

**Internal Phosphorus Loading in Spring Lake
11 Years Following Alum Treatment**

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EXECUTIVE SUMMARY

An analysis of internal phosphorus loading and benthic macroinvertebrate community structure in Spring Lake, MI, was conducted in September 2016, ~11 years following alum treatment. Measurements were made of water quality, benthic invertebrate community structure, sediment metals, and phosphorus release rates, and compared to prior measurements (2003/2004: pre-alum, 2006: 8 mo post-alum, and 2010: 5 yr post-alum) taken at the same sites and using comparable methods.

The total phosphorus (TP) concentrations in the Spring Lake surface water samples from September 2016 were similar to those measured in 2006 and 2010 (38-45 $\mu\text{g/L}$ vs. 20-80 $\mu\text{g/L}$, respectively) at all sites; however, TP concentrations in the near-bottom water at Sites 1 and 2 were very elevated (~250 and 1,000 $\mu\text{g/L}$, respectively) compared to 2006 and 2010, suggesting internal loading may be increasing, at least at these sites. However, maximum phosphorus release rates from the 2016 sediments were modest, ranging from 0.63 to 1.94 $\text{mg P/m}^2/\text{d}$ under anoxic conditions, similar to or lower than 2010 rates, and still an order of magnitude lower than in 2003/2004, before alum was applied. Loosely sorbed sediment SRP concentrations were very low at all sites; the HCl-extractable SRP fraction declined substantially between 2010 and 2016, which may be explained by a change in extraction methodology.

In general, chlorophyll *a* (Chl-*a*) concentrations continued a trend of modest reduction at Sites 1 and 2, and modest increases at sites 3 and 4. The absolute concentrations of Chl-*a* were still relatively high (7-15 $\mu\text{g/L}$), and suggestive of mesotrophic to eutrophic conditions. The macroinvertebrate community continued its recovery from the decline that occurred shortly after alum application and was similar in density and composition to the 2010 results.

In conclusion, our 2016 results are suggestive, but not conclusive, that internal P loading is increasing in magnitude in Spring Lake at Sites 1 and 2 (the deeper, more southern locations). The overall TP and Chl-*a* concentrations in the water column of Spring Lake remain at higher than desired levels, and point to the continued need for reductions in external P sources in the Spring Lake watershed. Recommendations for the type and placement of Best Management Practices (BMPs) in the watershed have been provided previously, and we once again urge the local municipalities, decision makers, and stakeholders to evaluate their potential value, and to begin their implementation where feasible. Our results illustrate what has been cautioned in previous studies: alum application is a short-term solution to the longer-term problem of internal P loading, and its effectiveness is critically tied to concurrent reductions in external P loading.

INTRODUCTION

Internal nutrient loading is a frequent phenomenon in shallow, eutrophic lakes throughout the world, and may prevent lake water quality from recovering even after external loads are reduced (Sas 1989). Phosphorus (P) release from the sediments can occur via two different mechanisms: 1) release at the sediment-water interface during periods of anoxia or hypoxia, and the subsequent diffusion of dissolved phosphate into the water column (Boström et al. 1982); and 2) wind-induced resuspension and bioturbation at the sediment surface, especially in shallow lakes, whereby either the sediment pore water P can be released into the water column or the P adsorbed to sediment particles can desorb into the water column (Selig 2003; Steinman et al. 2006; Cyr et al. 2009; Wang et al. 2009; Matisoff et al. 2017). In eutrophic lakes, internal loading can account for a substantial amount of the total P load (Moore et al. 1998). Indeed, many studies have shown that reductions in external loading, to levels where water quality improvement should be detected, do not have the desired effect because of the counteracting release of P from sediments (Björk 1985; Graneli 1999; Steinman et al. 1999; Søndergaard et al. 2012; Spears et al. 2012).

Although many sediment management technologies exist to deal with internal loading, one of the most common practices is chemical treatment (Cooke et al. 1993). Chemical applications are intended to bind the P, and usually include aluminum sulfate (alum), lime, or iron (Cooke et al. 1993; Bakker et al. 2015), although lanthanum-modified bentonite (phoslock) is gaining acceptance, especially outside of the US (Robb et al. 2003; Spears et al. 2013, 2016). Alum is particularly effective due to its dual mode of action for P removal. Alum reacts with soluble P to form an insoluble precipitate (Stumm and Morgan 1996). In addition, alum will

form an insoluble aluminum hydroxide floc at pH 6 to 8, which has a high capacity to adsorb large amounts of inorganic P (Kennedy and Cooke 1982). By these two mechanisms, an alum application can irreversibly bind P and inhibit diffusive flux from sediments.

Historically, Spring Lake had some of the highest P concentrations measured in western Michigan lakes; between 1999 and 2002, TP levels averaged 100 $\mu\text{g/L}$ and ranged from 6 to 631 $\mu\text{g/L}$ during ice-free periods (T. Groves, Progressive AE, personal communication). In response to concerns from residents regarding impaired water quality in the watershed, laboratory-based studies to assess internal phosphorus loading were conducted in 2003 and 2004 using sediment cores from Spring Lake. Results indicated that internal loading accounted for between 55 and 65% of the TP entering the lake water column on an annual basis, and that an alum application of 24 mg Al/L should be effective at reducing TP release from the sediments (Steinman et al. 2004). As a consequence, we concluded that alum application may be an effective tool to reduce P flux from sediments in Spring Lake, but noted that the longevity of its effectiveness would be related to external P load reduction.

In the fall of 2005, an alum treatment of between 10 and 20 mg/L alum was applied as a liquid slurry to the surface of Spring Lake, in locations where depths were ≥ 15 ft. The permit from Michigan Department of Natural Resources and Environment (MDNRE) approving this application mandated that the rate of internal phosphorus loading be measured following treatment and at various intervals thereafter. We measured rates of internal P loading and evaluated ecological effects of the alum application in summer 2006, 8 months after treatment. Our results indicated that the alum treatment effectively reduced internal P loading in Spring Lake, but water column phosphorus concentrations remained high and overall benthic invertebrate density had been reduced (Steinman and Ogdahl 2008). We repeated our analyses in

September 2010, ~5 years post-treatment. We recorded the following observations at that time: 1) water column TP was still significantly lower than during pre-alum conditions, but had increased from August 2006; 2) Chl-*a* concentrations in the water column were lower than what were measured in previous years, but still remained near or above the eutrophic level; 3) maximum internal P loading rates averaged from 1.68 to 2.81 mg P/m²/d under anoxic conditions, rates that were an order of magnitude lower than before alum was applied, but had increased since 2006, possibly indicating that the alum treatment was becoming less efficient at retaining P (Steinman and Ogdahl 2012).

This report contains the results from our 2016 sampling campaign, and compares them with previous studies. By using the same or comparable methods, we can rigorously assess the efficacy of the alum treatment, ~11 years after it was applied.

METHODS

Field Methods: All samples except macroinvertebrates were collected on 12 September 2016, from the same 4 locations that were sampled in previous studies (Fig. 1).

