Internal Phosphorus Loading in Spring Lake

Eight Months Following an Alum Treatment

Submitted by:

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EXECUTIVE SUMMARY

An analysis of internal phosphorus loading in Spring Lake, MI was conducted during August 2006, eight months following an alum treatment. Sediment cores were removed from 4 sites (that had been sampled previously in 2003 and 2004) and incubated in the laboratory under aerobic (with oxygen) and anaerobic (without oxygen) conditions. Phosphorus flux from the sediments into the overlaying water column were measured over a 22-day period and compared to rates measured from sediment cores collected previously from these sites.

Field measurements showed reduced soluble reactive and total phosphorus concentrations the summer following the alum application, but chlorophyll and irradiance levels were not significantly affected. It is unclear if more frequent sampling would detect differences. Overall macroinvertebrate density declined significantly in 2006 compared to 2004, with chaoborids and oligochaetes experiencing the greatest reductions.

Mean internal phosphorus release rates in Spring Lake sediments ranged from -0.52 to 0.877 mg TP/m^2/d in anaerobic conditions and from -0.206 to 0.272 mg/m^2/d in aerobic conditions. These internal loading rates were substantially lower than those measured before the alum treatment was applied. The NaOH-extractable SRP fraction was significantly lower in 2006 compared to 2003, whereas the HCl-extractable SRP fraction showed the exact opposite pattern. These results were counterintuitive, and may be related to exchange reactions whereby the alum floc that is loosely bound to phosphorus becomes replaced with calcium. More research is needed to elucidate the biogeochemical mechanisms operating in the sediments.

Overall, these results indicate that the alum treatment effectively reduced internal P loading in Spring Lake. However, it appears that chlorophyll levels remain a problem. This likely reflects continued inputs of external loads. Ultimately, a holistic approach that includes

reducing both internal and external loads is necessary to address the cultural eutrophication of Spring Lake.

INTRODUCTION

Internal 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; 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). 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.

Spring Lake has some of the highest P concentrations measured in western Michigan lakes; TP levels averaged 100 µg/L and ranged from 6 to 631 µg/L during ice-free periods from 1999 through 2002 (T. Groves, Progressive AE, personal communication). In response to concerns from residents regarding impaired water quality in the watershed, laboratory-based studies 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). Additional experiments showed that 1) P release rates at alum concentrations ≥10 mg/L were no different than release rates at concentrations of 25 mg/L, and 2) resuspension of sediments substantially increased TP concentrations, even at high alum concentrations, but total soluble P concentrations remained low in the water as long as alum was present (Steinman et al. 2006a). 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. As part of the permit from MDEQ approving this application, measurement of the rate of internal phosphorus loading was mandated. This report addresses that requirement.

METHODS

Field Methods: All samples were collected in July, 2006 from the same 4 locations that were sampled in 2003 and 2004 (Fig. 1; Steinman et al. 2004). At each site, vertical profiles of

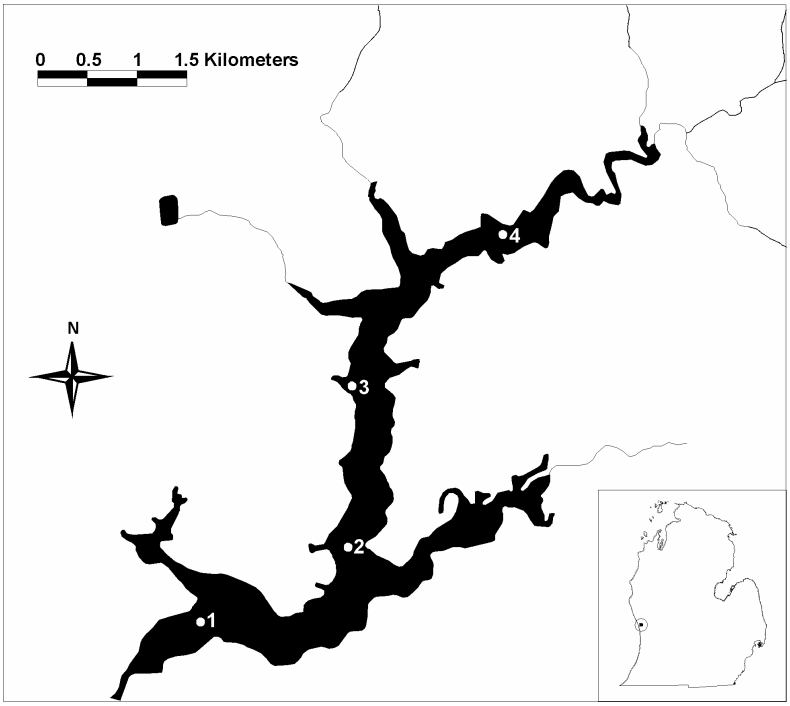
dissolved O_2, pH, temperature, specific conductance, redox potential, turbidity, chlorophyll *a*, and total dissolved solids were measured using a Hydrolab DataSonde 4a (2003, 2004) or a YSI 660 multi-parameter sonde (2006). Photosynthetically active radiation (PAR) profiles were measured using a Li-Cor LI-193SA spherical quantum sensor. Secchi disk depth also was measured to estimate water clarity. Water samples for phosphorus analysis were collected with a Van Dorn 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, always within 5 h of collection. TP samples were stored at 4°C and SRP samples were frozen until analysis. 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).

