Internal Phosphorus Loading in Spring Lake

5 Years Following Alum Treatment

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EXECUTIVE SUMMARY

An analysis of internal phosphorus loading in Spring Lake, MI, was conducted in September 2010, ~5 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 and 2006: 8 mo post-alum) taken at the same sites and using the same methods.

The total phosphorus concentration in the Spring Lake water column in September 2010 was significantly lower than during pre-alum conditions, but was greater than in August 2006, 8 months post-application. Chlorophyll *a* concentrations in the water column were lower than what were measured in previous years, but still remained near or above the eutrophic level. The macroinvertebrate community recovered from the decline that occurred shortly after alum application and was similar in density and composition to pre-alum conditions. Iron and aluminum concentrations in the sediment were higher in 2010 than 2006, while concentrations of iron and magnesium were similar between 2010 and 2006.

Maximum internal phosphorus loading rates in Spring Lake averaged from 1.68 to 2.81 mg $P/m^2/d$ under anoxic conditions. Although these rates are an order of magnitude lower than in 2003/2004, before alum was applied, they are substantially higher than in 2006. The NaOH-extractable SRP fraction has increased since 2006 and was similar to pre-alum concentrations, suggesting that the aluminum hydroxide floc has successfully bound phosphorus in the sediments. Further confirmation of phosphorus retention in the sediment was found in the increased sediment total phosphorus, which was greater than pre-alum concentrations at most sites.

Our results illustrate that the alum treatment continues to be effective at reducing internal loading rates and binding phosphorus in the sediments. However, its efficiency has declined slightly since 2006. Furthermore, the still-elevated water column phosphorus and chlorophyll concentrations point to the continued need for reductions in external phosphorus loads to Spring Lake.

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, 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). 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).

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). 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 μg/L and ranged from 6 to 631 μg/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 extremely 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 external P load reduction must accompany alum application to address the long-term impacts associated with cultural eutrophication.

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 again after a 5-yr interval (i.e., 2010). We measured rates of internal phosphorus 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).

Per the MDNRE permit, AWRI was contracted to repeat the same suite of internal phosphorus loading experiments and ecological analyses in September 2010, ~5 years post-treatment. This report contains our 2010 results, comparisons with previous studies, and an assessment of the longer-term effects of the alum application.

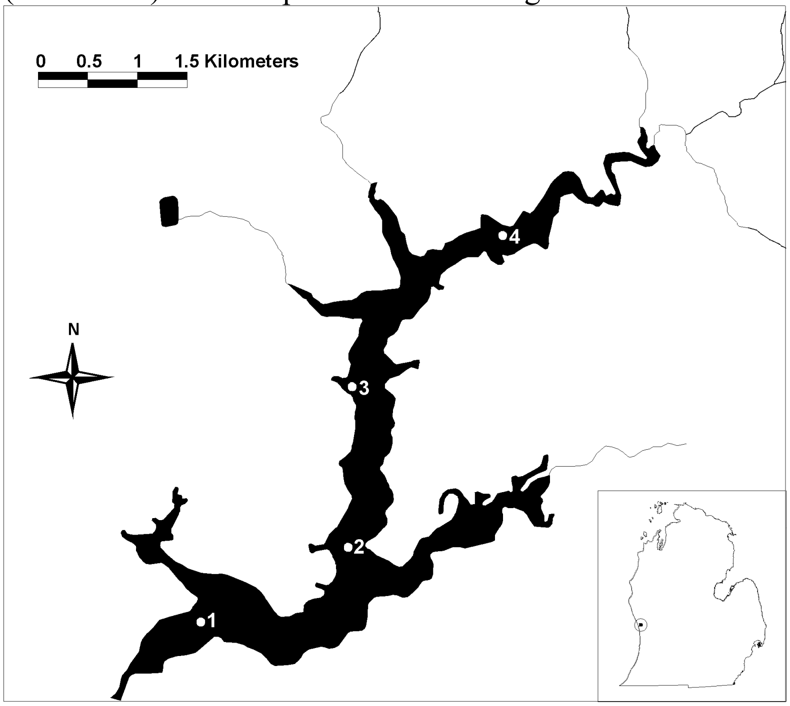
METHODS

Field Methods: All samples were collected on 9 September 2010, from the same 4 locations that were sampled in previous studies (Figure 1). 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-µm membrane filters into scintillation vials. Samples were stored on ice until transported to the laboratory, within 5 h of collection. TP samples were stored at 4°C and SRP samples were frozen 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-µm 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 (Figure 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). Inset: location of Spring Lake (circled dot) in lower peninsula of Michigan.



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 N_2 (with 330 ppm CO_2) 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-µm membrane filter and frozen for analysis of soluble SRP. SRP and TP were analyzed on a Bran+Luebbe Autoanalyzer (US EPA 1983). SRP values below detection were calculated as ½ the detection limit (5 µg/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 (at the same time as the cores were removed).

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

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

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. 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, 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 (Moore and Reddy 1994) to determine the fraction of phosphorus bound to iron and calcium minerals in the sediments. Porewater was filtered, frozen, and analyzed for SRP as described previously. Residual sediment was shaken for 17 h with 0.1M NaOH, centrifuged, filtered, frozen, and analyzed for SRP. This fraction is referred to Al- and Fe-bound phosphorus and represents a mineral association that can become soluble under anoxic conditions. After this extraction, the sediment was extracted for 24 h with 0.5M HCl, centrifuged, filtered, frozen, and analyzed for SRP. This fraction is referred to as Ca- and Mg-bound phosphorus and represents a stable mineral association.

RESULTS

Field results

Depth, Temperature, Dissolved Oxygen, and Chlorophyll a: Sites 1 and 2 were deeper than sites 3 and 4 (Table 1). Temperature, DO, and chlorophyll *a* were relatively constant throughout the water column at all sites (Table 1). Water temperature was 20-21 °C and DO was 4-7 mg/L at all sites except Site 4, where it was 10-11 mg/L. Chlorophyll *a* concentrations were similar among sites, ranging from 14-19 µg/L, except for Site 3, which had lower concentrations (9-10 µg/L; Table 1). Near-surface chlorophyll *a* concentrations were lower in 2010 than in 2006 (all sites) and 2003 (Sites 1 and 2; Table 1). Valid comparisons of chlorophyll *a* concentrations at Sites 3 and 4 are not possible with the 2003 data because of an algicide treatment that occurred shortly before sample collection in 2003 (Steinman and Ogdahl 2008). Chlorophyll *a* concentration near the bottom of the lake was greater at Sites 1 and 2 in 2010 than in previous years, most likely because of stratification (as evidenced by the DO data) at those sites during previous sampling events (Table 1). The 2010 sampling event occurred later in the year when stratification was not evident (Table 1), although episodic storm events also could be responsible for water column mixing.