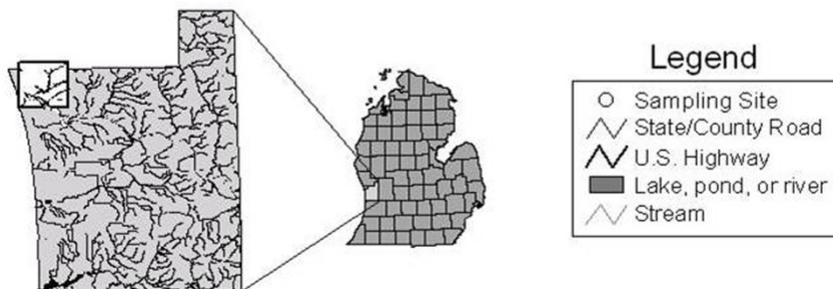
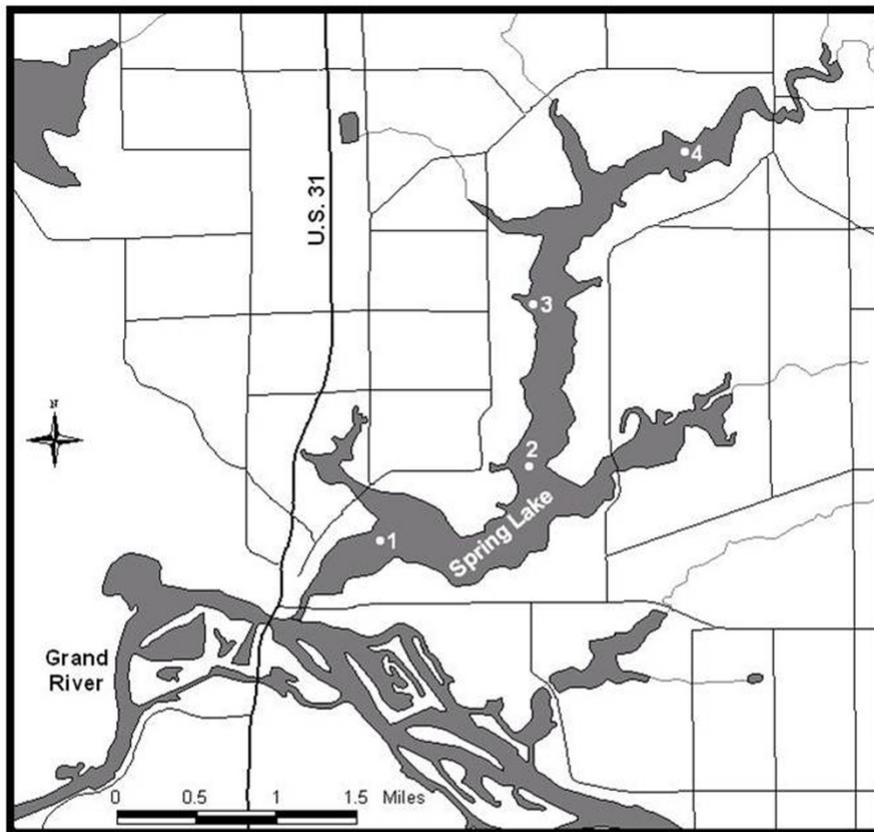
Macroinvertebrates were collected on 4 October 2016. At each site, dissolved oxygen, pH, temperature, specific conductance, chlorophyll *a*, and total dissolved solids were measured at the surface, middle, and bottom of the water column using a YSI 6600 sonde. Photosynthetically active radiation (PAR) 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 phosphorus 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. TP and SRP samples were stored at 4°C until analysis.

At each of the four Spring Lake coring sites, three replicate benthic samples were collected for invertebrate analysis using a petite Ponar dredge. Upon collection, the benthic samples were washed through a 500- μ m sieve under gentle pressure. Each sample was saved in its entirety and preserved in 95% ethanol. Rose Bengal stain was added to the ethanol to aid in sorting invertebrates from organic debris, and samples were stored until identification in the laboratory.

Sediment core sampling and laboratory incubation followed the procedures of Steinman et al. (2004). Sediment cores were collected from the same four sites as the water quality and invertebrate samples (Fig.1). Six sediment cores were collected from each site using a piston corer (Fisher et al. 1992, Steinman et al. 2004). The corer was constructed of a graduated 0.6-m long polycarbonate core tube (7-cm inner diameter) and a polyvinyl chloride (PVC) attachment assembly for coupling to aluminum drive rods. The piston was advanced 20 to 25 cm prior to deployment to maintain a water layer on top of the core during collection. The corer was positioned vertically at the sediment–water interface and pushed downward with the piston cable remaining stationary. After collection, the 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. The piston was then bolted to the top of the core tube to keep it stationary during transit. Core tubes were placed in a vertical rack and maintained at ambient temperature during transit. An additional core was collected from each site for sediment chemistry analysis; top 5 cm was removed for the analysis of TP, metals, ash-free dry mass [AFDM], and % solids in the lab (see below).

Figure 1. Map of Spring Lake, showing sampling locations (1-4). Below: location of Ottawa County (shaded white) with blow up of Spring Lake, located in upper NW region of the county.



Laboratory methods. Invertebrate samples were placed in a shallow white pan for sorting. All organisms were identified using a stereo microscope to the family level, with the exception of oligochaetes, which were identified to class level.

The 24 sediment cores (6/site) were placed in a Revco environmental growth chamber, with the temperature maintained to match ambient conditions in Spring Lake at the time of collection. The water column in three of the cores from each site was bubbled with N₂ (with 330 ppm CO₂) to create buffered anoxic conditions, while the remaining three were bubbled with oxygen 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, 1 d, 2 d, 4 d, 8 d, 12 d, 16 d, 20 d, and 25 d. Immediately after removal, a 20-mL subsample was refrigerated for analysis of TP, and a 20-mL subsample was filtered through a 0.45- μ m membrane filter and stored at 4°C for analysis of soluble SRP. SRP and TP were analyzed on a Seal AQ2 Discrete Analyzer (US EPA 1993). SRP values below detection were calculated as ½ the detection limit (5 μ g/L). The 40-mL subsample was replaced with filtered water collected from the corresponding site in the lake; this maintained the original volume 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):

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

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, V is the volume of water in the water column, and A is the planar surface area of the sediment cores. Maximum P release rate was calculated over the time period that resulted in the maximum apparent release rate, with the caveat that the initial and final samplings could not be consecutive dates to avoid potential short-

term bias. This is consistent with how release rates were calculated in previous studies, and allows for easy comparison of alum efficacy over time. For this report, only the TP internal loading data are presented; many of the SRP concentrations were below detection, thereby limiting the ability to make any definitive conclusions.

Following the incubations, the top five cm of sediment was removed from each core. The sediment was homogenized and subsampled for metals (Fe, Al, Ca, Mg) analysis and AFDM. Metals were analyzed using EPA method 6010b (US EPA 1996). The ashed material was analyzed for TP as described previously. Another subsample (5 g) of wet sediment was centrifuged to remove excess porewater and sequentially fractionated (Psenner et al. 1988). Unfortunately, there was insufficient water in the sediment after centrifuging to analyze SRP-P porewater concentrations but the residual sediment was subject to the 4-part sequential fractionation. The 1.0 M NH_4Cl extraction produces the loosely sorbed P; the 0.1 M 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 anoxic conditions; and finally, the 0.5 M HCl extraction produces Ca- and Mg-bound P, which represents a stable mineral association (see Psenner et al. 1988 for details).

RESULTS

Field results

Depth, Temperature, Total Dissolved Solids TDS), Light Extinction (K_d), and Secchi

Depth: Sites 1 and 2 were deeper than sites 3 and 4 (Table 1). Surface and bottom temperatures were similar at all sites with the exception of site 2 bottom, which was substantially cooler than all other locations. Temperature profiles were generally uniform at sites 1, 3, and 4 suggesting a

well-mixed water column. TDS values ranged from 0.312 to 0.377 g/L, with slightly lower values at sites 3 and 4 than sites 1 and 2; values were generally similar to previous years. Light extinction coefficients were lower than those measured in prior years, but Secchi depths were much shallower than prior years, and consistent with the light extinction coefficients (K_d) values, which were as much as 50% of previous years (Table 1). This reduced irradiance through the water column is not due to TDS, since concentrations were similar as in the past when transmittance values were higher, or to Chl-*a* concentrations (see below, as they were similar or lower than in previous years). We suspect the shallow Secchi depths may be related to dissolved organic matter, although this parameter is not measured.

Dissolved Oxygen (DO), Chlorophyll a (Chl a), Total Phosphorus (TP), Soluble Reactive Phosphorus (SRP), and pH.

Surface DO ranged between 7.4 and 9.7 mg/L at all sites (Table 2); however, bottom DO was hypoxic at sites 1 and 2, but above 6 mg/L at sites 3 and 4. The very low bottom DO at sites 1 and 2 mimic the conditions in 2006, and would likely promote internal P loading to the water column if the alum is no longer effective. Chlorophyll *a* concentrations ranged from 6.7 (site 2 bottom) to 14.5 (site 4 bottom) $\mu\text{g/L}$, and were generally lower than in prior years (Table 2). SRP concentrations from near-surface were below detection (DL = 5 $\mu\text{g/L}$) at all sites (Table 2); they were below detection in near-bottom samples at the relatively shallow sites 3 and 4, but reached concentrations of 175 and 932 $\mu\text{g/L}$ at sites 1 and 2, respectively (Table 2). Moderately high TP concentrations (~40-50 $\mu\text{g/L}$) were measured in the near-surface samples at all sites, as well as the near-bottom at shallow sites 3 and 4, but similar to SRP concentrations, were elevated at deeper sites 1 and 2 (Table 2). Mean surface water SRP and TP concentrations in 2016 remained similar to, or lower than, surface water concentrations from 2006 and 2010 (Table 2). In

addition, bottom water concentrations at sites 3 and 4 in 2016 were very similar to what we measured in 2006 and 2010 (Table 2). However, the very elevated 2016 near-bottom water concentrations at sites 1 and 2 compared to 2006 and 2010 suggest internal loading may be starting to develop at these deeper sites. pH values generally were more alkaline than in prior years, with some sites increasing by 0.6 to 0.8 points (Table 2).

Table 1. Selected physical limnological characteristics of sampling sites in Spring Lake. **2003 data in red**; 2006 and 2010 data in black (2nd and 3rd lines within a cell, respectively); 2016 in **black bold** (4th line). 2003 data were collected from Sites 1 and 2 on June 10 -11 and from Sites 3 and 4 on July 16. 2006 data were collected on August 1, 2010 data were collected on September 9, and 2016 data were collected on September 12.