In 2004, three replicate benthic samples were collected for invertebrate analysis from each of the four Spring Lake coring sites 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 field 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 overlaying 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 and the top 5 cm removed for the analyses of sediment chemistry in the lab.

Figure 1. Map of Spring Lake, showing sampling locations (1-4) of the sediment cores. 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 of invertebrates. All organisms were identified using a stereo microscope to the family level, with the exception of worms, which were identified to class level of Oligochaeta and Nematoda.

The 24 sediment cores (6/site) were placed in a Revco environmental growth chamber, with the temperature maintained to match ambient bottom-water 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 anaerobic conditions, while the remaining three were bubbled with oxygen to create aerobic 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 12 h, 1 d, 2 d, 4 d, 8 d, 12 d, 16 d, 19 d, and 22d after time 0. The 40-mL subsample was replaced with filtered water collected (at the same time as the cores were removed) from the corresponding site in the lake; this maintained the original volume in the core tubes. 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 reactive P (SRP). P was analyzed as described previously.

Flux (P release rate) calculations were based on the increase 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 or retention 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 overlaying the sediment cores, and A is the planar surface area of the sediment cores. P release rate was calculated using two approaches: 1) from the approximate time when P concentrations stabilized in the water column (day 4) until the final sampling date (day 22); and 2) 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. For this report, only the TP internal loading data are presented; most of the SRP concentrations were below detection, thereby limiting the ability to make any definitive conclusions.

Following the incubations, the top 5 cm of sediment was removed from each core. The sediment was homogenized and subsampled for metals (Fe, Ca, Mg, Al) analysis and AFDM. The ashed material was analyzed for TP as described previously. Another subsample (5 g) from the 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 and centrifuged. The supernatant was drawn off, 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, and the supernatant 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; Fig. 2). Water depths were slightly greater in 2006 than 2003. Temperatures were relatively constant throughout the water column at Sites 1, 3, and 4, but there was some evidence of stratification at Site 2 (Table 1; Fig. 2). Concentrations of DO declined

with depth at all sites, with Sites 1 and 2 having concentrations < 1 mg/L; in 2003, only Site 2 had DO levels < 1 mg/L (Table 1).

Chlorophyll *a* concentrations showed similar profiles at Sites 1 and 2, with concentrations between 15 and 20 µg/L through much of the water column and then declining to near 5 µg/L at the bottom (Fig. 2). Chl *a* concentrations increased with depth at Site 3, and were considerably higher at Site 4 than the other sites (Fig. 2). At sites 1 and 2, the 2006 near-surface chl *a* concentrations were somewhat lower than in 2003, but near the bottom of the water column chl *a* concentrations were greater in 2006 than in 2003 (Table 1). At sites 3 and 4, the chl *a* concentrations were much greater at both the near-surface and near-bottom in 2006 than in 2003, despite the application of alum (Table 1).

