive during the June to September period (summer AF of nearly 0.9). Runoff inputs appeared to mix the upper water column that increased the surface DO, as observed during several rainfall events in the 2020 season. Duckweed cover was persistent and dense from July until mid October. Thermal stratification appeared to weaken intermittently during the growing season (2019 and 2020) and pond turnover was observed by late Fall.

#### Pond 42

In Pond 42, the water column DO was extremely low (<1 mg/L), producing top-to-bottom anoxic conditions from June through October of both 2019 and 2020. Almost the entire pond area was anoxic during 2019 and 2020 (summer AF = 0.95). Thermal stratification was not as strong since the pond appeared to mix intermittently, but it did not oxygenate the water column. Duckweed cover ramped up quickly in early summer and was persistent and dense until mid to late October, suggesting the strong influence on oxygen levels in the pond water column. This pond is heavily sheltered by trees that likely prevented complete pond mixing.

#### Pond 849 W

Pond 849\_W was also strongly stratified and experienced persistent anoxia from June to September in 2019, 2020, and 2021. The entire water column had low DO such that a majority of the pond area was under anoxic conditions from June or July through September (summer AF > 0.85). The pond mixing dynamics in 2020 is shown using RTRM and contour plots in Figure 9. Poor mixing of the water column despite stormflow inputs is indicated by the relatively small decreases in RTRM associated with runoff events (e.g., late June, mid August) and thus mixing events appear to be mostly from wind or heat exchange (especially the cold snap in early September, and some windy days in mid July). The pond has a small contributing watershed, so the minimal result of watershed runoff is logical. Conversely, stratification strength tends to build (as increase in RTRM) during dry periods, such as during early July and late August, and even a few periods during September. Duckweed cover was dense and pervasive during the sustained stratified and anoxic conditions during every growing season. There is heavy wind sheltering by mature trees around the pond. In all three years, thermal stratification was eroded by heat loss typically by mid to late October when the water column appeared to be fully mixed.



Figure 9. 849\_W Pond time series of rain (cm; from MSP Airport), water depth (cm), wind speed (km/h), RTRM (for upper water column and for whole water column 'top-btm'), DO profiles (mg/L; as contours) during the 2021 monitoring season. RTRM, wind, and water level measured by monitoring stations and averaged into daily values). Other data from site visits.

Conductivity levels were also monitored in the ponds (contour plots shown in the Appendix). Conductivity measurements greater than 500  $\mu$ S/cm are likely due to runoff containing road salt applied during the winter months (Granato and Smith 1999). High conductivity (~400 to 1400  $\mu$ S/cm) was measured in the bottoms of Aquila Pond, BC-P4.10C, 849\_W, and Pond 42 during all three monitoring seasons. The high conductivity in the bottom measured during early summer was gradually flushed out by July in Pond 42 but not until late August or September in the other three ponds. Aquila Pond typically had high conductivity levels that did not get flushed out until very late in the field season. In Bren Pond, the low conductivity (<300  $\mu$ S/cm) in the pond bottom indicates little salt signal, although relatively high measurements were taken during the 2021 season. High specific conductivity, attributed to chlorides contributed by road salt input, can make water denser and more resistant to vertical mixing (Novotny et al. 2009). This phenomenon of chemostratification has been observed in some ponds that exhibited strong summertime stratification with low DO and high conductivity in the pond bottoms (Taguchi et al. 2018, Janke et al. 2021). It is possible that the conductivity levels contributed to the summertime stratification in the ponds studied, although the extent of the effect was not determined in this study.

# 3.2.2 Phosphorus water quality

Phosphorus concentrations (TP and SRP) in the ponds varied over each growing season and across the five sites (see time series plots in the Appendix). The mean phosphorus (TP, TDP and SRP) concentrations during each field season are summarized in Table 4. The general patterns of pond phosphorus concentrations are discussed first, including possible impacts of precipitation, pond stratification status, and duckweed cover on the pond water quality. The post-treatment water quality in the iron-treated ponds are discussed in section 3.2.2.1.

Table 5. Mean phosphorus concentrations in the ponds during 2019, 2020, and 2021 field sampling. The average concentrations of total phosphorus (TP), total dissolved phosphorus (TDP), and phosphate (SRP) in the pond surface (epilimnion) and hypolimnion (~0.25 m above pond bottom) during the May to October/November period are summarized. The surface water samples were collected below the duckweed cover. Post-iron treatment years are marked with an asterisk (\*). n/a represents no data.