Secchi Depth, Light Extinction Coefficient, and TDS. Secchi disk depth was 2 m at all sites (Table 1). This is greater than the transparency in 2006, when Secchi depths were <1 m (Table 1; Steinman and Ogdahl 2008). However, this comparison is based on single sampling dates, so conclusions regarding improved overall clarity are premature. Neither Secchi depth nor the light extinction coefficient appeared to be related to chlorophyll concentrations (Table 1). Total dissolved solids (TDS) concentration was similar among all sites (Table 1), was generally greater than in 2006 but less than in 2003, and did not show any obvious relationship to Secchi depth or light extinction data (Table 1).

SRP and TP. SRP concentrations were below detection (DL = 5 µg/L) at all sites except near-bottom at Site 3, where it was still very low at 5 µg/L (Table 1). TP concentrations were moderate at all sites (40-60 µg/L; Table 1). Overall, mean TP was lower in 2010 than in 2003, but the difference was statistically significant only for the near-surface measurements ($t=3.938$; $p=0.007$), not for the near-bottom measurements ($t=1.671$; $p>0.05$). In contrast, TP concentrations were greater in 2010 compared to 2006, but the differences were not statistically significant. TP concentration in near-surface waters declined by 41% between 2003 and 2010, but increased by 85% between 2006 and 2010. These changes in water column TP concentration, declining between 2003 and 2006 (after the alum treatment), but then increasing between 2006 and 2010, are consistent with the trends in the internal loading measurements (see below).

Table 1. Selected limnological characteristics of sampling sites in Spring Lake. 2003 data in red; 2006 data in black; 2010 in black **bold**. 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 and 2010 data were collected on September 9.

Parameter	Site 1		Site 2		Site 3		Site 4	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Depth (m)	8.2 8.8 **9.1**		10.1 10.9 **10.7**		6.7 7.0 **7.9**		4.9 5.5 **5.8**	
Temp (°C)	17.8 26.5 **20.3**	16.6 24.6 **19.8**	17.8 27.2 **20.6**	15.3 20.6 **19.6**	24.4 28.6 **20.8**	22.7 27.2 **20.3**	24.8 28.5 **20.8**	23.6 27.8 **20.4**
DO (mg/L)	11.3 7.4 **6.1**	6.0 0.3 **5.6**	9.3 8.6 **6.9**	0.6 0.5 **3.9**	6.1 9.8 **6.6**	1.5 7.1 **4.1**	5.4 9.8 **10.6**	4.2 6.6 **10.0**
Chl a (µg/L)	23.9 20.4 **15.2**	6.2 8.6 **18.9**	21.7 15.9 **14.4**	3.3 6.4 **15.7**	5.3 10.5 **9.6**	3.8 16.7 **8.7**	3.6 22.4 **17.2**	4.9 25.9 **14.3**
SRP (mg/L)	<0.01 <0.005 **<0.005**	< 0.01 < 0.005 **<0.005**	< 0.01 <0.005 **<0.005**	0.04 0.006 **0.005**	0.03 <0.005 **<0.005**	0.04 <0.005 **0.005**	0.04 <0.005 **<0.005**	0.03 <0.005 **<0.005**
TP (mg/L)	0.06 0.03 **0.06**	0.04 0.05 **0.06**	0.11 0.03 **0.05**	0.08 0.02 **0.05**	0.10 0.02 **0.05**	0.08 0.03 **0.06**	0.12 0.04 **0.05**	0.08 0.04 **0.04**
TDS (g/L)	0.386 0.304 **0.365**	0.378 0.302 **0.386**	0.362 0.290 **0.337**	0.372 0.300 **0.374**	0.362 0.281 **0.333**	0.384 0.284 **0.344**	0.353 0.275 **0.311**	0.381 0.278 **0.312**
pH	8.6 8.3 **8.0**	8.2 7.6 **8.0**	8.6 8.4 **8.0**	7.9 7.4 **7.9**	8.5 8.5 **8.0**	8.0 8.2 **7.9**	8.4 8.5 **8.5**	8.3 8.1 **8.5**
K_d	1.44 1.26 **1.33**		1.52 1.52 **1.26**		1.72 1.35 **1.42**		2.25 2.32 **1.97**	
Secchi depth (m)	1.25 0.5 **2.0**		1.0 0.7 **2.0**		1.0 0.5 **2.0**		0.75 0.5 **2.0**	

Invertebrates. Four major groups of benthic invertebrates were identified in the Spring Lake sediments (Figure 2). Chaoborids were the dominant invertebrate in 2010, in contrast to 2004 and 2006, when oligochaetes dominated the benthic community (Figure 2). Grand means (i.e., across all sites) of chaoboridae and chironomidae densities were not significantly different in 2010 than in 2004 (Figure 2, Table 2). Chironomid density significantly decreased and chaoborid density significantly increased from 2006 to 2010 (Figure 2, Table 2). Oligochaete density was significantly lower in 2010 than in 2004, but was greater than in 2006, although that difference was not statistically significant (Figure 2, Table 2). Ceratopogonidae density was significantly greater in 2010 than in 2004 and 2006, but remained low (Figure 2, Table 2).

Chironomidae density was significantly lower in 2010 than in 2004 only at Site 1 (Figure 3, Table 2). Mean chironomidae density decreased at all sites between 2006 and 2010, but the decrease was significant only at Sites 3 and 4 (Figure 3, Table 2). Chaoborid density was greater in 2010 than in 2004 and 2006 at all sites, except at Sites 2 and 3 where it was similar in 2004 (Figure 3, Table 2). Inter-annual patterns in oligochaete density varied throughout the lake. Mean oligochaete density was similar across years at Site 1, greater in 2010 than in other years at Site 2, and lower in 2010 than in other years at Sites 3 and 4 (Figure 3, Table 2). Ceratopogonidae density was not significantly different between years at any site, despite the significantly higher grand mean density in 2010 (Figure 2, Table 2).

Analysis of total invertebrate density revealed an increase in 2010 from the decline that was observed in 2006, with the exception of Site 4 (Figure 4). The grand mean density, as well as densities at Sites 1 and 2, was not significantly different between 2004 and 2010 (Figure 4, Table 3). Total invertebrate density remained significantly lower in 2010 than in 2004 at Sites 3 and 4, despite the significant increase at Site 3 since 2006 (Figure 4, Table 3).

Table 2. Mean (± SE) invertebrate densities (organisms/m^2) for each major taxonomic group observed in Spring Lake sediments in 2004, 2006, and 2010. Significant comparisons between years were determined using t-test or Mann-Whitney Rank Sum test.