Secchi Depth, Light Extinction Coefficient, and TDS. Secchi disk depths at all sites were < 1m, suggesting very low transparency, and showed no apparent relationship with chlorophyll concentration. The light extinction coefficient data tracked the chlorophyll data better, as indicated at site 4, where the high chlorophyll concentrations corresponded to the higher extinction coefficient (Table 1). Secchi disk depths were lower at all sites in 2006 than in 2003; extinction coefficients were generally similar between the two dates. Total dissolved solids (TDS) were slightly greater at sites 1 and 2 than at sites 3 and 4 (Table 1), and did not show any obvious relationship to secchi disk or light extinction data. TDS levels were lower in 2006 than in 2003 at all sites and all depths (Table 1).

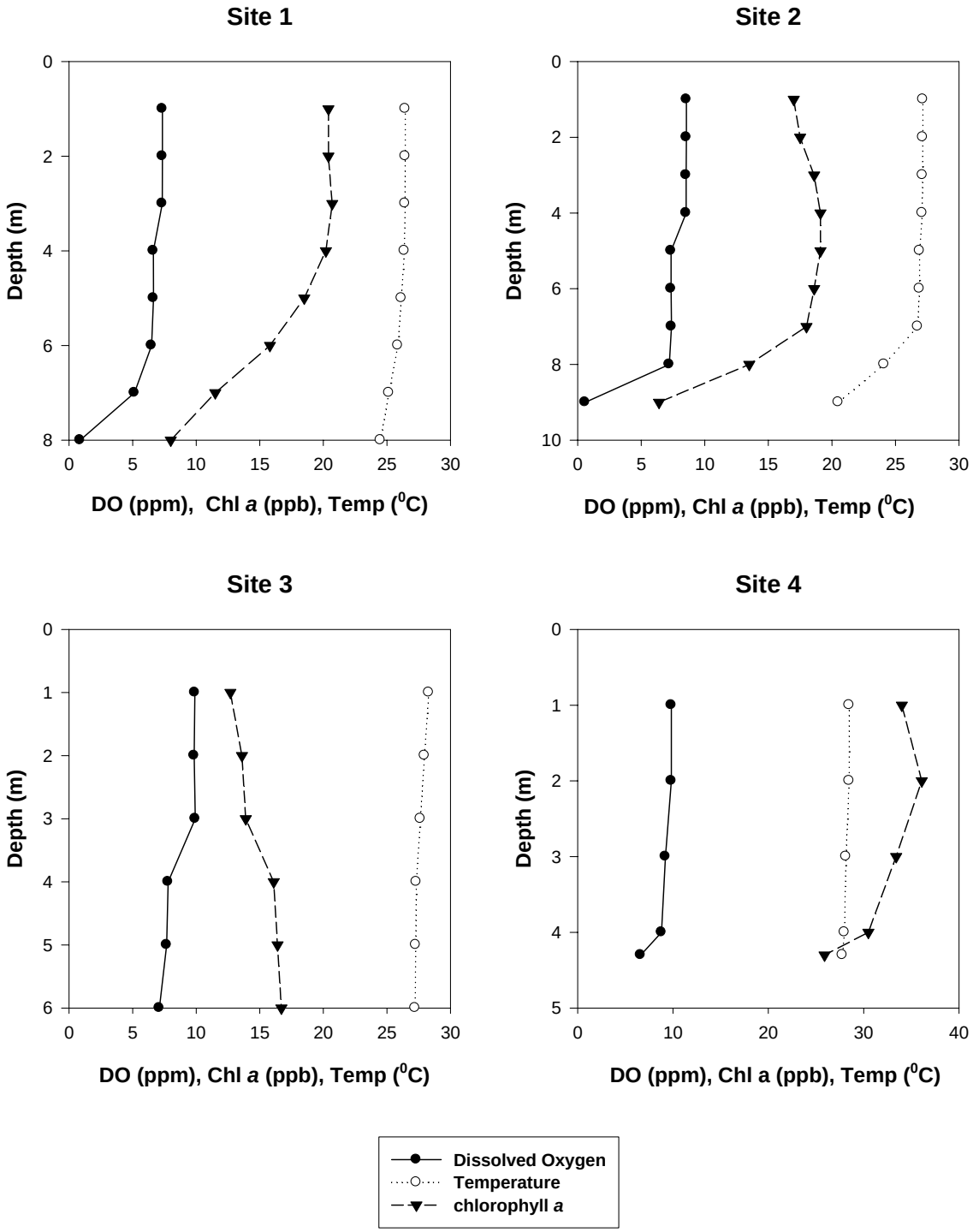
SRP and TP. SRP concentrations were below detection (DL = 0.005 µg/L) at all sites except near-bottom at site 2, where it was still very low at 0.006 µg/L (Table 1). The lower SRP concentrations at site 1 in 2006 reflect an improved detection limit, and hence it is unclear if this difference is real or not; however, the lower SRP concentrations in 2006 at the other sites