	Iron	Field	Mean phosphorus concentration (mg/L)											
Pond	filings treatment	Season	Season Surface Surface Surface FP TDP SRP		Нуро ТР	Hypo TDP	Hypo SRP							
	<b>N</b> T .	2019	0.161	n/a	0.042	0.168	n/a	0.039						
Aquila	Not treated	2020	0.330	0.059	0.032	0.284	0.051	0.032						
Pond BC- P4.10C	treated	2021	0.321	0.100	0.052	0.329	0.113	0.058						
Dand DC		2019	0.139	n/a	0.037	0.213	n/a	0.107						
Pond BC- P4 10C	2/19/19	2020*	0.167	0.039	0.025	0.200	0.033	0.015						
P4.10C		2021*	0.187	0.050	0.025	0.307	0.044	0.021						
	2/24/20	2019	0.191	n/a	0.055	0.176	n/a	0.052						
Bren Pond		2020	0.182	0.048	0.021	0.171	0.048	0.022						
		2021*	0.160	0.049	0.015	0.251	0.048	0.013						
		2019	0.127	n/a	0.012	0.116	n/a	0.012						
Pond 849 W	2/21/19	2020*	0.270	0.023	0.013	0.401	0.030	0.009						
		2021*	0.187	0.025	0.012	0.311	0.027	0.013						
		2019	0.173	n/a	0.061	0.210	n/a	0.066						
Pond 42	Not treated	2020	0.270	0.074	0.047	0.329	0.072	0.043						
	treated	2021	n/a	n/a	n/a	n/a	n/a	n/a						

# Aquila Pond

The surface TP dynamics in Aquila Pond showed a general pattern of increased surface and hypolimnion TP during the wetter periods (for example, mid-August period in 2019, 2020 and 2021), likely reflecting watershed inputs and mixing of the hypolimnion. The overall TP concentrations measured in 2019 were lower than in both 2020 and 2021. In 2021, TP concentrations were relatively high earlier in the season (July to August). The SRP concentrations in the surface and hypolimnetic were similar, and showed minimal variation over the monitoring period in 2019 and 2020. During 2021, SRP concentrations peaked during the onset of the wet period as observed for TP.

# Pond BC-P4.10C

In Pond BC-P4.10C, the surface TP gradually increased over the season until August and the P concentrations generally decreased over the remainder of the season, which were typically dry. SRP concentrations were more variable over the 2019 season than in 2020 and 2021. The 2020 and 2021 seasons were also the post-treatment monitoring season for this pond. With some notable exceptions, the hypolimnetic TP and SRP concentrations were similar to the average concentrations of TP and SRP in the pond surface water.

# Bren Pond

In Bren Pond, the surface and hypolimnetic TP responded to the wet periods in 2019 (mid-August), likely due to TP input and mixing of hypolimnion. The trend was less apparent in 2020 and 2021, which showed minimal variation in surface TP and SRP over much of the season. The hypolimnetic TP and SRP concentrations were similar to the average concentrations of TP and SRP in the pond surface water, with the exception of summer 2021 when higher hypolimnetic TP was measured early in the season. In the post-treatment summer of 2021, lower surface TP and SRP concentrations were sampled than previous years.

# Pond 849 W

The increase in surface TP in Pond 849\_W generally coincided with onset of rainfall events (mid-August in 2019, June-July 2020). The 2020 and 2021 seasons were the post-treatment monitoring season for this pond. In 2021, surface TP concentrations were higher in May (when it was dry) and concentrations remained low throughout the rest of the season. The SRP levels in 849\_W were typically very low (<  $20 \mu g/L$ ) and less variable in all three seasons. One reason for such low phosphate concentrations could be due to uptake by the floating plant biomass and submerged macrophytes in the pond.

#### Pond 42

The surface TP concentrations in Pond 42 were generally similar from June to September in 2019 and P concentrations did not appear to fluctuate during rainfall events. In 2021, surface TP

increased during the wet period in August. Hypolimnetic TP increased toward the end of the season during both years, likely indicating mixing of pond. The overall TP concentrations measured in 2020 were higher than 2019 levels. Surface SRP was higher at the beginning and end of the season, suggesting possible plant uptake of phosphate during peak growing season.

All five ponds were covered with duckweed and *Wolffia*; peak areal coverage of nearly 100% was established in mid or late June that sustained until the end of August or September, and duckweed cover decrease at the beginning of October and mostly disappeared by mid-October (see duckweed cover time series plots in the Appendix). It must be noted that the measured P concentrations were in the water under the thick duckweed cover on the pond surface and, therefore, mostly exclude the phosphorus contained in the organic material (duckweed and algal mat) in the pond, which can be substantial. The effect of duckweed on the pond phosphorus concentrations, however, was not quantified in this study. In addition, it is believed that the reduction of TP concentration during the summer is impacted by the growth of macrophytes, which contain phosphorus and were not sampled. Still, the surface TP levels in the pond often exceeded the MPCA's 60  $\mu$ g/L TP standard for aquatic life and recreation in shallow lakes in the North Central Hardwood Forests region during the three monitored seasons [Minn. R. § 7050.0222; MPCA)].