	2004	2006	2010	Significant Comparisons
Chironomidae				
Grand Mean	155 ± 27	422 ± 126	94 ± 32	2006>2010, p=0.032
Site 1	173 ± 25	260 ± 216	29 ± 29	2004>2010, p=0.019
Site 2	58 ± 58	43 ± 0	29 ± 29	NS
Site 3	173 ± 66	433 ± 25	58 ± 14	2006>2004, p=0.021 2006>2010, p<0.001
Site 4	216 ± 25	952 ± 278	260 ± 50	2006>2004, p=0.058 2006>2010, p=0.07
Chaoboridae				
Grand Mean	1125 ± 393	76 ± 23	1919 ± 318	2004>2006, p=0.02 2010>2006, p<0.001
Site 1	43 ± 25	188 ± 29	2366 ± 658	2006>2004, p=0.019 2010>2004, p=0.024 2010>2006, p=0.030
Site 2	1904 ± 1039	87 ± 25	2684 ± 195	2010>2006, p<0.001
Site 3	2438 ± 225	29 ± 14	2280 ± 232	2004>2006; p<0.001 2010>2006; p<0.001
Site 4	115 ± 14	0 ± 0	346 ± 50	2004>2006; p=0.001 2010>2004; p=0.011 2010>2006; p=0.002
Oligochaeta				
Grand Mean	3502 ± 994	555 ± 135	1021 ± 342	2004>2006, p=0.013 2004>2010, p=0.043
Site 1	2193 ± 731	967 ± 270	2611 ± 863	NS
Site 2	274 ± 76	101 ± 63	678 ± 29	2010>2004; p=0.008 2010>2006; p=0.001
Site 3	2727 ± 225	736 ± 325	649 ± 205	2004>2006; p=0.007 2004>2010; p=0.002
Site 4	8815 ± 806	418 ± 72	144 ± 63	2004>2006; p<0.001 2004>2010; p<0.001 2006>2010; p=0.046
Ceratopogonidae				
Grand Mean	7 ± 5	7 ± 5	76 ± 42	2010>2004, p=0.029 2010>2006, p=0.029
Site 1	0 ± 0	0 ± 0	14 ± 14	NS
Site 2	0 ± 0	0 ± 0	0 ± 0	NS
Site 3	14 ± 14	0 ± 0	43 ± 0	NS
Site 4	14 ± 14	29 ± 14	245 ± 138	NS

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

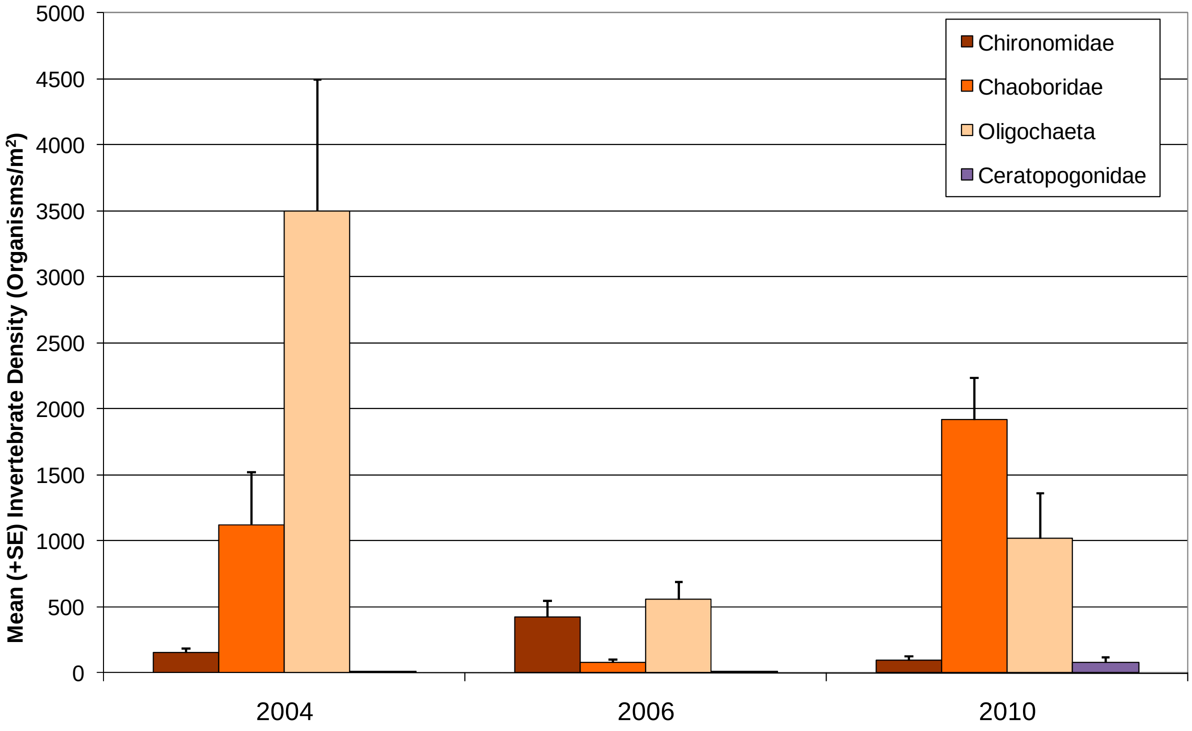


Figure 3. Mean (± SE) invertebrate density of each major taxonomic group identified at each site in Spring Lake in 2004, 2006, and 2010.