Parameter	Site 1		Site 2		Site 3		Site 4	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Depth (m)	8.2		10.1		6.7		4.9	
	8.8		10.9		7.0		5.5	
	9.1		10.7		7.9		5.8	
	8.3		10.6		7.0		5.4	
Temp (°C)	17.8	16.6	17.8	15.3	24.4	22.7	24.8	23.6
	26.5	24.6	27.2	20.6	28.6	27.2	28.5	27.8
	20.3	19.8	20.6	19.6	20.8	20.3	20.8	20.4
	23.6	21.7	23.9	15.4	23.9	23.6	24.4	23.7
TDS (g/L)	0.386	0.378	0.362	0.372	0.362	0.384	0.353	0.381
	0.304	0.302	0.290	0.300	0.281	0.284	0.275	0.278
	0.365	0.386	0.337	0.374	0.333	0.344	0.311	0.312
	0.356	0.377	0.342	0.355	0.332	0.330	0.314	0.312
Light Extinction K _d	1.44		1.52		1.72		2.25	
	1.26		1.52		1.35		2.32	
	1.33		1.26		1.42		1.97	
	0.84		0.86		0.76		1.14	
Secchi depth (m)	1.25		1.0		1.0		0.75	
	0.5		0.7		0.5		0.5	
	2.0		2.0		2.0		2.0	
	1.1		0.75		0.75		0.5	

Table 2. Selected chemical and biological limnological characteristics of sampling sites in Spring Lake. 2003 data in red; 2006 and 2010 data in black (2nd and 3rd lines within a cell, respectively); 2016 in black bold (4th line). 2003 data were collected from Sites 1 and 2 on June 10 -11 and from Sites 3 and 4 on July 16. 2006 data were collected on August 1, 2010 data were collected on September 9, and 2016 data were collect on September 12.

Parameter	Site 1		Site 2		Site 3		Site 4	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
DO (mg/L)	11.3	6.0	9.3	0.6	6.1	1.5	5.4	4.2
	7.4	0.3	8.6	0.5	9.8	7.1	9.8	6.6
	6.1	5.6	6.9	3.9	6.6	4.1	10.6	10.0
	7.4	0.3	9.0	0.6	8.0	6.4	9.7	8.0
Chl- <i>a</i> (µg/L)	23.9	6.2	21.7	3.3	5.3	3.8	3.6	4.9
	20.4	8.6	15.9	6.4	10.5	16.7	22.4	25.9
	15.2	18.9	14.4	15.7	9.6	8.7	17.2	14.3
	9.6	10.2	8.1	6.7	8.9	10.0	13.5	14.5
SRP (mg/L)	<0.01	< 0.01	< 0.01	0.04	0.03	0.04	0.04	0.03
	<0.005	< 0.005	<0.005	0.006	<0.005	<0.005	<0.005	<0.005
	<0.005	<0.005	<0.005	0.005	<0.005	0.005	<0.005	<0.005
	<0.005	0.175	<0.005	0.930	<0.005	<0.005	<0.005	<0.005
TP (mg/L)	0.06	0.04	0.11	0.08	0.10	0.08	0.12	0.08
	0.03	0.05	0.03	0.02	0.02	0.03	0.04	0.04
	0.06	0.06	0.05	0.05	0.05	0.06	0.05	0.04
	0.038	0.246	0.040	1.055	0.042	0.051	0.045	0.047
pH	8.6	8.2	8.6	7.9	8.5	8.0	8.4	8.3
	8.3	7.6	8.4	7.4	8.5	8.2	8.5	8.1
	8.0	8.0	8.0	7.9	8.0	7.9	8.5	8.5
	8.6	7.9	8.8	8.2	8.6	8.5	8.8	8.5

Invertebrates. Four major groups of benthic invertebrates were identified in the Spring Lake sediments (Fig. 2). The overall pattern of invertebrate density in 2016 was very similar to what was observed in 2010. Chaoborids continued to dominate the invertebrate fauna, in contrast to 2004 and 2006, when oligochaetes dominated the benthic community (Fig. 2). Chironomid and ceratopogonid densities were both very low, similar to 2010 (Fig. 2).

No one site dominated in terms of invertebrate density. In 2016, chironomids were most abundant at site 1, but densities were low at all four sites (Table 3, Fig. 3). In prior years, site 4 had the most chironomids, although densities have been relatively low at all sites since 2004 (Table 3, Fig. 3). Comparisons with prior years showed that chironomids were significantly

lower in 2016 than in 2004 and 2006 on a lakewide basis, and significantly lower than all other years at site 4 (Table 3).

Chaoborid density was $\sim 4\times$ higher at site 2 than at sites 1 and 3 in 2016—site 2 historically has had relatively high chaoborid densities, although not to this year's extent (Table 3, Fig. 3). In contrast to the temporal trend for chironomids, chaoborid densities significantly increased in 2016 compared to all other years at site 3, and on a lakewide basis relative to 2006 (Table 3).

Oligochaete density was highest at site 1 in 2016, where densities have not significantly changed over time (Table 3, Fig. 3). Overall, densities of this group plummeted in 2006 and 2010, especially at sites 3 and 4, and in 2016 continue to be significantly lower than in 2004 on a lakewide basis and at sites 3 and 4 (Table 3). Ceratopogonid density was low overall, similar to prior years, and they were absent entirely from sites 1, 2, and 3 (Table 3, Fig. 3).

Analysis of total invertebrate density revealed generally similar numbers in 2016 as what was observed in 2010 (Fig. 4), but was significantly greater than in 2006 (Table 3). The overall grand mean of 2904 organisms/m² is similar to our measurements in 2010 (3109/m²), and remains lower than prior to the alum treatment but not significantly so (Table 3). Sites 1 and 2 had higher invertebrate densities than sites 3 and 4 in 2016, which is reversed from our observations in 2004 (Table 3, Fig. 4). The overall densities in 2016 are heavily biased by one invertebrate group at one site: chaoborids at site 2 (Table 3). Overall densities at sites 3 and 4 were still significantly lower in 2016 than in 2004 (Table 3, Fig. 4).

Table 3. Mean (\pm SE) invertebrate densities (organisms/m²) for each major taxonomic group observed in Spring Lake sediments in 2004, 2006, 2010, and 2016. Significant comparisons between years were determined using t-test or Mann-Whitney Rank Sum test; comparisons involving 2016 are in bold.

	2004	2006	2010	2016	Statistics
Chironomidae					
Grand Mean	155 \pm 27	422 \pm 126	94 \pm 32	76 \pm 27	2004>2016, p=0.044 2006>2010, p=0.032 2006>2016, p=0.019
Site 1	173 \pm 25	260 \pm 216	29 \pm 29	144 \pm 80	2004>2010, p=0.019
Site 2	58 \pm 58	43 \pm 0	29 \pm 29	72 \pm 29	NS
Site 3	173 \pm 66	433 \pm 25	58 \pm 14	14 \pm 14	2004>2016, p=0.079 2006>2004, p=0.021 2006>2010, p<0.001 2006>2016, p<0.001
Site 4	216 \pm 25	952 \pm 278	260 \pm 50	72 \pm 52	2004>2016, p=0.067 2006>2004, p=0.058 2006>2010, p=0.07 2006>2016, p=0.036 2010>2016, p=0.060
Chaoboridae					
Grand Mean	1125 \pm 393	76 \pm 23	1919 \pm 318	2034 \pm 1089	2004>2006, p=0.02 2010>2006, p<0.001 2016>2006, p<0.001
Site 1	43 \pm 25	188 \pm 29	2366 \pm 658	1342 \pm 468	2006>2004, p=0.019 2010>2004, p=0.024 2010>2006, p=0.030 2016>2004, p=0.050 2016>2006, p=0.070
Site 2	1904 \pm 1039	87 \pm 25	2684 \pm 195	5194 \pm 1386	2010>2006, p<0.001 2016>2006, p=0.021
Site 3	2438 \pm 225	29 \pm 14	2280 \pm 232	1399 \pm 265	2004>2006, p<0.001 2010>2006, p<0.001 2016>2004, p=0.041 2016>2006, p=0.007 2010>2016, p=0.067
Site 4	115 \pm 14	0 \pm 0	346 \pm 50	202 \pm 63	2004>2006, p=0.001 2010>2004, p=0.011 2010>2006, p=0.002 2016>2006, p=0.033
Oligochaeta					
Grand Mean	3502 \pm 994	555 \pm 135	1021 \pm 342	743 \pm 313	2004>2006, p=0.013 2004>2010, p=0.043 2004>2016, p=0.013
Site 1	2193 \pm 731	967 \pm 270	2611 \pm 863	1573 \pm 420	NS
Site 2	274 \pm 76	101 \pm 63	678 \pm 29	216 \pm 25	2010>2004, p=0.008 2010>2006, p=0.001 2010>2016, p<0.001
Site 3	2727 \pm 225	736 \pm 325	649 \pm 205	303 \pm 50	2004>2006, p=0.007 2004>2010, p=0.002 2004>2016, p=0.100
Site 4	8815 \pm 806	418 \pm 72	144 \pm 63	880 \pm 399	2004>2006, p<0.001 2004>2010, p<0.001 2004>2016, p<0.001 2006>2010, p=0.046