# 3.2.2.1 Pretreatment vs. post-iron treatment phosphorus concentrations

A reduction in surface SRP concentrations was observed after treatment in BC-P4.10C and Bren Pond, and their hypolimnetic SRP levels were especially lower post treatment (Table 4). The SRP levels in Pond 849\_W were low during all three years. In Figure 10, we show the mean surface TP concentrations measured during each monitoring season in the five RPBCWD ponds and in other ponds across the Twin Cities metro region. The Shoreview Commons Pond, located in the Ramsey Washington Metro Watershed District, is a fourth pond that was treated with iron filings in February 2021.



Figure 10. Mean surface TP concentrations in the five RPBCWD ponds and other ponds in the Twin Cities Metro area during the 2019, 2020, and 2021 field seasons. Mean concentration for the May to October period is plotted. Error bars represent standard deviation of the mean. The ponds treated with iron filings are marked with an asterisk (dates of iron application are 2/19/20 in BC-P4.10C, 2/21/20 in 849\_W, 2/24/21 in Bren Pond and Shoreview Commons Pond). Alameda, Arrow, and Cleveland/R are ponds located in Roseville, Ponds B and K are located in Eden Prairie, and Shoreview Commons Pond is located in Shoreview. Except Pond K and Arrow Pond, all other ponds have dense floating vegetation (duckweed and watermeal) cover during the peak growing season.

In the untreated ponds (Aquila, Bren, 42, Alameda, Cleveland/R, Arrow, B, K), surface TP concentrations measured in 2020 were generally higher than their 2019 concentrations. Aquila Pond can be used as a control for the RPBCWD region, where TP was seen to increase greatly from 2019 to 2020, and then stayed about the same in 2021. In Pond BC-P4.10C, the average TP went up after treatment with iron filings in February 2020, but not as substantially as the Aquila Pond. In Bren Pond, the average TP decreased after treatment in February 2021 but the TP showed a slight reduction in all three years. In Pond 849\_W, average TP went up after treatment in 2020 but then reduced in 2021. A similar reduction can be seen in comparing average TP for Shoreview Commons Pond to the Alameda Pond, where Shoreview Commons Pond had a reduced average TP in 2021 after iron filings addition and the Alameda Pond, with no iron filings addition, did not have a reduction in TP; these ponds had similar TP levels in previous years.

Precipitation and runoff patterns, watershed phosphorus inputs, pond hydrologic balance, and floating plant growth are some of the important factors that drive pond phosphorus concentrations. Rainfall during the monitored period was lowest in 2021 than 2020 and 2019. The year-to-year variation in phosphorus levels in the ponds thus complicates the interpretation of the measured phosphorus concentrations and treatment effectiveness. The iron filings treatment seems to have had some effect on TP levels, but rainfall and runoff are at least as important for pond water quality. For most of these ponds, adding iron filings can be a part of the solution to reduce TP in the water, but must be implemented with other remediation techniques.

#### 3.3 Effects of iron filings treatment on pond sediments

#### 3.3.1 Phosphorus release from iron-treated sediments

Phosphorus release from the iron-amended sediments of Bren Pond was determined through column tests (Figure 11). Under the oxic phase, the water column phosphate and TP mass decreased over time. The concentrations continued to remain low after low DO condition (DO < 1 mg/L) was established during the unmixed phase (starting day 39 in Figure 11). Even under an anoxic state, there were no significant changes in the water column phosphate concentrations in four cores, which means sediment phosphate release did not occur from these iron-amended sediments. Only one core (Bren 2) exhibited a small release of phosphate after 24 days of anoxic conditions (under N<sub>2</sub> bubbling; day 99). A gradual increase in TP was observed in all columns during the anoxic phase; biofilm growth was observed in a few columns indicating bacterial contribution to particulate phosphorus mass accumulation in the columns.



Figure 11. Phosphate (SRP) and total phosphorus (TP) concentrations in the water columns of the iron-treated sediment cores from Bren Pond during the laboratory study. The sediment cores were collected eight months after iron filings application in Bren Pond.