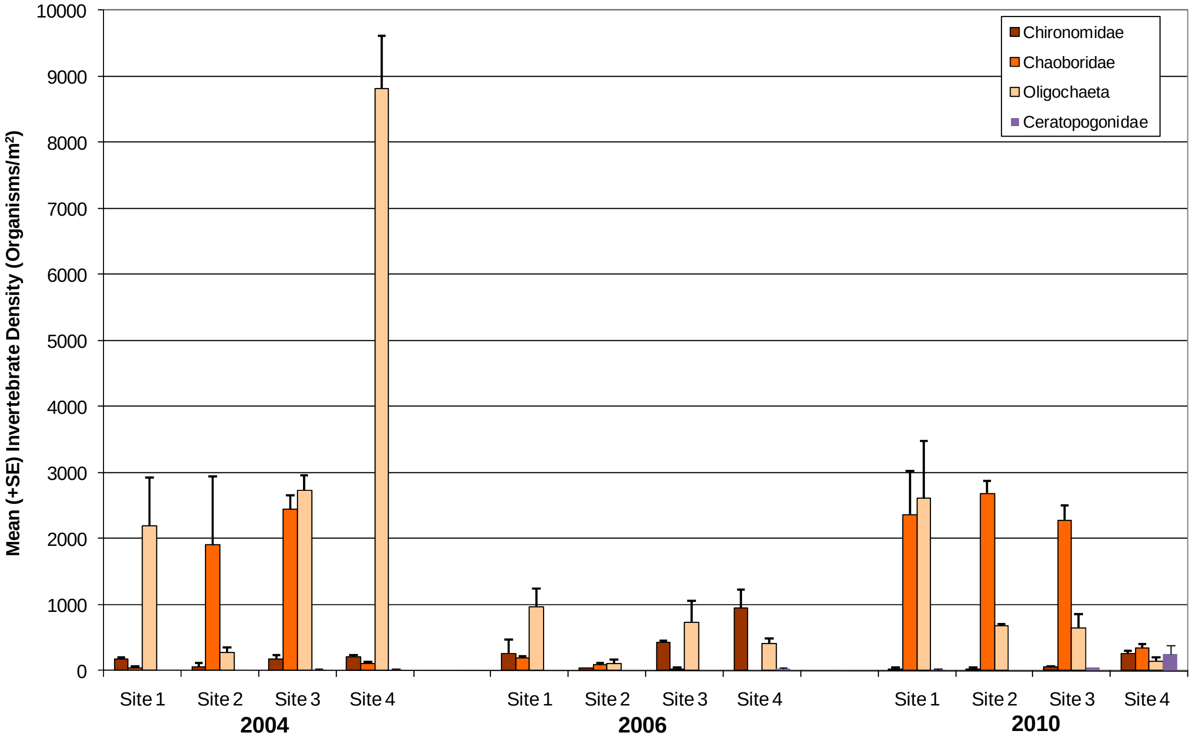
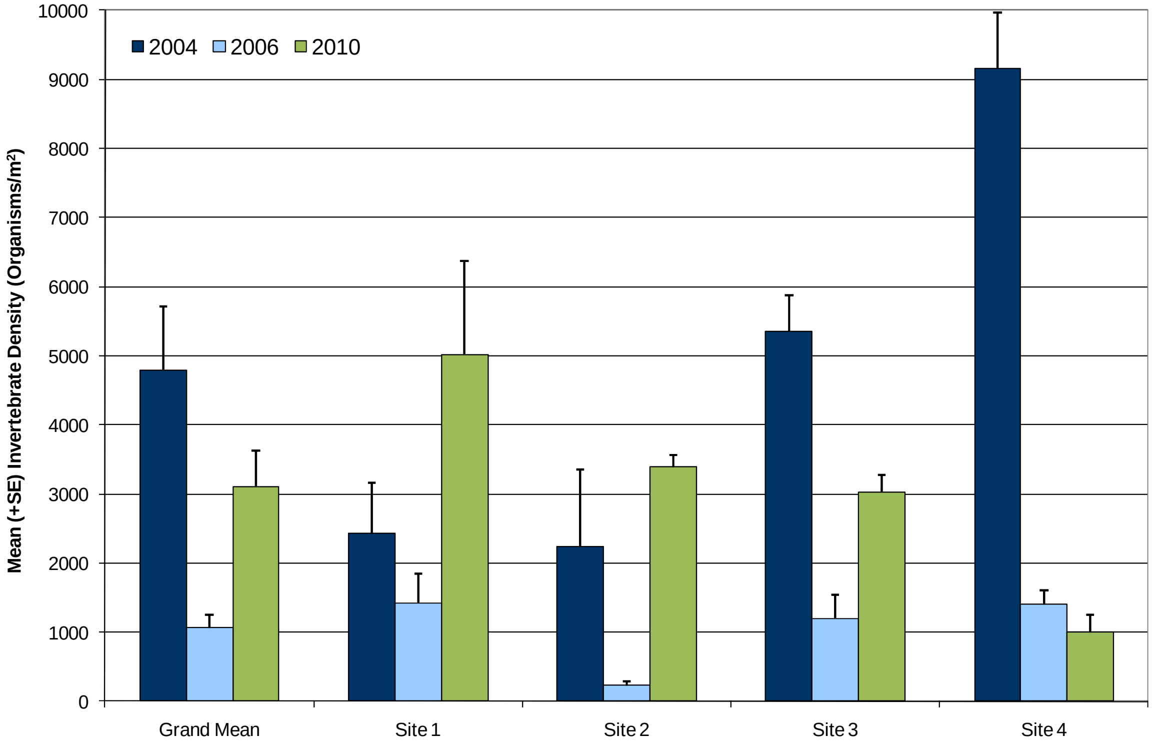


Table 3. Mean (± SE) total invertebrate densities (organisms/m^2) observed in Spring Lake sediments in 2004, 2006, and 2010. Significant comparisons between years were determined using t-test or Mann-Whitney Rank Sum test.

	2004	2006	2010	Significant Comparisons
Grand Mean	4794 ± 917	1064 ± 192	3109 ± 526	2004>2006; p=0.002 2010>2006; p=0.002
Site 1	2424 ± 732	1428 ± 425	5021 ± 1350	NS
Site 2	2236 ± 1115	231 ± 52	3390 ± 166	2010>2006; p<0.001
Site 3	5353 ± 525	1197 ± 336	3030 ± 246	2004>2006; p=0.003 2004>2010; p=0.016 2010>2006; p=0.012
Site 4	9161 ± 813	1399 ± 200	995 ± 254	2004>2006; p<0.001 2004>2010; p<0.001

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



Laboratory results

Maximum apparent TP flux rates under anoxic conditions ranged from 1.68 to 2.81 mg TP/m^2/d, which were still an order of magnitude lower than in 2003, prior to alum treatment (Table 4). However, the 2010 rates were 2 to 8 times higher than in 2006. These data suggest that there has been some decrease in alum efficiency in Spring Lake over the last 5 years, although the alum is still resulting in a substantial reduction in internal P loading.