Ceratopogonidae					
Grand Mean	7 ± 5	7 ± 5	76 ± 42	50 ± 50	2010>2004, p=0.029 2010>2006, p=0.029 2010>2016, p=0.096
Site 1	0 ± 0	0 ± 0	14 ± 14	0 ± 0	NS
Site 2	0 ± 0	0 ± 0	0 ± 0	0 ± 0	NS
Site 3	14 ± 14	0 ± 0	43 ± 0	0 ± 0	2010>2016, p=0.100
Site 4	14 ± 14	29 ± 14	245 ± 138	202 ± 142	NS
Total Invertebrates					
Grand Mean	4794 ± 917	1064 ± 192	3109 ± 526	2904 ± 614	2004>2006; p=0.002 2010>2006; p=0.002 2016>2006, p=0.009
Site 1	2424 ± 732	1428 ± 425	5021 ± 1350	3059 ± 784	NS
Site 2	2236 ± 1115	231 ± 52	3390 ± 166	5482 ± 1395	2010>2006; p<0.001 2016>2006, p=0.020
Site 3	5353 ± 525	1197 ± 336	3030 ± 246	1717 ± 300	2004>2006; p=0.003 2004>2010; p=0.016 2004>2016, P=0.100 2010>2006; p=0.012 2010>2016, p=0.028
Site 4	9161 ± 813	1399 ± 200	995 ± 254	1356 ± 633	2004>2006; p<0.001 2004>2010; p<0.001 2004>2016, p=0.002

Figure 2. Mean (\pm SE) invertebrate density across all sites (“grand mean”) for each major taxonomic group identified in Spring Lake in 2004, 2006, 2010, and 2016.

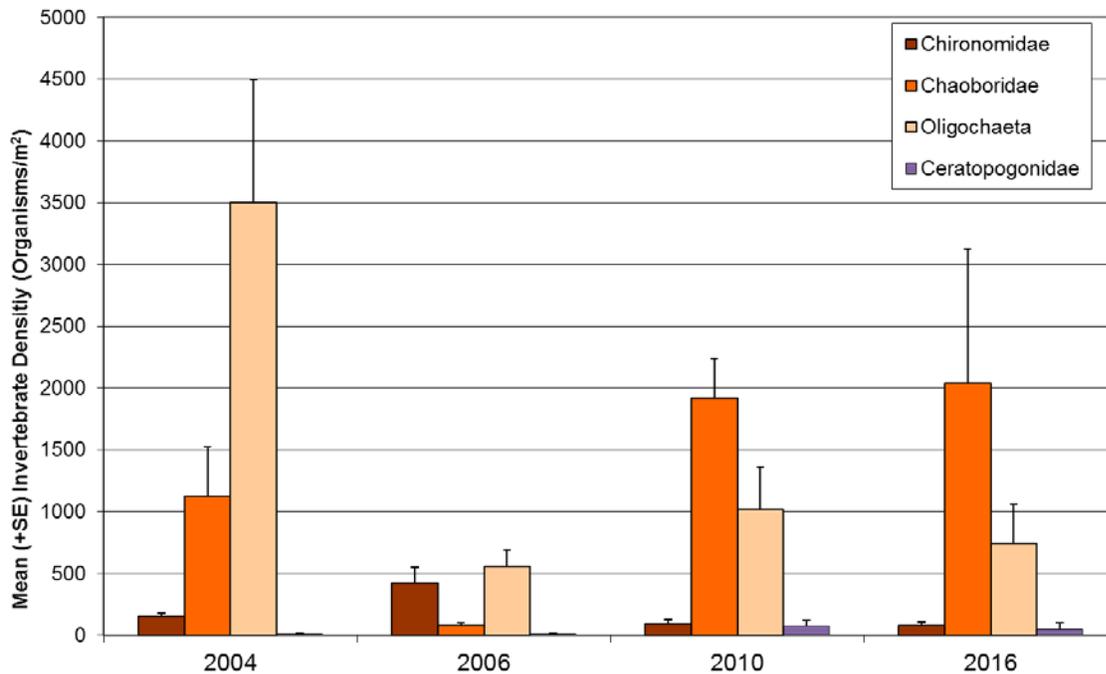


Figure 3. Mean (\pm SE) invertebrate density of each major taxonomic group identified at each site in Spring Lake in 2004, 2006, 2010, and 2016.

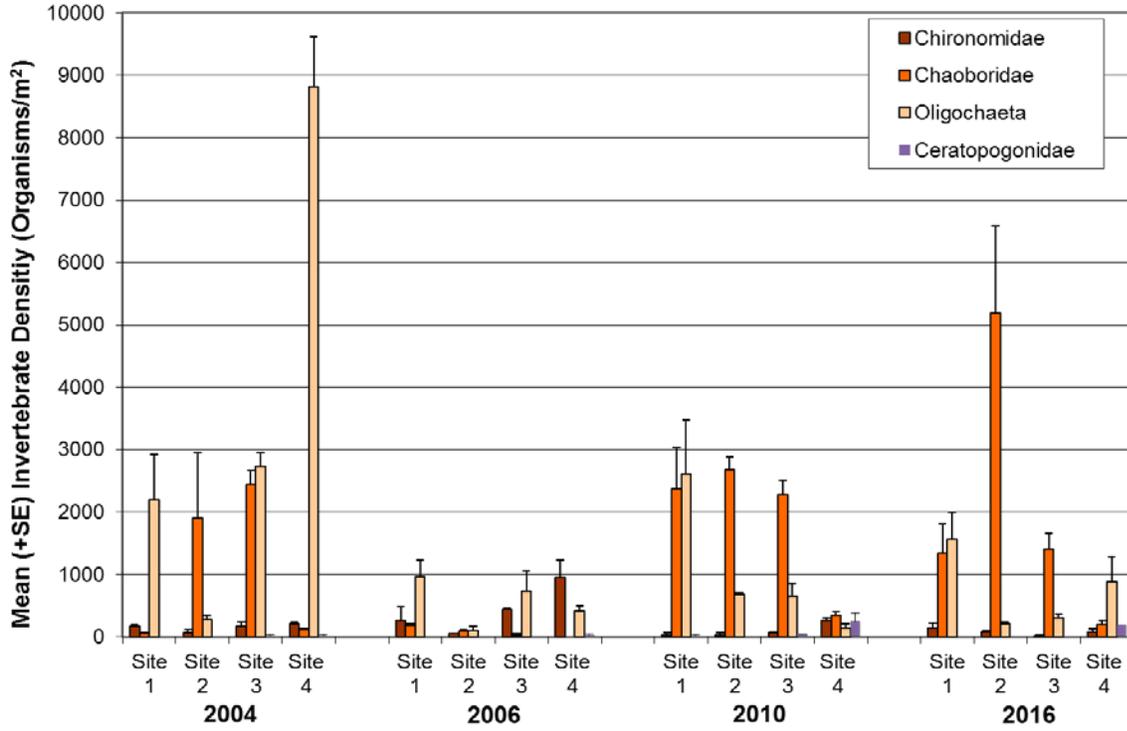
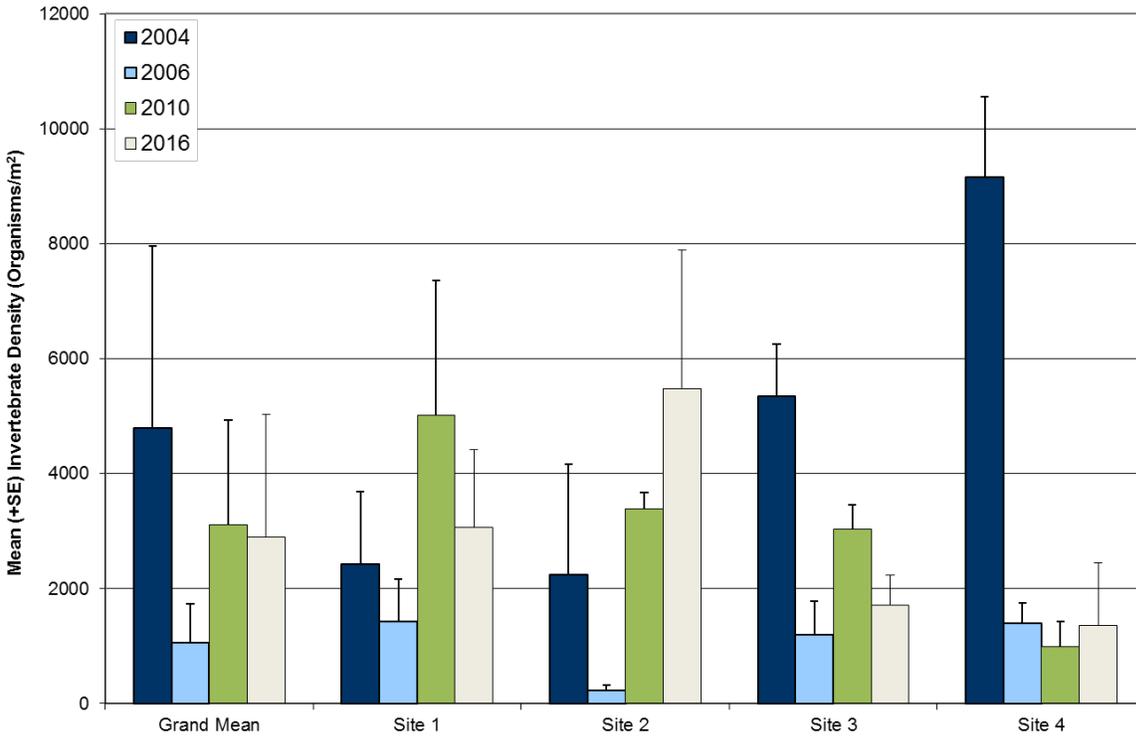