Figure 12 further illustrates the positive impact of iron filings addition on sediment phosphorus flux from Bren Pond sediments. Also shown are results for the Shoreview Commons Pond (located in the Ramsey Washington Metro Watershed District), which was treated with iron filings at the same time as Bren Pond. Both oxic and anoxic sediment phosphorus releases were effectively controlled by the addition of iron filings to the pond sediments. The anoxic flux was substantially reduced due to the enhanced iron concentrations in the sediments. The mean sediment oxygen demand (SOD) was also lower for the iron-treated sediments. The reason for lower SOD is not clear, since the sediment organic content was similar in the sediments collected before and after iron filings treatment (mean organic content in upper 2 cm depth was 28% before and 27% after treatment).



Figure 12. Oxic and anoxic sediment phosphate (SRP) release measured before and after iron filings application in Bren Pond and Shoreview Commons Pond. The mean SRP flux and sediment oxygen demand (Smax) for five sediment cores are plotted for each pond. Error bars represent 67% confidence interval of the mean. Sediment cores were collected from Bren pond in March 2019 (before iron treatment) and in October 2021 (after iron treatment).

#### 3.3.2 Sediment phosphorus composition in iron-treated sediments

The effect of iron addition on the concentrations of the redox-sensitive P species that release under low DO conditions and the labile organic P that releases by bacterial mineralization was examined (concentration profiles of all P fractions shown in the Appendix). The mean redox-P concentration (i.e., loosely- and iron-bound P) was found to be elevated in the upper 3 cm depth of Pond BC-P4.10C sediments and only in the upper 2 cm depth of Bren Pond sediments (Figure 13). In the 849\_W pond sediments, redox-P increased substantially up to the 6 cm depth. It is likely that the iron filings pieces deposited across the top 6 cm depth of the "muckier" sediments and produced a higher P mass sorption within that depth. The labile organic P in the upper 4 cm depth of treated sediments were lower than the pretreatment concentrations, especially in Pond 849 W sediments.



Figure 13. Vertical profiles of redox-sensitive (iron-bound P + loosely-bound P) and labile organic phosphorus fractions in the pond sediments before treatment (unamended) and after treatment (treated) with iron filings. The average concentration (dry sediment weight basis) in five sediment cores is plotted for each pond.

The increase in Fe-P formation changed the relative P mass distribution (as % of total sediment P), especially in the upper 4 cm depth (see pie charts in the Appendix). The average total sediment P was nearly the same in the unamended and treated sediment samples (change in TP mass was -0.72% in Pond BC-P4.10C, 8.9% in Pond 849 W and 6.7% in Bren Pond post treatment), making the before vs. after comparison of P fractionation meaningful. In Pond BC-P4.10C, the Fe-P mass increased from 19% to 27% of the total sediment P, with a concomitant decrease in the loosely-bound P (-0.58% change) and labile organic P mass (-7.5% change). In Pond 849 W, the Fe-P mass increase (+16% change) was accompanied with loss in looselybound P (-4.1% change) and labile organic P mass (-15% change). The speciation change in Bren Pond sediments were less substantial in the top 4 cm depth; Fe-P mass increased by 2.3% and labile organic P mass reduced by 6.7%. The change in relative mass of the remaining unavailable P fractions was marginal. It is hypothesized that the loss in loosely-bound P (primarily porewater phosphate) and labile organic-P can partially or fully manifest as an increase in iron-bound P due to the formation of iron-phosphate minerals in the presence of enhanced iron mass in the sediments (Natarajan et al. 2017). The decrease in labile organic P can be attributed to its breakdown and conversion into phosphate that can be captured by not only iron but also aluminum and calcium minerals in the sediments, although loss to the water column and biota is also possible. The role of organic matter inputs such as leaf litter and plant biomass may also influence the organic phosphorus levels in pond sediments (Janke et al. 2017).

It must be noted that the Fe-P profiles were spatially variable across the pond area. The Fe-P mass in the upper 2-3 cm sediment depth were much higher than the deeper sediments in only three cores (Bren Pond) or four cores (BC-P4.10C and 849\_W ponds) out of the five cores collected from each pond. First, a perfectly uniform distribution of iron filings over the entire pond surface is difficult to achieve during application. The physical characteristics (bulk density) of the surficial sediments can influence the vertical deposition of iron filings pieces into the sediments and thus the amount of iron available for biding P. Second, it is probable that some locations in the pond receive and accumulate a lower amount of incoming debris (and P) due to the runoff flow patterns and pond configuration. We found similar patterns in an iron-treated pond in St. Cloud (Natarajan and Gulliver 2022).