Table 4. Maximum Apparent TP Release Rate (anoxic conditions): mg P/m^2/d

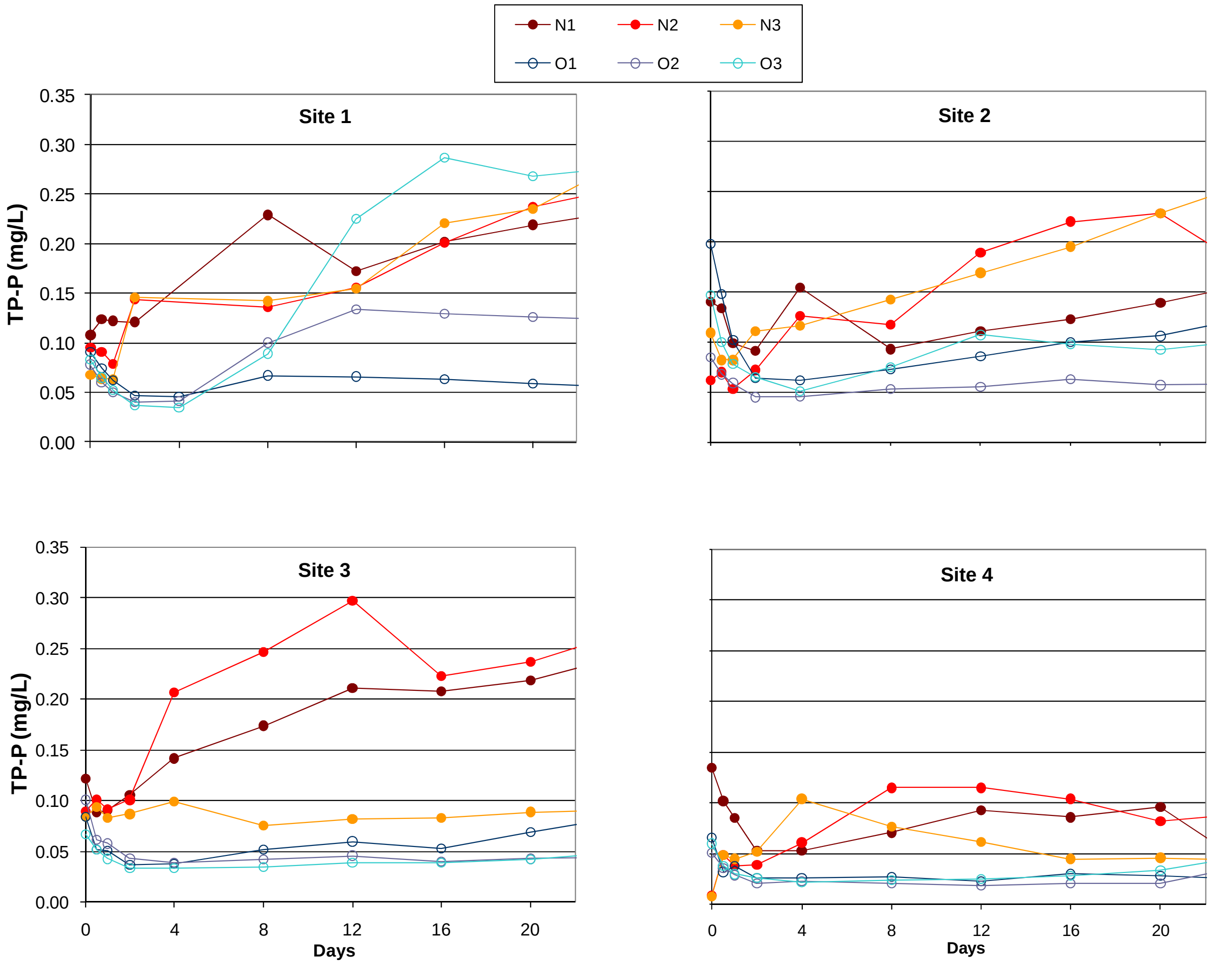
Site	**2003**	**2006**	**2010**
1	29.54±0.95	0.33±0.31	2.81±1.02
2	17.33±4.89	0.88±1.52	1.68±0.53
3	13.33±8.36	0.49±0.55	2.33±2.46
4	11.67±4.08	-0.05±0.09	2.25±1.40

In general, TP concentrations in the overlying water quickly declined once the cores were placed in the incubation chamber, regardless of site or treatment (Figure 5). TP concentrations usually began to increase by day 2. Release concentrations were lowest at Site 4 (Figure 5). Notably, even the highest TP concentrations were <300 µg/L; although this is clearly a very high P concentration, it is substantially less than the maximum concentrations measured in 2003 (Table 5).

Table 5. Mean TP Saturation Concentration (i.e., maximum concentration) measured under anoxic conditions. Units in µg/L.

Site	**2003**	**2006**	**2010**
1	1420	30	260
2	850	110	220
3	610	60	220
4	770	20	110

Figure 5. TP concentrations in the water overlying sediment cores from 4 sites in Spring Lake sampled in September 2010. 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 (as a function of dry weight) prior to incubation ranged from 1025 mg/kg (Site 1) to 2049 mg/kg (Site 2; Figure 6). Post-incubation concentrations were similar to initial values except at Site 1, where post-incubation TP was greater. Redox state did not affect sediment TP concentration (Figure 6). Post-incubation sediment TP was greater in 2010 than in 2004 or 2006 at all sites except Site 1, where concentrations were similar to those measured in 2004 (Figure 7).

Figure 6. TP concentration (mg/kg) in cores collected in 2010, as a function of dry weight. Initial = prior to incubation; O = oxygen (oxic condition); N = nitrogen (anoxic condition).