Figure 4. Mean (\pm SE) total invertebrate densities in Spring Lake in 2004, 2006, 2010, and 2016.



Laboratory results

Maximum mean apparent TP flux under anoxic conditions ranged from 0.63 to 1.94 mg TP/m²/d, which was slightly lower than the mean rates measured in 2010 at sites 1 and 2, but not statistically significant (Table 4). The 2016 mean fluxes were still significantly lower than those measured in 2003 at all sites, prior to the alum application (Table 4). These data are consistent with the relatively low TP concentrations measured near-bottom at sites 3 and 4 (~0.05 µg/L), but are in conflict with the near-bottom TP concentrations at sites 1 and 2 (Table 2), where TP concentrations of ~250 and 1000 µg/L, respectively, suggest the presence of internal loading at these sites.

Table 4. Maximum Apparent TP Release Rate (anoxic conditions): mg P/m²/d. P-values annotated with * represent log(x) transformed data for that comparison. Comparisons involving 2016 data are in bold.

Site	2003	2006	2010	2016	Statistics
1	29.54±0.95	0.33±0.31	2.81±1.02	1.94±0.69	2003>2006; p<0.001 2003>2010; p<0.001 2003>2016; p<0.001 2010>2006; p=0.016 2016>2006; p=0.021
2	17.33±4.89	0.88±1.52	1.68±0.53	1.62±0.37	2003>2006; p=0.005 2003>2010; p=0.005 2003>2016; p=0.005
3	13.33±8.36	0.49±0.55	2.33±2.46	0.81±0.32	2003>2016; p=0.005*
4	11.67±4.08	-0.05±0.09	2.25±1.40	0.63±0.24	2003>2006; p=0.008 2003>2010; p=0.022 2003>2016; p<0.001* 2010>2006; p=0.047 2016>2006; p=0.010

With the exception of site 2, the TP concentrations in the overlying water in the sediment core tubes started at or below ~100 µg/L (Fig. 5). In the anoxic treatments, TP concentrations increased over time at sites 1, 3, and 4 until about day 4-8, and then declined; at site 2, TP concentration started much higher, between 200-500 µg/L (Fig. 5), and increased slightly over

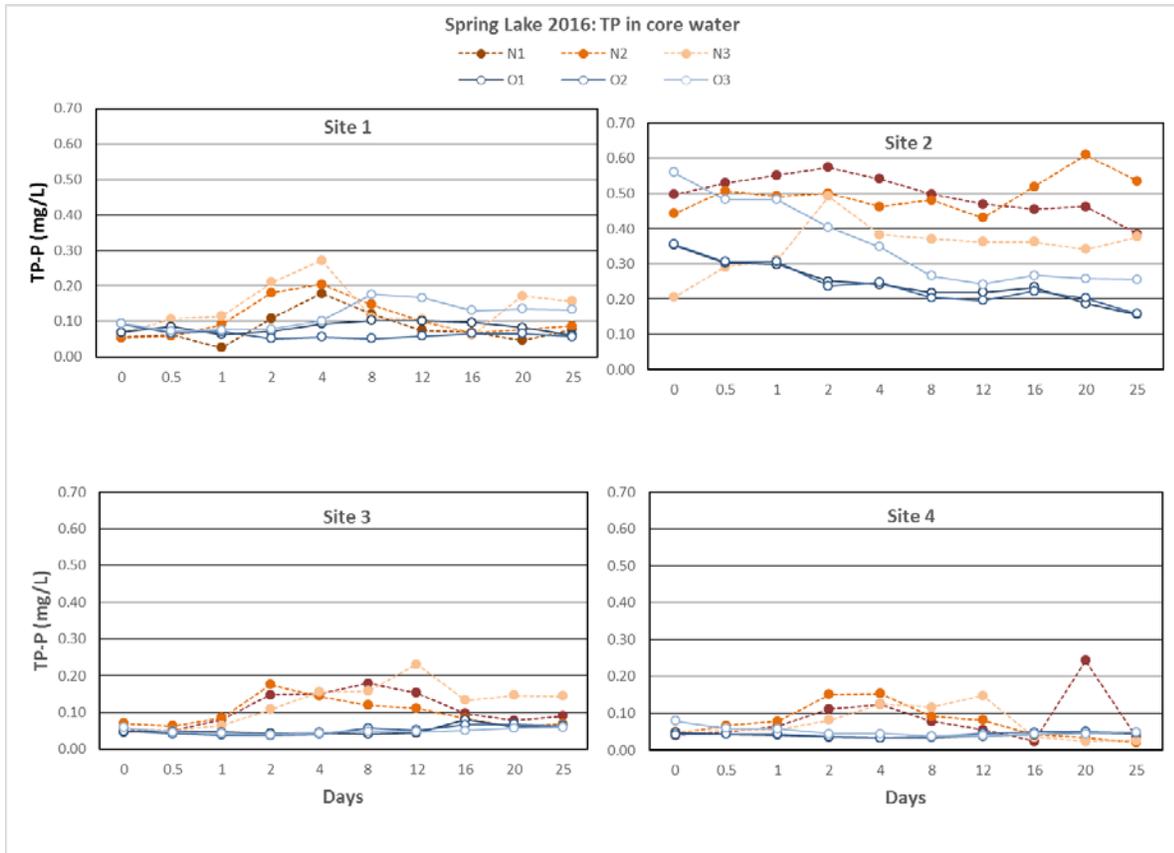
the first few days in two replicates, and rose more sharply in the remaining replicate (Fig. 5). In the oxic treatments, TP concentrations either increased at a modest rate over the experimental period or declined over time (site 2; Fig. 5). Interestingly, there was no statistically significant difference (t-test) between the maximum oxic and anoxic release rates at any of the sites in 2016, although site 2 was marginally significant ($p = 0.086$).

Table 5. Mean TP Saturation Concentration (i.e., maximum concentration) measured under anoxic conditions from 2003 (pre-alum), 2006, 2010, and 2016. Units in $\mu\text{g/L}$.

Site	2003	2006	2010	2016
1	1420	30	260	220
2	850	110	220	560
3	610	60	220	200
4	770	20	110	180

The maximum mean TP concentration from the anoxic treatments increased between 2010 and 2016 at sites 2 and 4, and declined slightly at sites 1 and 3 (Table 5). All the maximum mean concentrations are well below those measured from pre-alum sediment cores, although the 2016 TP concentration at site 2 more than doubled since 2010 (Table 5).

Figure 5. TP concentrations in the water overlying sediment cores from 4 sites in Spring Lake sampled in September 2016. The letter in the legend refers to redox state (N = nitrogen, anoxic condition; O = oxygen, oxic condition); the number refers to replicate number (1-3).