#### 3.3.3 Iron concentrations in treated sediments

The objective of these measurements is to find correlation based upon sediment analysis that can replace sediment release analysis, which is a time-consuming effort requiring several months. As expected, the iron filings application increased the overall sediment iron (Fe) concentration in the surficial sediments. In BC-P4.10C pond, the average Fe level in 0-4 cm depth increased from 29 mg/g to 45 mg/g, which corresponds to Fe:P (by mass) increase from 24:1 to 40:1. In 849\_W pond, the 0-4 cm iron concentration increased from 18 mg/g (Fe:P = 12:1) to 61 mg/g (Fe:P = 32:1). The metal analysis of Bren Pond sediments was not completed at the time of writing this report. High Fe availability in the surface sediments has been related to the reduced availability of phosphate in the pore water and release to the overlying water in lakes; a ratio above 15 Fe:P has been recommended for controlling internal P release by keeping the surface sediment oxidized (Jensen et al. 1992, Geurts et al. 2008). This is because a high Fe:P in the sediments would provide more sorption sites for phosphate ions on iron hydroxide mineral surfaces under oxic conditions.

Within a pond, the iron concentration profiles at the five coring locations were variable; i.e., elevated Fe concentrations (predominantly in the upper 4 cm depth) was evident in some cores but not all (data summarized in the Appendix). These differences are expected due to an uneven distribution of iron filings during application. As noted earlier, the iron-bound P profiles also exhibited spatial variation, likely a result of differences in available iron and phosphate in these sediments. Figure 14 depicts the correlation between iron-bound-P and Fe concentrations in the upper 10 cm depth of sediments (linear  $R^2 = 0.39$ ); the scatter in the plot suggests that a high Fe concentration did not directly correspond to higher iron-bound P mass in the sediments.



Figure 14. Correlation plot showing the sediment concentrations of total iron (Fe) and ironbound phosphorus (P) fraction in the upper 10 cm depth of sediments from three iron filingstreated ponds. Dark circles are data for BC-P4.10C and 849\_W ponds, and open circles are data for St. Cloud Pond 52.

# 4 Findings and interpretations

#### 4.1 Summary

Five ponds, Aquila Pond (in Bloomington), Pond BC-P4.10C (in Chanhassen), Bren Pond (in Eden Prairie), Pond 849\_W (in Minnetonka) and Pond 42 (in Shorewood), were evaluated in this two-part study.

- a) In the pretreatment study, column studies with pond sediment cores showed a moderatelyhigh flux of phosphate release from anoxic sediments. Oxic phosphate release was observed only for BC-P4.10C and Bren pond sediments. The sediment phosphorus chemistry analysis indicated that the mobile P in the sediments (redox-P which is releasable under low oxygen conditions and labile organic P which is releasable by microbacterial degradation under both oxic and anoxic conditions) constituted 41% (Pond 42) to 63% (849\_W) of the total sediment phosphorus, and influence internal phosphorus release under anoxic conditions.
- b) In situ monitoring during the growing season showed that all ponds, except for Aquila Pond, had a stratified water column that was anoxic from top to bottom from June to September. Aquila Pond appeared to partially mix intermittently although bottom DO was still low during certain periods. At all five pond sites, floating vegetation (duckweed and watermeal) covered the entire pond surface from June to September, and likely influenced the DO dynamics (Janke et al. 2021).
- c) The application of iron filings was recommended to reduce phosphate release from the pond sediments. Ponds BC-P4.10C and 849\_W were treated with iron filings in February 2020 and Bren Pond was treated in February 2020. Aquila Pond can be used as a control for the RPBCWD region, where surface water TP was seen to increase greatly from 2019 to 2020,

and then stayed about the same in 2021. In Pond BC-P4.10C, the average TP went up after treatment with iron filings in February 2020, but not as substantially as the Aquila Pond. In Bren Pond, the average TP had a slight reduction in all three years. In Pond 849\_W, the average TP went up in 2020 but then reduced in 2021. A similar reduction can be seen in comparing average TP for an iron-treated pond (Shoreview Commons Pond) and an untreated pond (Alameda Pond) located near Roseville.

- d) Laboratory analysis of the iron-treated sediments showed the anoxic sediment phosphate flux was significantly lower in treated sediments when compared to untreated sediments. The addition of iron filings had resulted in an enhanced iron-bound P mass and decreased labile organic P mass in the treated ponds, suggesting the partial or full movement of phosphate from the organic P form and loosely-bound P to iron-phosphate minerals in the sediments (Natarajan et al. 2017).
- e) The post-treatment water quality at the three iron-treated ponds showed reductions in SRP concentrations but changes in TP levels were less obvious, especially considering the year-to-year variation in rainfall and runoff patterns that also influence the pond phosphorus levels.