indicated a real reduction in SRP after the alum application. TP concentrations in 2006 were relatively low at all sites (≤ 50 µg/L; Table 1). A 2-way analysis of variance revealed significantly lower TP concentrations in 2006 vs 2003 ($F = 21.19$, $p < 0.001$) but no significant effect of depth ($p > 0.50$) or the year x depth interaction ($p > 0.17$).

Table 1. Selected limnological characteristics of sampling sites in Spring Lake. 2003 data located above 2006 data within each cell. For 2003 data, collections were made from Sites 1 and 2 on June 10 and 11, respectively, and from Sites 3 and 4 on July 16. Data from all sites in 2006 were collected on August 1.

Parameter	Site 1		Site 2		Site 3		Site 4	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Depth (m)	8.2 8.8		10.1 10.9		6.7 7.0		4.9 5.5	
Temp (ºC)	17.8 26.5	16.6 24.6	17.8 27.2	15.3 20.6	24.4 28.6	22.7 27.2	24.8 28.5	23.6 27.8
DO (mg/L)	11.3 7.4	6.0 0.3	9.3 8.6	0.6 0.5	6.1 9.8	1.5 7.1	5.4 9.8	4.2 6.6
Chl a (µg/L)	23.9 20.4	6.2 8.6	21.7 15.9	3.3 6.4	5.3 10.5	3.8 16.7	3.6 22.4	4.9 25.9
SRP (mg/L)	<0.01 <0.005	< 0.01 < 0.005	< 0.01 <0.005	0.04 0.006	0.03 <0.005	0.04 <0.005	0.04 <0.005	0.03 <0.005
TP (mg/L)	0.06 0.03	0.04 0.05	0.11 0.03	0.08 0.02	0.10 0.02	0.08 0.03	0.12 0.04	0.08 0.04
TDS (g/L)	0.386 0.304	0.378 0.302	0.362 0.290	0.372 0.300	0.362 0.281	0.384 0.284	0.353 0.275	0.381 0.278
pH	8.6 8.3	8.2 7.6	8.6 8.4	7.9 7.4	8.5 8.5	8.0 8.2	8.4 8.5	8.3 8.1
K_d	1.439 1.26		1.525 1.52		1.721 1.35		2.247 2.32	
Secchi depth (m)	1.25 0.5		1.0 0.7		1.0 0.5		0.75 0.5	

Figure 2. Selected limnological characteristics (temperature, dissolved oxygen, and chlorophyll *a*) at Sites 1-4. Note different scales for the depth axis.



Invertebrates. Five major groups of benthic invertebrates were identified from the Spring Lake sediments (Table 2). In general, oligochaetes were the dominant invertebrate, followed by

chironomids, and chaoborids, with very sparse numbers of ceratopogonids and nematomorphs. The last two groups were excluded from statistical analysis because of their low abundances. Chironomidae density showed no significant difference between 2004 and 2006 at sites 1 and 2, were significantly greater ($F = 13.50$, $P < 0.025$) or marginally significantly greater ($F = 6.94$, $P = 0.058$) in 2006 than in 2004 at sites 3 and 4, respectively (Fig. 3, Table 2). Mean density of Chaoboridae was significantly greater in 2006 at site 1 ($F = 14.256$, $P < 0.02$), but declined at the three remaining sites (Fig. 3); differences were not significant between 2006 and 2004 at sites 2 and 4, but were significantly lower in 2006 at site 3 ($F = 113.83$, $P < 0.001$; Table 2). Mean density of Oligochaeta declined at all sites in 2006 compared to 2004 (Fig. 3), but these declines were statistically significant only at sites 3 and 4 ($F = 25.392$, $P < 0.01$: site 3; $F = 107.668$, $P < 0.001$: site 4; Table 2).