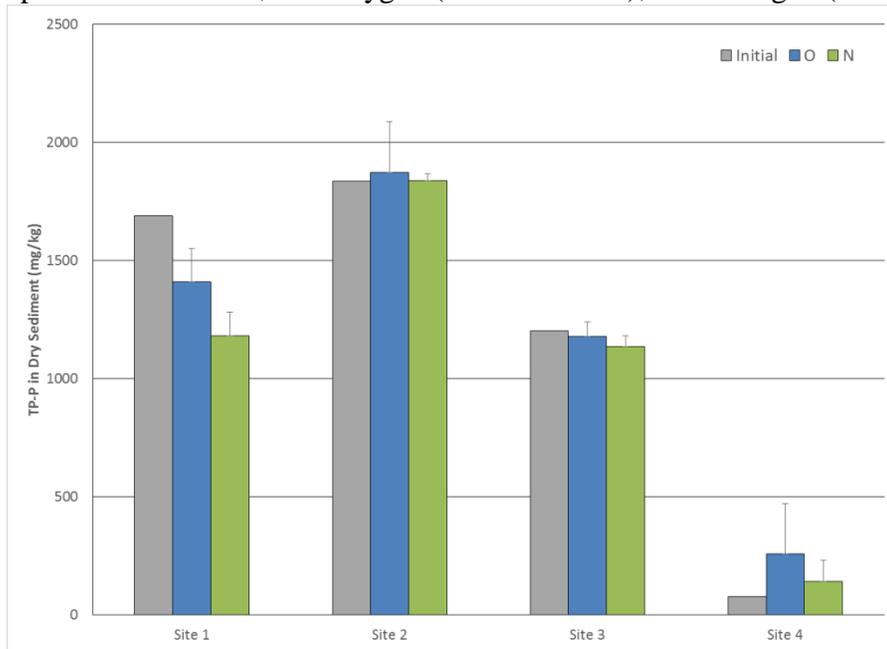


Sediment TP in 2016 (as a function of dry weight) prior to incubation ranged from 77 (site 4) to 1837 (site 2) mg/kg (Table 6, Fig. 6). The 2016 sediment TP concentrations were generally similar to those measured in 2010 with the very distinct exception of site 4, where the sediment TP concentration was remarkably lower than in 2010 (Fig. 7). It is likely that despite returning to the same site (based on GPS coordinates), we encountered an area of high inorganic deposits, which hold less organic matter and would therefore contain lower TP concentrations. Indeed, both the dry mass and ash-free dry mass at site 4 were $\sim 5\text{-}12\times$ greater at site 4 than the other sites (Table 6). Even when sediment TP is not normalized by mass, the absolute TP concentrations are much lower at site 4 (Table 6).

Table 6. Sediment dry mass, ash-free dry mass, and TP from Spring Lake sites 1-4.

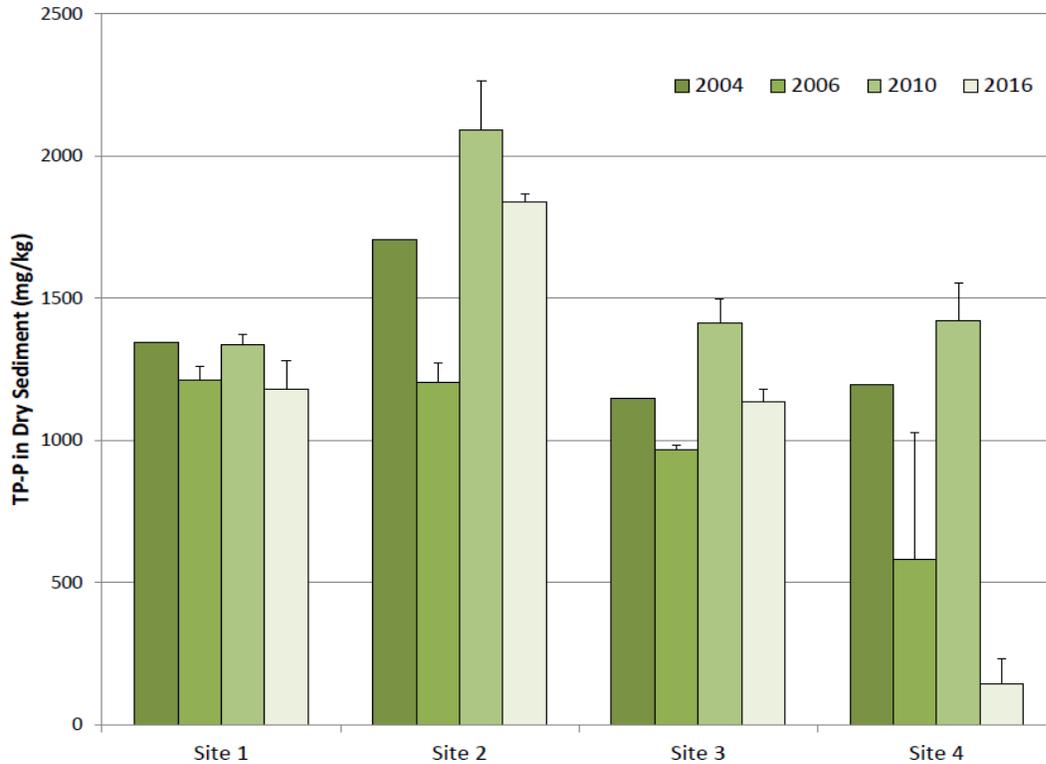
Site	Dry mass (%)	Ash-Free Dry Mass (%)	TP (mg/kg)
1	15.16	13.08	1690
2	6.64	5.63	1837
3	15.74	13.29	1203
4	70.71	68.87	77

Figure 6. TP concentration (mg/kg) in cores collected in 2016, as a function of dry weight. Initial = prior to incubation; O = oxygen (oxic condition); N = nitrogen (anoxic condition).



Mean sediment TP concentrations were lower in the anoxic vs. oxic treatments at Sites 1 and 4, but similar to each other at Sites 2 and 3 (Fig. 6). Mean post-incubation sediment TP concentrations declined at all sites in 2016 compared to 2010 (Fig. 7); the decline was most precipitous at Site 4, consistent with the prior data.

Figure 7. TP concentration (mg/kg) in cores collected in 2004, 2006, 2010, and 2016 as a function of dry weight. To facilitate comparisons among years, the data shown represent post-anoxic incubation conditions.



There was insufficient water in the sediment after centrifuging to analyze SRP-P porewater concentrations. However, the fractionation methodology allows us to measure extractable SRP. In 2016, we used a 4-part fractionation to assess loosely sorbed SRP, a fraction we did not previously measure. However, the different methodology does introduce a potential confounding factor when comparing across years (Table 7). We calculated the 2016 data both will all 4 sites and excluding site 4, given the anomalous sediment results for this site. Excluding site 4 data does increase the extractable SRP in all fractions, but only by 20-30% on average (Table 7). Comparing the two fractions that were examined previously (NaOH and HCl) revealed considerably lower extractable SRP concentrations in 2016 compared to prior years (Table 7). Two trends were observed in all sites: 1) within each individual site, the patterns for extractable

SRP were very similar for both the oxic and anoxic treatments; and 2) NH_4Cl -extractable SRP fractions (loosely bound P) were very low at all sites (Fig. 8). At sites 1 and 3, the dominant extractable fractions were BD and HCl, whereas HCl alone was dominant at Site 4 (Fig. 8). Only at Site 2 did the NaOH fraction have the highest mean SRP concentration (Fig. 8).

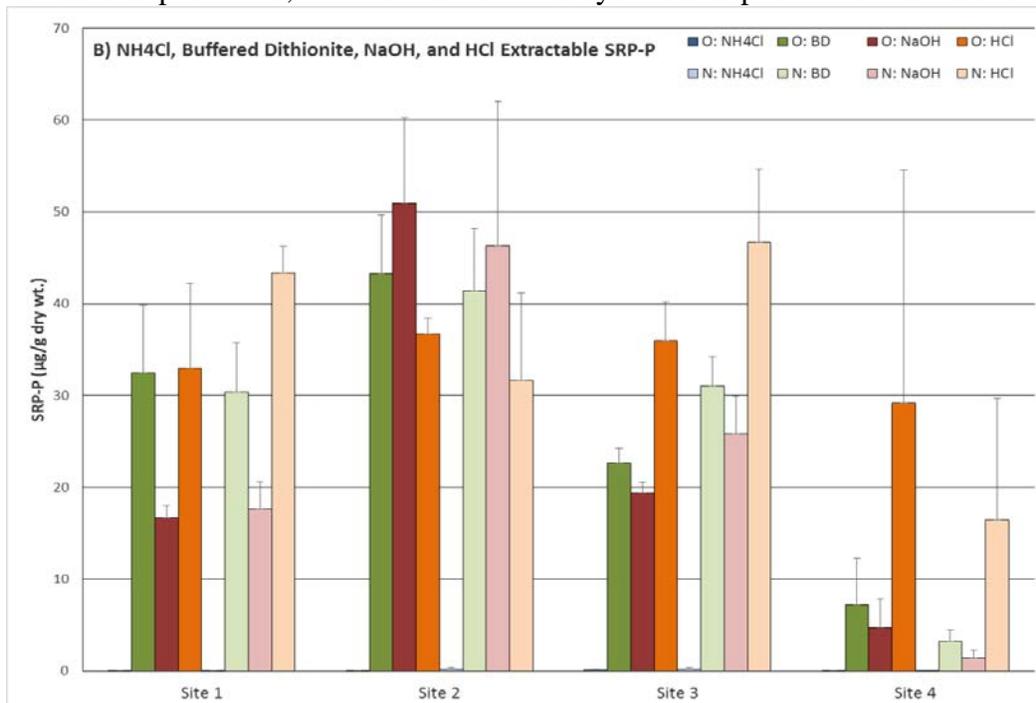
Table 7. Comparison of grand mean (\pm SD) values of porewater soluble reactive phosphorus (SRP) concentrations (mg/L) for 2003/4, 2006, and 2010 only, and NH_4Cl - (2016 only), BD- (2016 only), and NaOH- and HCl-extractable (all years) SRP concentrations ($\mu\text{g/g}$ dry wt) from Spring Lake sediments under anoxic conditions. The 2016 mean values are shown with and without site 4 (see text).