# 4.2 Recommendations for pond remediation

Since the five ponds monitored in this study are under anoxia for much of the summer and only rarely undergo mixing, there are substantial risks for internal phosphorus loading in those ponds. Some of the potential measures, other than chemical treatment of sediments using iron filings, to lower the potential for internal loading on these and other ponds in the RPBCWD will be discussed in this section.

a) Chemical treatment of sediments

The application of a phosphorus-adsorbing chemical to inactivate the sediment phosphorus is a commonly used in-lake treatment method for internal phosphorus load reduction. Alum, iron, and calcium compounds have been applied in lakes for phosphorus control with varying degrees of success. The effectiveness of the chemical treatment is influenced by a number of factors including the dosing, existing conditions, and control of external phosphorus load input (Steinman and Spears 2019, MPCA 2020). In a recent study of wet pond maintenance (Taguchi et al. 2022), chemical treatment of sediments was found to be the most cost-effective means of reducing phosphorus export from the ponds studied.

Iron chloride has been successfully applied in several lakes (Orihel et al. 2016), although the iron treatment was combined with continuous or intermittent artificial aeration in some cases for long-term reduction in lake phosphorus levels (Engstrom 2005). The experimental addition of iron filings to lake sediments in the laboratory showed that sediment phosphorus release was reduced under oxic and anoxic conditions (Natarajan et al. 2017), and this was tested for three pond sediments in this study. The RPBCWD is the first organization to test the effectiveness of

iron filings treatment under field conditions. The result is that some reduction in expected TP levels has been observed, but the three ponds still had an abundance of floating plants. The external loading of phosphorus and dissolved oxygen concentration in the pond need to be remediated along with chemical treatment of sediments.

Alum ( $[Al_2(SO_4)_3]$  has been widely applied in lakes and more recently in ponds for sediment phosphorus inactivation. The alum dose is devised to primarily target the highly-mobile redox-P fraction (loosely-bound P + iron-bound P) in the sediments and convert it to the immobile aluminum-bound P which is not sensitive to changes in DO conditions. Depending on the water alkalinity, a buffered alum treatment (i.e., alum with sodium aluminate buffer) may be required to prevent the pH from dropping below 6 during the application. At least 85% reduction in sediment phosphorus release has been observed with alum dosing in lakes, although other factors such as high external load can impact the overall reduction in lake phosphorus levels (NALMS alum workshop 2019). The longevity of alum treatment has varied from 1 to 11 years in shallow lakes and from 4 to 21 years in stratified lakes (MPCA 2020). While alum is a well-known lake treatment, there have been no studies of the effectiveness of alum treatment in ponds, which have a much higher sedimentation rate. It is likely that for many ponds, alum addition would need to be a part of a larger remediation effort that includes watershed-based phosphorus control options.

Another proprietary chemical that has been recently applied in lakes, primarily in Australia, Europe, and Canada, is a lanthanum-modified bentonite (Phoslock®) that forms a highly stable mineral with phosphate even under anoxic conditions. Similar to alum, Phoslock doses are added to inactivate phosphate in the water and the mobile P in the sediment, and have shown reduction in lake TP levels (Spears et al. 2005, Nürnberg and LaZerte 2016). The effectiveness and longevity of the Phoslock additive is, however, unclear because of the relatively few known applications so far (MPCA 2020).

# b) Mechanical aeration

Taguchi et al. (2022) also found that mechanical aeration designed to destratify the pond can be an effective treatment for water column concentration of TP at stormwater retention ponds. This is especially true if, under oxic conditions, the pond sediments had a measured phosphate adsorption rate. Outflow must also be considered to estimate a reduction in the export of phosphorus.

Mechanical aeration in combination with the application of iron filings or alum may be good remediation strategy for ponds that have low DO and substantial phosphate release from the sediments.

# c) Develop wind corridors by reducing sheltering

Taguchi et al. (2022) also found that a reduction of sheltering did not provide much additional mixing of the four ponds that they were studying, and therefore did not substantially reduce total

water column phosphorus concentration. This could result from one or all of three observations: the ponds have a shot wind fetch, relative to lakes, the banks on the pond cause sufficient separation of the wind and sheltering of the ponds to reduce the potential wind shear, and the upwind roughness, such as houses, trees around the houses and buildings have a fairly large effect on the wind's ability to generate shear stress on the ponds. Wind has a greater effect on ponds that are more exposed to wind, but in a residential area with trees around the pond, similar to the ponds studied herein, developing wind corridors would not be an effective treatment.