Table 2. Mean ± 1SE density (organisms/m^2) of the three most abundant invertebrate groups observed in Spring Lake sediments in 2004 (pre-alum application) and in 2006 (post-alum application). Site pairs in bold indicate statistically significant differences between 2004 and 2006.

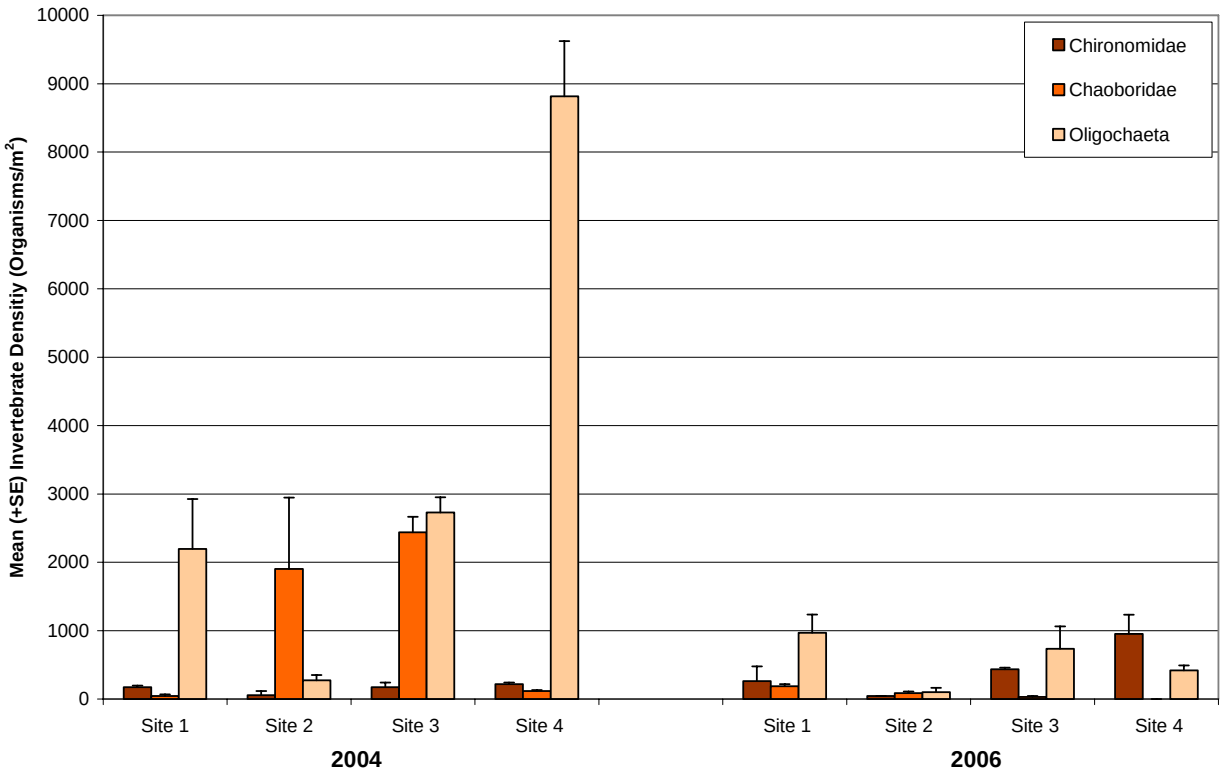
Taxon	**Site 1**		**Site 2**		**Site 3**		**Site 4**	
	2004	2006	2004	2006	2004	2006	2004	2006
Chironomidae	173 ± 25	260 ± 216	58 ± 58	43 ± 0	**173 ± 66**	**433 ± 25***	216 ± 25	952 ± 278
Chaoboridae	**43 ± 25**	**188 ± 29***	1904 ± 1039	87 ± 25	**2438 ± 225**	**29 ± 14*****	115 ± 14	0 ± 0
Oligochaeta	2193 ± 731	967 ± 270	274 ± 76	101 ± 63	**2727 ± 225**	**736 ± 325****	**8815 ± ± 806**	**418 ± 72*****