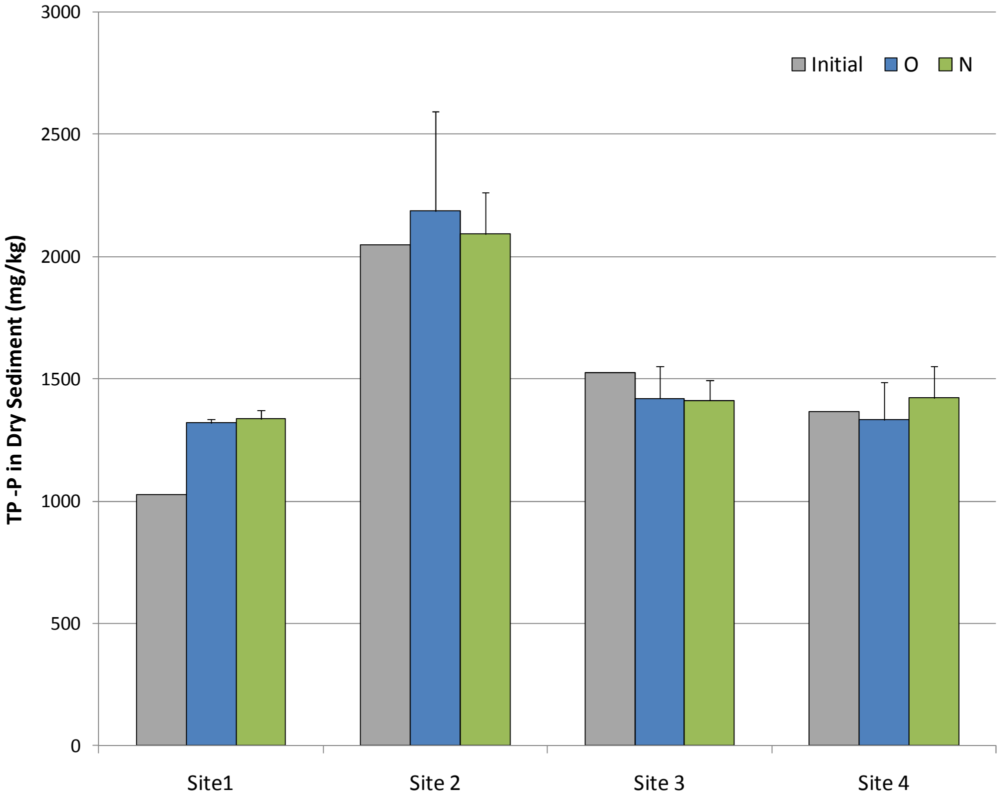
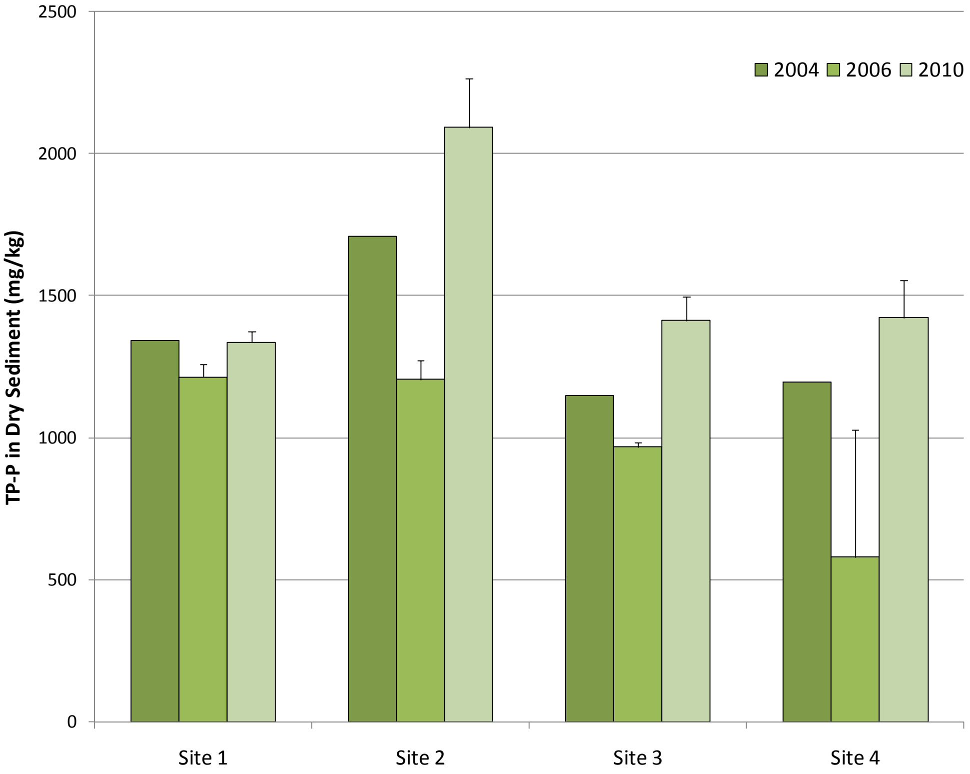


Figure 7. TP concentration (mg/kg) in cores collected in 2004, 2006, and 2010, as a function of dry weight. To facilitate comparisons among years, the data shown represent post-anoxic incubation conditions.



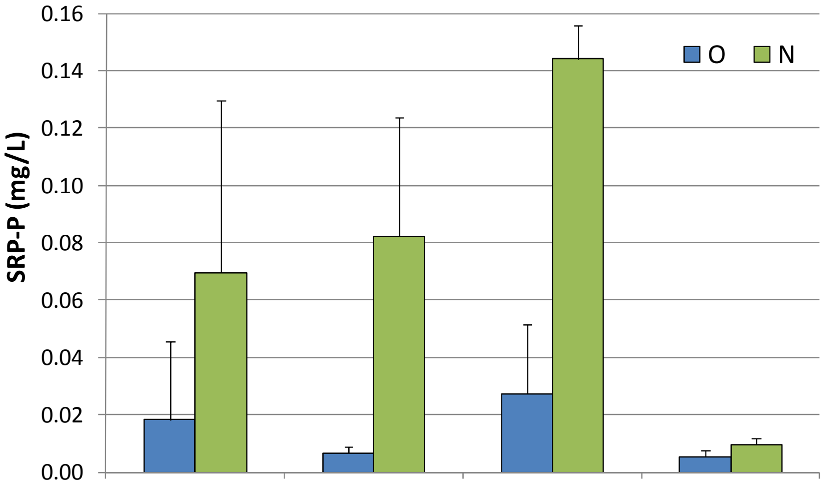
Porewater SRP measured in sediments following the 25-d incubations ranged from below detection in several oxic cores to an average of 0.14 mg/L in anoxic cores taken from Site 3 (Figure 8). Site influenced porewater SRP only in anoxic treatments, with Site 3 having the highest concentrations (H=8.843; p=0.031). Porewater SRP was significantly greater in anoxic than oxic treatments (H=9.512; p=0.002; Figure 8). The porewater SRP concentrations measured in anoxic cores in 2010 were greater than those measured in 2006, although the difference was not statistically significant (Table 6). Porewater SRP was not statistically different in 2010 than in pre-alum conditions (Table 6).

Extractable SRP was analyzed in a three-way ANOVA to examine the effects of site, redox state, and extractant. Overall, there were clear differences between the NaOH-extractable and HCl-extractable fractions of SRP, with SRP from the HCl extraction greater than from the NaOH extraction (F=101.488; p<0.001; Figure 8). However, analysis of the data on an individual site basis revealed that there was no significant extractant effect at Site 2 (p=0.450). Extractable SRP significantly varied by site (F=32.170; p<0.001). This was especially pronounced for the NaOH-extractable fraction, which was greater at Site 2 than at all other sites. The HCl-extractable fraction was greater at Site 2 than at Site 4. The site X extractant term was also highly significant (F=17.455, p<0.001), as the effect of site was influenced by the type of extraction; there was a significant site effect for both the NaOH (p<0.001) and HCl (p=0.037) fractions. Redox had no significant effect on extractable SRP (p=0.822). The redox X extractant interaction term was not significant (p=0.307), but the site X redox X extractant interaction term was significant (p=0.049).

Mean NaOH-extractable SRP was not significantly different from pre-alum conditions in either redox treatment, despite the decrease that was observed in 2006 (Table 6). However, HCl-extractable SRP in 2010 remained greater than in pre-alum concentrations and similar to 2006 levels.

Figure 8. A) Porewater SRP concentrations in sediment cores at the end of the incubation period. B) NaOH and HCl-extractable SRP concentrations from sediment cores at the end of the incubation period. O = oxic incubation conditions; N = anoxic incubation conditions.