#### d) Watershed-based reduction of phosphorus inflow

Watershed-based methods (reducing inflow concentrations and volumes) are an effective means of reducing TP exports for all ponds because the stormwater TP inflows are a major component of the overall TP mass balance in each pond (Taguchi et al. 2022). Reducing inflow volumes (through the installation of infiltration practices) can led to increased TP concentrations in a ponds since constituents in the pond water will not be as diluted by inflow volumes. This approach resulted in very low TP export but do not reduce TP concentration for ponds that are treated as amenities where pond water quality is also a priority. Reducing inflow TP concentrations and overall pond TP export in a more predictable way.

Volume inflow reduction and phosphorus concentration reduction, however, are generally less cost-effective than in-pond options at reducing total phosphorus concentration when sediment phosphate release rate is high. They are more effective on newer ponds with a low phosphate release rate).

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# Appendix

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*Figure A- 1. Map showing the locations of the five RPBCWD ponds monitored in this study (<www.maps.google.com>).* 



Figure A- 2. Maps showing the locations of surface water sample collection (1-5 red circles) and profile measurement (deepest location) in the RPBCWD ponds sampled from 2019-2021. Hypolimnion water samples were collected at the deepest location (typically pond center except for Aquila). Sediment cores for laboratory phosphorus release study were collected close to the marked locations.







Figure A- 3. Dissolved oxygen (DO) and temperature contour plots for Bren Pond, Pond 849\_W and Pond 42. Color indicates values per the scale at right, with water depth relative to the pond bottom on the y-axis, and time along the x-axis. Vertical dashed lines are dates of site visits when profiles were collected; linear interpolation used to fill in the gaps between profile dates. A contour for 1.0 mg/L DO indicates levels below which the pond is considered anoxic.







Figure A- 4. Conductivity contour plots for Aquila Pond, Pond BC-P4.10C, Bren Pond, Pond 849\_W and Pond 42. Color indicates values per the scale at right, with water depth relative to the pond bottom on the y-axis, and time along the x-axis. Vertical dashed lines are dates of site visits when profiles were collected; linear interpolation used to fill in the gaps between profile dates.







# 849\_W





Figure A- 5. Phosphorus concentrations (TP and SRP) in the surface and hypolimnion of the ponds and duckweed cover for the 2019, 2020 and 2021 field seasons. Average surface concentrations plotted are based on surface water samples collected from five locations in the pond. The hypolimnion samples were collected from the approximate center of the pond and  $\sim 0.25$  m above the pond bottom.



Figure A- 6. Daily precipitation measured at the Minneapolis Flying Cloud Airport (44.822, -93.458). The five RPBCWD ponds are located within a 10 mile radius of the airport.



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Figure A- 9. Composition of the sedimentary phosphorus pool (as % of total P) in the BC-P4.10C, 849\_W, and Bren Pond before and after the application of iron filings to the sediments. The pretreatment ("before") concentrations were determined in cores collected in February 2019 for BC-P4.10C and Bren Pond, and in April 2017 for 849\_W. The post-treatment ("after") concentrations were determined in cores collected in October 2020 for BC-P4.10 and 849\_W ponds and in October 2021 for Bren Pond. The loosely-bound P, iron-bound P, and labile organic P represent the releasable P in the sediments, where this P is released by redox changes and bacterial mineralization. The other P forms (Al-P, mineral-P, and residual organic P) are generally not available for sediment P release.

Table A- 1. Total metal concentrations in the sediments cores collected from Pond BC-P4.10C in October 2020. The results provided are on dry sediment weight basis (mg/kg). The 0 cm depth represents the sediment-water interface. Concentrations below the laboratory detection limit (LOD) are indicated as < LOD value. Figure A-2 in Appendix A shows the approximate coring locations (1-5). Iron filings were applied to the sediments in February 2020. The average metal concentrations in the 0-4 cm depth of the pond sediments collected in February 2019 are also included in the table.