*P < 0.05

**P < 0.01

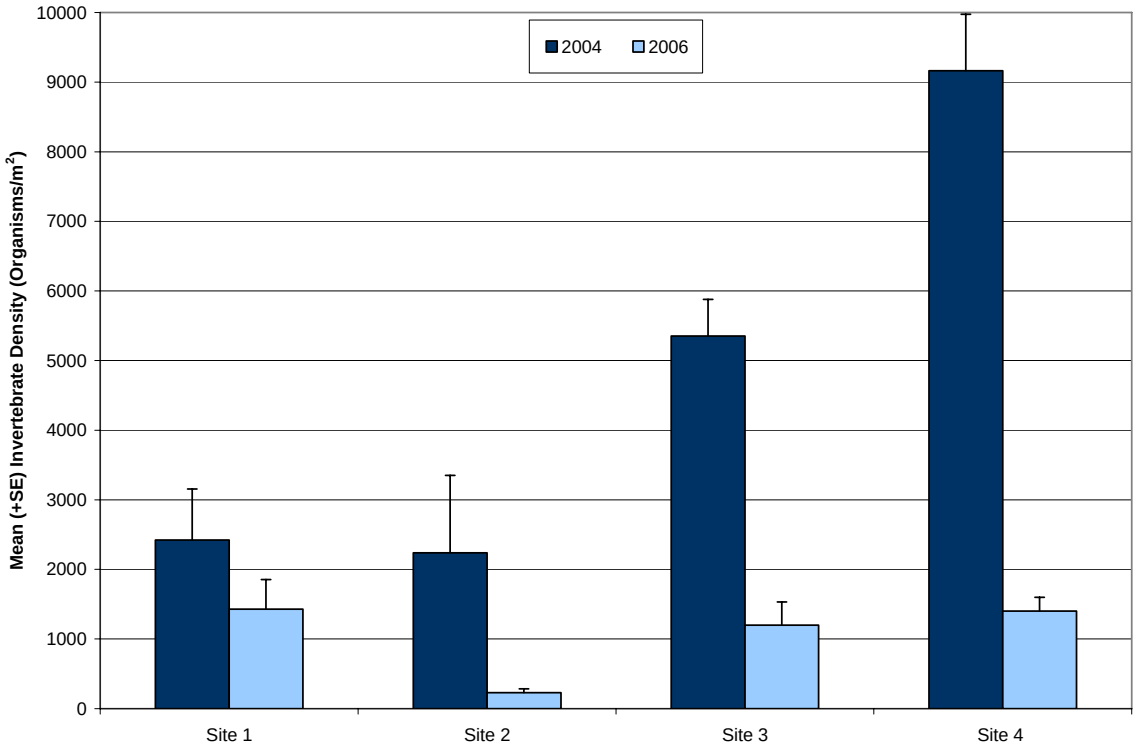
***P < 0.001

Figure 3. Mean + 1SE invertebrate densities (organisms/m^2) of major groups in Spring Lake in 2004 and 2006.



The differences in mean density between 2004 and 2006 are apparent when total invertebrate density is measured (Fig. 4). Mean total invertebrate density declined between 2004 and 2006 at all sites, although this decline was statistically significant only at sites 3 ($F = 44.474$, $P < 0.01$) and 4 ($F = 86.016$, $P < 0.001$).

Figure 4. Mean + 1SE total invertebrate density (organisms/m^2) in Spring Lake in 2004 and 2006.



Laboratory results

Regardless of whether TP flux in 2006 was calculated based on the time period when maximum release occurred or over a defined period of time (i.e., days 4-22), redox had no significant affect on mean flux ($P > 0.2$). This is in contrast to the 2003 data, when the flux rates in the anaerobic treatment were significantly greater than in the aerobic treatment. In addition, mean TP flux was dramatically reduced in 2006 compared to 2003 (Table 2).