A) Porewater SRP-P



B) NaOH- and HCl-Extractable SRP-P

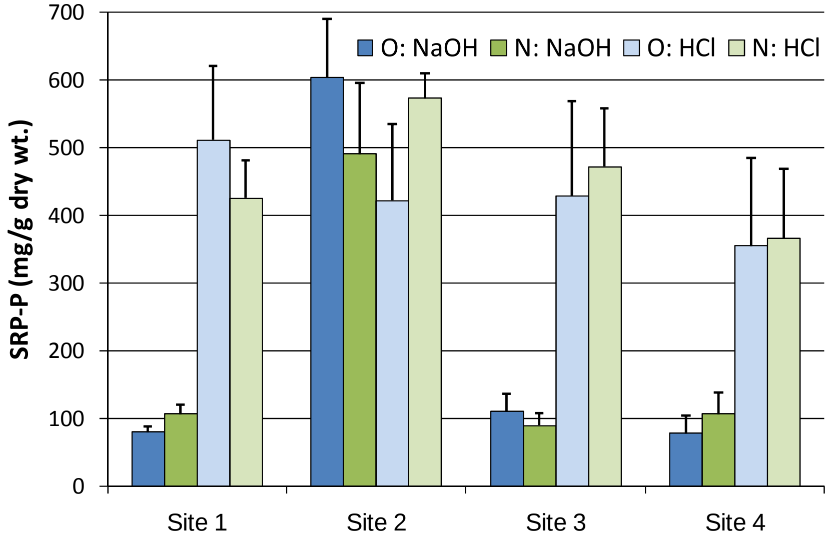
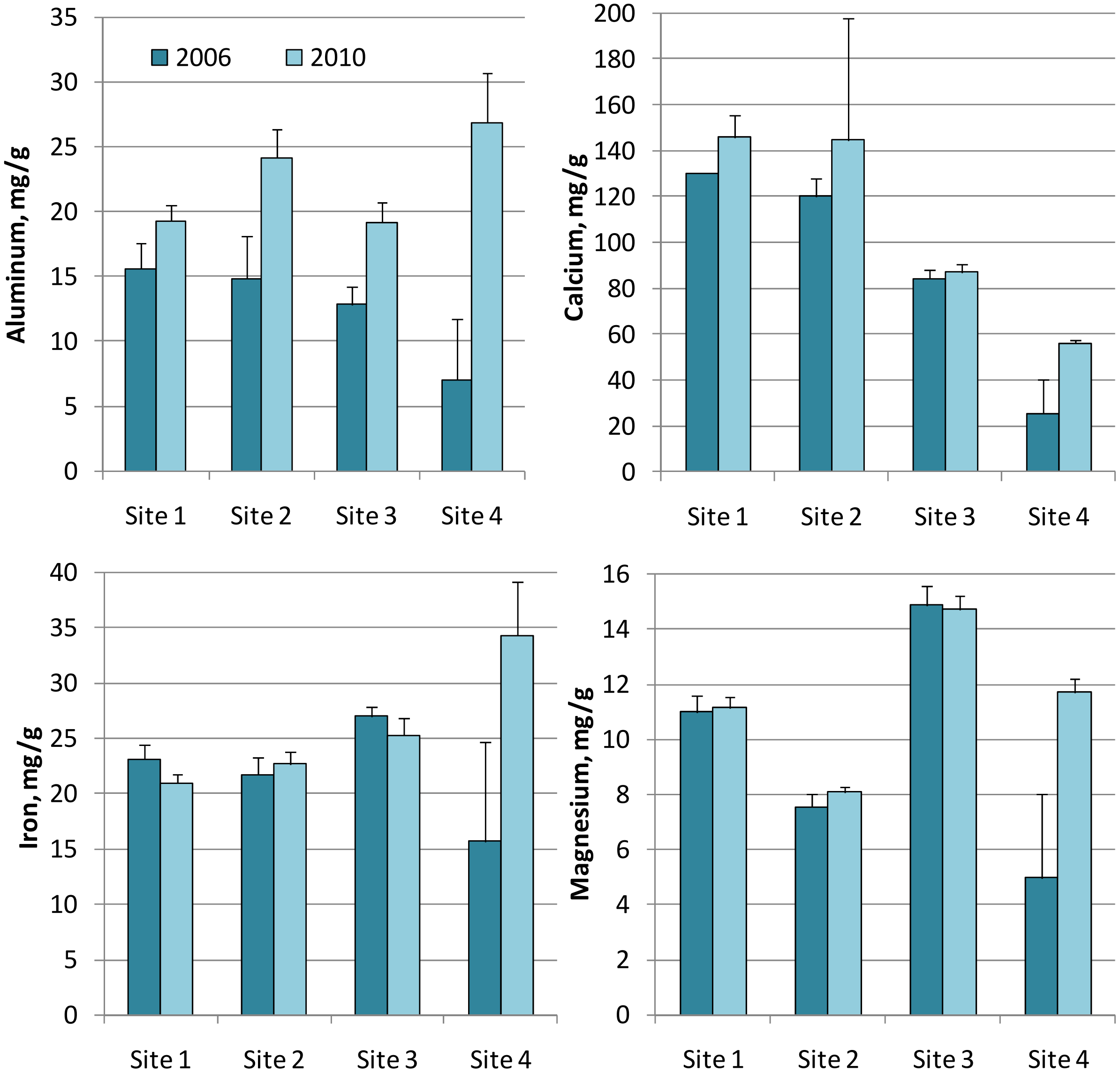


Table 6. Comparison of grand mean values of porewater soluble reactive phosphorus (SRP) (±SD) concentrations (mg/L) and NaOH- and HCl-extractable SRP concentrations (µg/g dry wt.) from Spring Lake sediments pre- (2003 or 2004) and post-alum (2006, 2010) treatment under oxic and anoxic conditions.

Measurement	Pre-Alum (2003 or 2004)	8 Mo. Post-Alum (2006)	5 Yr. Post-Alum (2010)	Significant Comparisons
Anoxic Conditions				
Porewater SRP	0.18 ± 0.19	0.03 ± 0.02	0.08 ± 0.03	NS
NaOH-extractable SRP	140.98 ± 16.19	127.83 ± 22.87	198.46 ± 41.89	2003>2006; 2010>2006; p<0.001
HCl-extractable SRP	285.57 ± 125.71	453.55 ± 135.11	458.79 ± 70.47	2006>2003; 2010>2003; p=0.001
Oxic Conditions				
Porewater SRP	0.03 ± 0.03	0.01 ± 0.00	0.01 ± 0.01	2003>2006; p=0.006
NaOH-extractable SRP	157.95 ± 28.83	91.01 ± 9.25	217.49 ± 37.79	2003>2006; p=0.006
HCl-extractable SRP	276.64 ± 119.31	539.00 ± 48.69	429.14 ± 123.22	2006>2003; 2010>2003; p=0.003

Calcium was the most abundant metal measured at any site (Figure 9). Redox had no effect on sediment metals concentration; therefore, all analyses were performed on grand means of all cores for each site (i.e., initial, oxic, anoxic). Concentrations of iron and aluminum were greater in 2010 than in 2006, while iron and magnesium were similar between the two years. One notable exception is Site 4, which had greater concentrations of all 4 metals in 2010.