Sediment Core ID	Depth interval (cm)	Al	В	Ca	Cd	Cr	Cu	Fe	К	Mg	Mn	Na	Ni	Р	Pb)	Zn
	0-2	15401	39	59163	3.040	33	58	31245	2421	12038	932	646	33	988	26	183
1	2-4	10777	18	46839	2.108	26	48	23928	1769	10782	724	290	33	762	21	122
1	4-6	10918	14	31476	0.608	25	27	18849	1865	9457	573	232	28	617	29	81
	6-10	11313	15	28328	< 0.001	23	25	18885	1835	8412	553	224	29	631	15	68
	0-2	7358	49	123737	< 0.001	132	296	98338	1683	8892	1623	404	166	1652	40	145
2	2-4	9056	37	128421	< 0.001	140	350	87246	1730	11198	1435	343	148	1380	21	182
Z	4-7	9871	24	130653	0.361	78	162	44147	1885	13141	1085	401	63	1182	17	175
	7-10	12991	20	116641	0.456	28	39	30789	2263	11135	1096	365	37	977	17	137
	0-2	8522	51	123541	< 0.001	62	139	82190	1816	10026	2223	534	92	1862	18	197
2	2-4	9365	42	107481	< 0.001	190	468	113505	1753	10843	2244	431	167	1444	20	215
5	4-7	11510	22	109866	0.381	36	70	40192	2088	13205	1250	600	45	1166	18	206
	7-10	12767	19	77581	0.402	42	71	38345	2327	13562	1177	588	36	1066	19	167
	0-2	10704	39	154251	< 0.001	62	158	39752	2053	11997	1515	420	52	1166	16	210
4	2-4	11281	28	124054	0.447	25	42	27128	2085	10513	1188	446	31	1064	16	192
4	4-7	15070	29	130317	0.483	31	43	30616	2635	11536	1260	464	33	1049	16	181
	7-10	15261	20	100419	0.330	30	34	30784	2719	11565	1217	381	31	926	19	128
	0-2	13967	39	66701	0.378	33	38	35817	2708	14046	933	352	35	887	19	124
5	2-4	9975	15	65166	0.371	50	88	33250	1986	12948	819	287	50	725	17	100
3	4-7	13908	16	53730	0.324	35	35	27680	2603	14079	703	324	35	646	18	101
	7-10	10300	12	36664	< 0.001	38	40	21696	2008	12664	481	250	43	581	17	69
Average in 2019	0-4	12185	34.06	156092	0.427	30	47	29340	2165	14634	1281	620	34	1250	19	237

Table A- 2. Total metal concentrations in the sediments cores collected from Pond 849\_W in October 2020. The results provided are on dry sediment weight basis (mg/kg). The 0 cm depth represents the sediment-water interface. Concentrations below the laboratory detection limit (LOD) are indicated as < LOD value. Figure A-2 in Appendix A shows the approximate coring locations (1-5). Iron filings were applied to the sediments in February 2020. The average metal concentrations in the 0-4 cm depth of the pond sediments collected in July 2016 are also included in the table.

Sediment Core ID	Depth interval (cm)	Al	В	Ca	Cd	Cr	Cu	Fe	к	Mg	Mn	Na	Ni	Р	Pb)	Zn
	0-2	7635	34	29411	0.456	32	116	37121	2674	9742	543	1323	35	2197	29	155
1	2-4	6297	19	28415	< 0.001	113	271	57528	1366	9623	630	535	113	1580	27	131
1	4-7	7759	14	30665	< 0.001	126	325	59803	1500	12267	668	517	94	1256	31	134
	7-10	9532	15	31010	0.458	35	133	22802	1768	12755	424	613	33	1189	39	138
	0-2	4228	16	25917	< 0.001	127	300	72426	1077	3344	824	530	128	1619	19	44
2	2-4	2659	10	17488	< 0.001	446	1213	285234	504	2593	1899	385	445	982	35	33
Z	4-7	4307	10	23584	< 0.001	92	315	58680	684	3723	728	477	79	1029	18	35
	7-10	5522	10	26329	< 0.001	19	137	15253	874	4378	498	529	20	1057	21	44
	0-2	9729	17	21648	0.388	47	247	46583	1754	6525	923	872	36	1936	40	118
2	2-4	8226	15	21218	< 0.001	55	261	57318	1491	6642	980	1020	71	1751	38	108
3	4-7	8487	16	22315	0.432	68	336	61201	1565	6637	1100	967	77	1641	40	116
	7-10	9079	16	22635	0.418	68	315	55985	1592	6650	1134	717	56	1563	42	115
	0-2	8126	14	22493	0.405	35	363	38848	1405	5010	1006	614	34	1437	39	92
4	2-4	8764	16	23257	0.484	23	320	31538	1508	5521	976	872	25	1470	38	91
4	4-7	7532	14	22847	0.524	23	232	21699	1326	4835	971	777	20	1437	32	73
	7-10	6763	13	25353	0.431	17	195	18751	1172	4558	1107	704	15	1364	26	64
	0-2	5616	12	18951	< 0.001	263	783	109720	1032	4377	1155	574	241	1425	36	68
E	2-4	7777	14	22702	0.397	78	421	47617	1426	5615	718	870	63	1369	37	85
3	4-7	7662	14	21796	0.447	92	459	54843	1360	5303	778	726	86	1392	37	78
	7-10	8810	14	23872	0.535	41	382	39582	1525	6055	637	802	41	1358	40	85
Average in 2016	0-4	10254	18	27433	1	21	283	17502	1865	7518	859	896	20	1488	51	109