Measurement	Pre-Alum (2003/2004)	8 mo. Post- Alum (2006)	5 Yr Post-Alum (2010)	11-Yr Post-Alum (2016)	
				(Sites 1-3)	(Sites 1-4)
Porewater SRP	0.18 \pm 0.19	0.03 \pm 0.02	0.08 \pm 0.03	ND	ND
NH_4Cl -SRP	ND	ND	ND	0.28 \pm 0.17	0.22 \pm 0.13
BD-SRP	ND	ND	ND	81 \pm 10	62 \pm 8
NaOH-SRP ¹	141 \pm 16	128 \pm 23	198 \pm 42	71 \pm 5	54 \pm 4
HCl-SRP ²	286 \pm 126	454 \pm 135	459 \pm 70	90 \pm 4	74 \pm 8

¹NaOH extract was 1.0 M in 2016 and 0.1 M in previous years

²HCl extract was incubated for 16 hrs in 2016 and 24 hrs in previous years

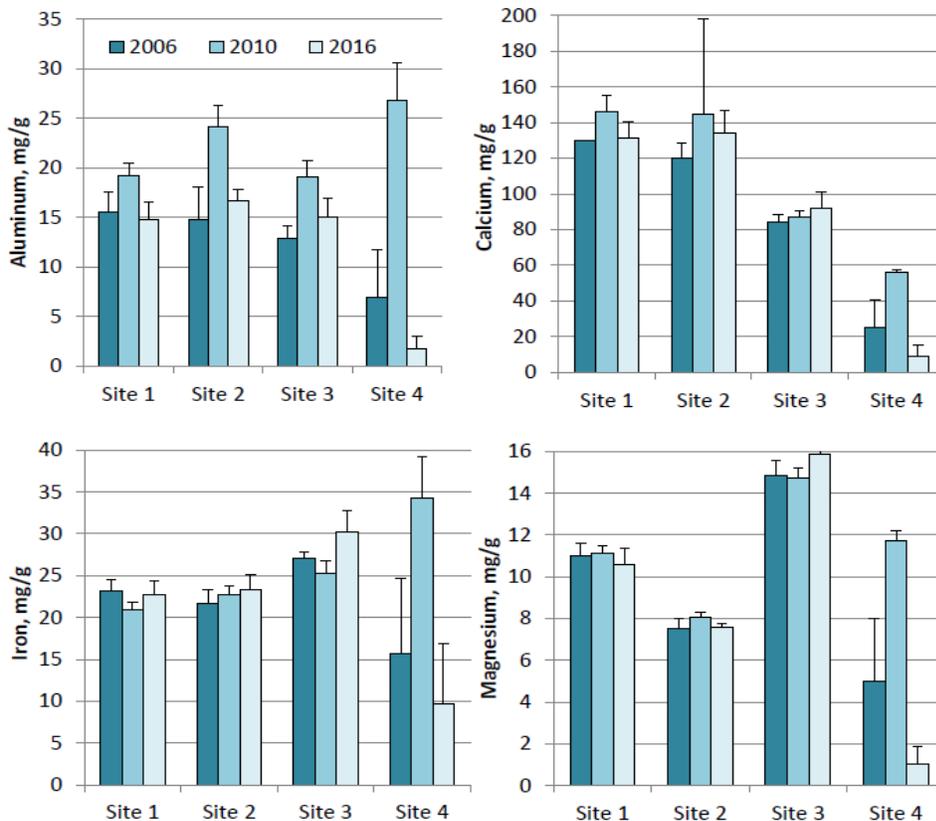
Figure 8. Extractable SRP concentrations from sediment cores at the end of the incubation period. O = oxic incubation conditions; N = anoxic incubation conditions. Note due to insufficient porewater, we were unable to analyze SRP-P porewater concentrations.



As was the case in prior years, calcium was the most abundant metal at all sites (Fig. 9).

Aluminum concentrations declined between 2010 and 2016, with the decline most dramatic at Site 4 (Fig. 9). Calcium, iron, and magnesium concentrations were relatively similar over the years at Sites 1-3, except again for the decline between 2010 and 2016 at Site 4 (Fig. 9).

Figure 9. Grand means (\pm SD) of aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg) in sediment cores from Spring Lake in 2006, 2010, and 2016. Metals were not measured in 2003/2004. Note different scales for the y-axes.



DISCUSSION

Internal P loading can be a significant source of nutrients in shallow, eutrophic lakes, and can result in serious impairment to water quality (Welch and Cooke 1995, 1999; Søndergaard et al. 2001; Matisoff et al. 2016; Nürnberg and LaZerte 2004, 2016; Qin et al. 2016). Even when

external loading rates are relatively low, high diffusive flux and internal loading from bioturbation or sediment resuspension can help trigger and/or sustain algal blooms. The ecological and societal implications of internal P loading rates, including aesthetic issues and potential human health concerns (Zhao et al. 2016) often prompt management strategies in lakes where rates are high.

Although prior studies have shown that alum treatments usually have short-term benefits (Cooke et al. 1993, Welch and Schriever 1994, Welch and Cooke 1999, Egemose et al. 2010), the question of long-term effectiveness is less clear. Effectiveness of alum treatments generally has ranged from ~4 to 20 years, and is dependent on many factors, including: 1) lake morphometry (Welch and Cooke 1995, 1999); 2) the amount of alum added to the system (Rydin and Welch 1998; Lewandowski et al. 2003; Jensen et al. 2015); 3) bioturbation (Van Rees et al. 1996; Matisoff and Wang 1998; Nogaro et al. 2016); 4) macrophyte cover (Welch and Schriever 1994; Welch and Cooke 1999); 5) water column pH (Rydin and Welch 1998; Lewandowski et al. 2003); 6) sedimentation rate (Lewandowski et al. 2003); 7) the magnitude of internal loading from shallow areas not treated by alum (Søndergaard et al. 1999; Nixdorf and Deneke 1995); and 8) perhaps most important of all, the degree to which external loads have been reduced following the alum treatment (Hansson et al. 1998; Lewandowski et al. 2003; Mehner et al. 2008), as continued inputs of high phosphorus loads will fuel the production of new biomass, which becomes the basis for future internal loads to the system (Carpenter 2005, Burger et al. 2008; Sharpley et al. 2013). A recent meta-analysis by Huser et al. (2015) found the three most important variables explaining alum treatment longevity were Al dose (47% of variation explained), an index related to lake hydraulic residence time (32% of variation explained), and lake morphometry (3% of variation explained).

The results from our 2016 study provide partial evidence that the Spring Lake alum treatment of 2005 is starting to lose its effectiveness. This conclusion is based largely on the water column SRP and TP data from the near-bottom of Sites 1 and 2 (Table 2), where concentrations greatly exceeded even the pre-alum P concentrations. The very high 2016 concentrations coincided with very low DO concentrations in the hypolimnion (Table 2), suggesting redox-catalyzed release of P that would be bound to Fe oxides and oxyhydroxides under oxic conditions (Boström et al. 1982). DO concentrations during the 2010 sampling were ≥ 3.9 mg/L at all near-bottom sites (Table 2), so it is not surprising that P concentrations were relatively low; however, in 2006, DO concentrations were ≤ 0.5 mg/L at the near-bottom of Sites 1 and 2, yet TP concentrations were < 50 $\mu\text{g/L}$, far less than the 250-1000 $\mu\text{g/L}$ measured at these sites in 2016. This suggests that the alum in 2006 was still effective in binding P even under low DO conditions, whereas by 2016, the P putatively released during anoxic conditions was no longer being trapped by the alum, and instead was accumulating in the hypolimnetic zone.