In general, flux rates quickly declined once placed in the incubation chamber, regardless of site or treatment (Fig. 5). In most cases, flux rates stayed flat after the initial decline, although one replicate core from sites 2 and 3 showed increases in the anaerobic treatments; however,

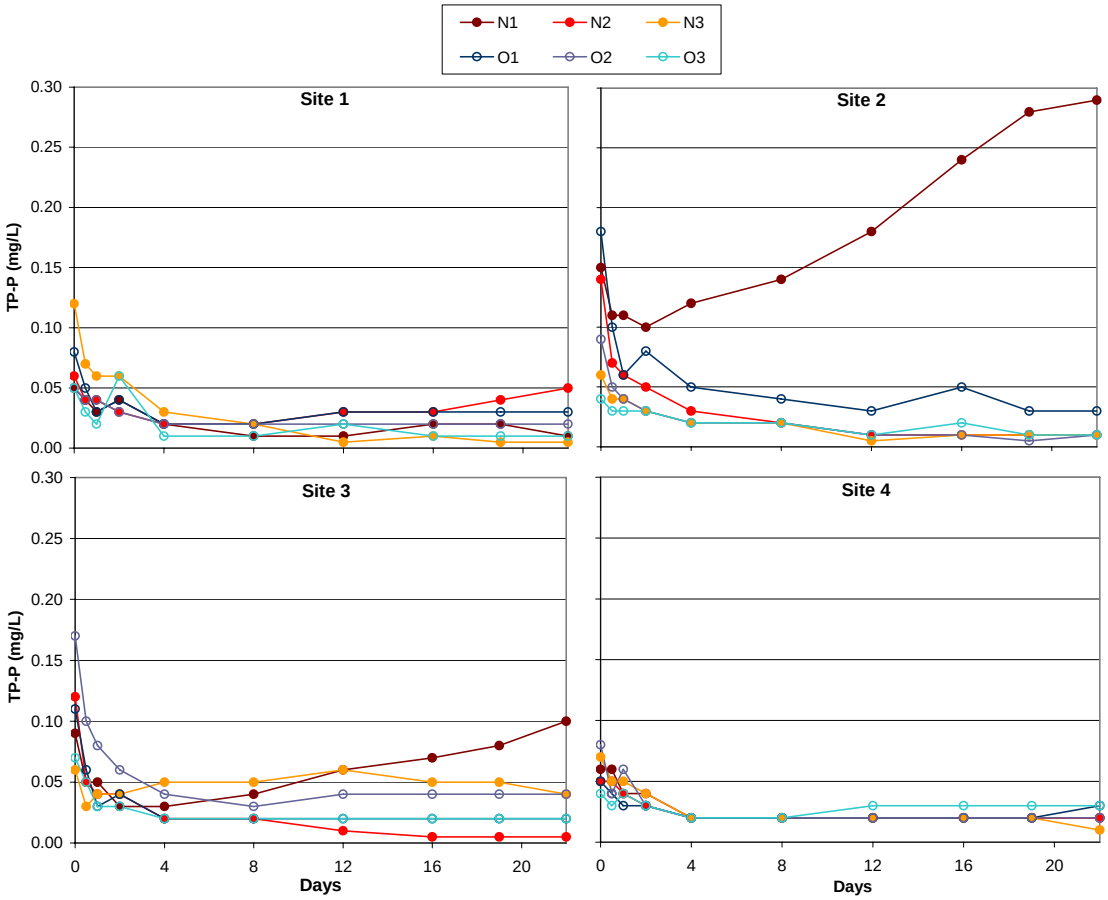
even those increases were relatively modest (maximum concentrations of 100 and 290 µg/L, respectively) compared to the maximum concentrations of > 1000 µg/L measured in 2003.

Mean maximum diffusive flux rates of TP in 2006 ranged from -0.52 to 0.877 mg TP/m^2/d in anaerobic conditions and from -0.206 to 0.272 mg/m^2/d in aerobic conditions (Table 2). The negative values suggest that the sediments could act as a sink for TP.

Table 2. Comparison of mean flux rates of TP from sediment cores collected from Spring Lake in summer 2006 (based on maximum release rates and days 4-22; see methods) compared to medium release rates measured in summer 2003.