Figure 9. Grand means (±SD) of aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg) in sediment cores from Spring Lake in 2006 and 2010. Metals were not measured in 2003/2004.



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; Steinman et al. 1999, 2004; Søndergaard et al. 2001; Nürnberg and LaZerte 2004). Even when external loading rates are relatively low, high diffusive flux rates can help trigger and/or sustain algal blooms. The ecological and societal implications of internal P loading rates 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 Schrieve 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); 3) bioturbation (Van Rees et al. 1996, Matisoff and Wang 1998); 4) macrophyte cover (Welch and Schrieve 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).

The data from Spring Lake show that the September 2010 total phosphorus concentrations in the water column remained significantly lower than the TP concentrations measured in June/July 2003, before alum was applied to the lake. However, the 2010 TP concentrations have increased compared to August 2006, which was 8 months following the alum treatment. Despite this increase in phosphorus, chlorophyll *a* concentrations were lower and Secchi depths were deeper in 2010 than in 2006. This suggests an improvement in water quality over the long term; however, both TP and chlorophyll *a* levels were still relatively high (40-60 μg/L and 9-19 μg/L, respectively). It is important to recognize that this apparent improvement is based on measurements from single sampling dates, which may not be representative of longer-term conditions. Furthermore, the 2010 sampling event occurred later in the season (September) than the previous studies (June-August); our field data indicate the lake was well mixed, in contrast to past years, which affects parameters such as temperature, dissolved oxygen, and chlorophyll. Therefore, comparisons of water quality among the three years must be viewed with caution.

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 reveal that overall benthic invertebrate density declined in Spring Lake the year after treatment, likely because of smothering by the alum floc, but that densities have recovered to near pre-alum application levels 5 years later. 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 also more closely resembled the pre-alum condition 5 years after the alum application. This was especially true for chironomid and chaoborid populations, which reversed their respective increasing and decreasing trends that were observed 8 months after treatment (Steinman and Ogdahl 2008). Overall, oligochaetes remained significantly lower in 2010 than prior to alum application, but recovery was apparent at Sites 1 and 2. We did observe a significant increase in ceratopogonids at one site (Site 4). Although these are generally tolerant organisms, their overall densities were low. One notable change in the invertebrate community was the shift in the dominant taxon, from oligochaetes prior to alum treatment to chaoborids 5 years after treatment. 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).

Our P release data suggest that the alum treatment continues to help reduce internal phosphorus loading in Spring Lake. Based on the maximum release rates (Table 4), however, the effectiveness of alum is beginning to decline. Maximum release rates under anoxic conditions in 2010 were still an order of magnitude lower than before alum was applied, but as of September 2010 are an order of magnitude higher than those measured 8 months after treatment. We also compared the mean (not maximum) internal phosphorus loading rates from various west Michigan lakes (Table 7); it is evident that while the mean anoxic rates for the 2010 Spring Lake sediments have increased slightly compared to 2006, the rates are still very low compared to White, Mona, and pre-alum Spring Lakes (Table 7), and remain well below the range measured in eutrophic systems (Nürnberg and LaZerte 2004).

Despite the relatively low internal release rates measured in 2010, the TP concentration in the Spring Lake water column remains relatively high (Table 1). These data suggest external phosphorus loadings are still a problem in the Spring Lake watershed, but are also consistent with the phosphorus release potential of the sediments. The maximum TP concentrations measured in the overlying water from the sediment core incubations were 2-9 times higher than the maximum concentrations measured in 2006 (although considerably less than in the pre-alum incubations; Table 5). Hence, the potential for Spring Lake sediments to liberate P has appeared to remain much lower than pre-alum conditions but has increased in the past 5 years. It is unknown if the decline in alum efficacy will continue, and if so, at what rate.

Table 7. Mean summer flux rates of TP from sediment cores collected from White Lake (2006: Steinman et al. 2009b), Mona Lake (2004 and 2005: Steinman et al. 2009a), and Spring Lake (2003: Steinman et al. 2004; 2006: Steinman and Ogdahl 2008; and 2010 (this study). Spring Lake rates differ slightly from those in Table 4 because data in Table 7 are mean release rates.

TP Release Rate (mg P/m^2/d)		
Site	**Anaerobic**	**Aerobic**
	White Lake (2006)	
1	7.78	-0.18
2	1.55	0.07
3	2.46	0.03
4	3.21	0.14
	Mona Lake (2004)	
1	6.46	-1.84
2	5.38	-2.41
3	13.63	0.99
4	12.82	0.30
	Mona Lake (2005)	
1	4.16	0.22
2	5.57	0.21
3	4.85	0.52
4	3.19	0.19
	Spring Lake (2003)	
1	26.71	0.40
2	16.02	-2.00
3	9.04	0.16
4	10.64	-1.04
	Spring Lake (2006)	
1	0.0	0.52
2	0.72	-0.21
3	0.26	0.0
4	0.0	0.10
	Spring Lake (2010)	
1	1.79	0.70
2	0.98	-0.53
3	1.12	-0.25
4	-0.04	-0.25

In 2006, we were surprised by the observed response of the sediment fractions to alum application: a decrease in NaOH-extractable SRP was unexpected, as increases in the Al- and Fe-bound phosphorus fraction after alum dosing have been observed in other lakes (Rydin and Welch 1999, Reitzel et al. 2005). Our measurements 5 years after alum application conformed to our initial expectations, and revealed an increase in the NaOH-extractible P fraction since 2006 to concentrations similar to pre-alum measurements (Steinman and Ogdahl 2008). The HCl-extractable P fraction remained greater than pre-alum concentrations and was similar to that measured in 2006 (Steinman and Ogdahl 2008). One possible interpretation of our results is that shortly after alum application, the P that was loosely bound to the alum floc may have become exchanged with soluble calcium, thereby causing an initial increase in the HCl-extractable SRP (Steinman and Ogdahl 2008). In the longer-term, soluble and particulate P likely was adsorbed or entrapped by the $Al(OH)_3$ floc formed by the dissociation of alum (Bottero et al. 1980, Galarneau and Gehr 1997, Omoike and Valoon 1999). Indeed, the increase in sediment TP in Spring Lake suggests that alum has been effective in removing P from the water column and retaining it in the sediments.

In conclusion, our 2010 results show that the efficacy of the alum treatment has declined over the past 5 years, but that the alum is still retaining P in Spring Lake sediments. However, this effect has not translated into a major reduction in water column phosphorus concentrations in Spring Lake. The relatively high water column P and chlorophyll concentrations point to the continued need for reductions in external P sources in the Spring Lake watershed. Our results illustrate what has been cautioned in previous studies (Steinman et al. 2006, Steinman and Ogdahl 2008): 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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