While these P concentrations suggest the alum treatment's efficiency is waning, the measured P release rates in 2016 were very similar, if not lower, than those measured in 2010 at Sites 1 and 2 (Table 5). This result was unexpected and the disparity is difficult to reconcile, as one would expect high release rates are needed to generate the high hypolimnetic P concentrations. However, if anoxic/hypoxic conditions persisted throughout the summer, it may be possible for P to accumulate in the deeper regions of the lake even at low release rates. The shallower Sites 3 and 4 continued to have both low release rates and relatively low P concentrations that have been measured in other post-alum treatment years; this is consistent with their shallow depths, where water mixing can oxygenate the entire water column. Indeed, the 2016 DO data at these sites were > 6 mg/L, even at the near-bottom (Table 2).

Another anomalous result was the lack of difference in P release rates for oxic vs. anoxic treatments. Under oxic conditions, phosphate binds to oxidized iron (Fe^{3+}) minerals, preventing P-rich porewater from diffusing into the water column (Mortimer 1941, 1942). However, under anoxic conditions, the Fe^{3+} is reduced to Fe^{2+} , and in the process liberating phosphate. Our prior studies in Spring Lake (Steinman et al. 2004, 2006; Steinman and Ogdahl 2008, 2012) have clearly shown much greater P release rates, especially at sites 1 and 2, under anoxic vs. oxic conditions, as expected. However, this was not the case in 2016; Fe sediment concentrations were similar in 2016 to past years in sites 1-3, although much lower at site 4, so it is unlikely that metal chemistry can account for similar oxic vs anoxic results. Mean (\pm SD) DO concentrations at the end of the incubations in core tube water were 8.85 ± 0.14 mg/L in oxygenated vs. 1.38 ± 0.18 mg/L in non-oxygenated waters, so the lack of increased internal loading in the “anoxic” treatments does not appear to be related to excess DO in the low-DO treatments.

The accumulation of P in the hypolimnion at Sites 1 and 2 appears to have had limited effect on phytoplankton biomass in the surface waters. Surface Chl-*a* concentrations at Sites 1 and 2 were $2.5\times$ lower than pre-alum and $\sim 2/3$ of concentrations measured in 2010. Of course, snapshot samples of a dynamic metric such as Chl-*a* can be misleading, as concentrations change quickly, so this comparison should be viewed cautiously. Chl-*a* concentrations at Sites 3 and 4 were relatively uniform through the water column, reflecting the water column mixing at these shallow sites; 2016 concentrations were similar to those of prior post-alum sampling years (Table 2). In general, Chl-*a* concentrations continued the trend of modest reduction at Sites 1 and 2, but modest increases at sites 3 and 4. Regardless of overall trends, the absolute concentrations of both TP and chlorophyll *a* were still high (38 - $1,000$ $\mu\text{g/L}$ and 7 - 15 $\mu\text{g/L}$, respectively).

In contrast to chemical water quality parameters, biological indicators, such as benthic macroinvertebrates, respond to and incorporate a wide range of environmental disturbance and quality gradients (Dixit et al. 1992, Karr 1993, Stemberger and Lazorchak 1994, Death 1996). Benthic invertebrate community composition and density have been shown to be effective indicators of water quality because they are comparatively easy to sample in a quantitative manner, and their relative narrow range of mobility, range of sensitivities to contaminants, and relatively long life histories allow them to integrate environmental conditions over time (Cook and Johnson 1974, Wiederholm 1984, Nalepa et al. 2000, Purcell et al. 2009).

Our post-alum application data revealed that overall benthic invertebrate density declined in Spring Lake the year after treatment, likely because of smothering by the alum floc, but that overall invertebrate density in 2016 was significantly greater than that measured in 2006, suggesting sustained recovery. However, pre-alum densities at Sites 3 and 4 remain significantly greater than 2016 densities. Densities in 2016 were similar to those measured in 2010, with the only statistically significant difference occurring at Site 3, where density was greater in 2010 compared to 2016. As noted in the 2010 report, these results are consistent with those of Smeltzer et al. (1999), who found that following an initial decline in invertebrate richness and density, recovery to pre-treatment levels occurred within 2 years and significant increases above pre-treatment levels were evident after 10 years.

Invertebrate community composition in 2016 also was very similar to that observed in 2010. Chironomid densities remained very low, with the Site 4 density in 2010 significantly greater than in 2016. Given the low absolute numbers, it is unlikely this statistically significant difference has any ecological relevance. Chaoborids were the most abundant group overall, as was the case in 2010, and were especially prominent at Site 2. Increases in chaoborid density

following alum application have been documented in other studies (Doke et al. 1995; Narf 1990) and attributed to a change in trophic structure and subsequent increases in food resources (Doke et al. 1995). Chaoborids can tolerate a wide range of water quality conditions, including pollution degradation (Hilsenhoff 1987).

Oligochaete density was not significantly different between 2016 and 2010 at any site. And although ceratopogonid density was significantly lower at Site 3 in 2016 compared to 2010, the absolute density was very low.

In 2016, we altered our fractionation scheme to include 4 instead of 2 fractions. In particular, we were interested in the amount of loosely sorbed (highly bioavailable) P in the sediment, which we had not measured previously. It is suggested that the calculation of how much alum to apply should focus on the readily available P in the sediment (loosely sorbed and redox sensitive) instead of simply total P (Pilgrim et al. 2007). Interestingly, the NH_4Cl -extractable SRP fraction (loosely sorbed) was extremely low in Spring Lake, regardless of site. Indeed, most SRP fractions were low and both the NaOH- and HCl-extractable SRP fractions dropped substantially between 2010 and 2016, even when site 4 data are excluded from the analysis. The lower NaOH-extractable SRP values in 2016 can be explained by the more detailed fractionation scheme; that is, the more coarse NaOH-extraction conducted in the 2010 scheme likely included both the BD- and NaOH-extractable fractions that were measured separately in 2016. Indeed, when these two fractions from 2016 are added together, the SRP concentration is reasonably close to that of 2010. The NaOH-extractable SRP reflects the Al- and Fe-bound phosphorus fraction, which usually increases after alum dosing (Rydin and Welch 1999, Reitzel et al. 2005). We speculate that after 11 years, the reduction in Al-bound P is due to either sediment movement or burial.

The explanation for the substantial decline in the HCl-extractable SRP fraction in 2016 is more difficult to explain. Given the relatively high Ca concentrations in the sediment, one would expect HCl-extractable P fraction to have remained high; previously, we speculated that the P that was loosely bound to the alum floc may have become exchanged with soluble calcium, thereby causing the increases we measured in 2006 and 2010 (Steinman and Ogdahl 2008, 2012). We see no evidence of that in 2016, however. It is possible that the change in extraction methodology may have resulted in less efficient Ca-P to be extracted compared to the 2010 method. For example, even though the HCl molarity was the same for both methods, the extraction time was 16 hr in 2016 and 24 hr in previous years. In addition, the NaOH molarity was 0.1M in 2010 vs. 1M in 2016. The shorter extraction time in 2016 plus the greater molarity of the NaOH solution may have reduced the efficiency of the HCl extraction.

In our 2010 report, we noted that the relatively high TP concentrations in the Spring Lake water column suggested that external phosphorus loadings are still a problem in the Spring Lake watershed. In 2016, we are now seeing evidence of very high TP concentrations accumulating in the bottom waters at Sites 1 and 2. Although maximum P release rates from the sediment remain relatively low, the P concentrations are suggestive that the alum treatment is losing its efficacy. This could be due to several factors, none of which are mutually exclusive: 1) the alum floc being focused to deeper waters in Spring Lake, and thus not covering as much of the sediment area as it did immediately after application; and 2) the alum's binding sites are becoming saturated, and can no longer effectively bind more P.

In conclusion, our 2016 study generated mixed results. The hypolimnetic P concentrations in the bottom waters at Sites 1 and 2 strongly suggest internal loading has returned to Spring Lake and is contributing significant phosphorus; however, the sediment

release rates remain relatively modest and very similar to those measured in 2010, when there was no evidence of significant P accumulating at Sites 1 and 2. More significantly, the overall TP and Chl-*a* concentrations in the water column of Spring Lake remain high, and point to the continued need for reductions in external P sources in the Spring Lake watershed.

Recommendations for the type and placement of Best Management Practices (BMPs) in the watershed have been provided previously (Steinman et al. 2015), and we once again urge the local municipalities, decision makers, and stakeholders to begin implementing them. Our results illustrate what has been cautioned in previous studies (Steinman et al. 2006; Steinman and Ogdahl 2008, 2012; Steinman et al. 2015): alum application is a short-term solution to the longer-term problem of internal P loading and its effectiveness is critically tied to concurrent reductions in external P loading.

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