TP Flux Rate (mg P/m^2/d)		
Site	**Anaerobic**	**Aerobic**
Spring Lake (2006) – maximum rates		
1	0.328	0.251
2	0.877	0.125
3	0.487	0.125
4	-0.052	0.272
Spring Lake (2006) – days 4-22		
1	0	0.052
2	0.722	-0.206
3	0.258	0
4	0	0.103
Spring Lake (2003) – medium rates		
1	26.71	0.40
2	16.02	-2.00
3	9.04	0.16
4	10.64	-1.04

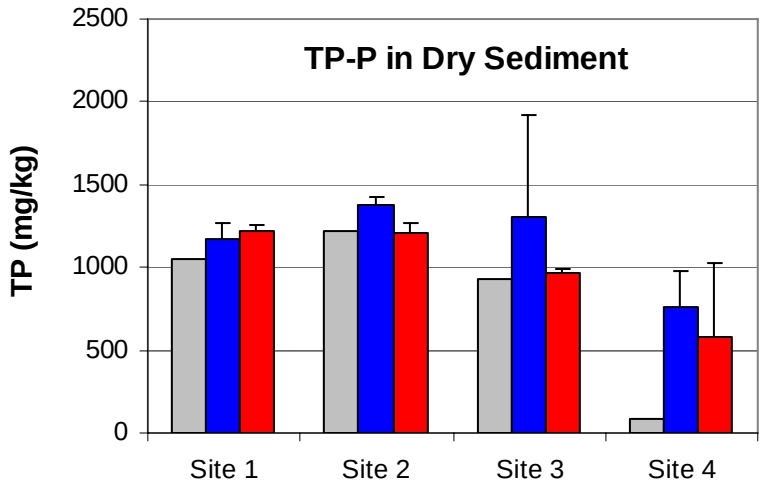
Figure 5. TP concentrations released from sediment cores from 4 sites in Spring Lake sampled in Summer, 2006. The first number in the legend refers to redox state (N = nitrogen, anaerobic condition; O = oxygen, aerobic condition); the second number refers to replicate number (1-3).



The TP concentration in the 2006 sediment cores (as function of dry weight) prior to incubation ranged from 80 (site 4) to 1217 mg/kg (site 2; Fig. 6). No inferential statistics were applied to these data as replicate cores were not sampled at each site. With the exception of site 4, these numbers are similar to those measured in Spring Lake (1135-1592 mg/kg) in 2004. Interestingly, at the end of the incubation, TP concentrations had increased substantially at site 4 compared to the initial value (Fig. 6). Redox state had no significant effect on post-incubation sediment TP ($P > 0.17$), although site was statistically significant ($F = 5.615$, $P < 0.01$) as the

sediment TP at site 4 was significantly lower than at sites 1 and 2, but not site 3 (Tukey's HSD). The interaction between site and redox was not statistically significant (P = 0.711).

Figure 6. TP concentration in dry sediment (mg/kg) from summer 2006 sediment cores analyzed prior to, and at the end of, the laboratory incubations. Gray bar = initial sample (prior to incubation); blue bar = end of incubation under aerobic conditions; red bar = end of incubation under anaerobic conditions.



SRP in the porewater at the end of the incubations ranged from below detection (<0.005 mg/L) to one high concentration of 0.15 mg/L in one core from site 2, with mean values of 0.03 and 0.006 mg/L in anaerobic and aerobic treatments, respectively (Table 3, Fig. 7). Overall, SRP porewater concentration was significantly influenced by both site (F = 43.20, P < 0.001), with Site 1 being significantly lower than site 3, and redox, with porewater SRP significantly greater in anaerobic than aerobic treatments (F = 4.924, P = 0.014; Fig. 7). The site x redox interaction term was marginally significant (F = 2.578, P = 0.092).

There were clear differences between the NaOH-extractable and HCl-extractable fractions of SRP, regardless of site (Fig. 7: bottom panel), with the SRP from the NaOH extraction significantly lower than the SRP from the HCl extraction (3-way ANOVA: F = 1058.25, P < 0.001). Site also was statistically significant (3-way ANOVA: F = 31.062, P < 0.001), with all sites being significantly different from another except sites 1 vs 2 (Fig. 7).

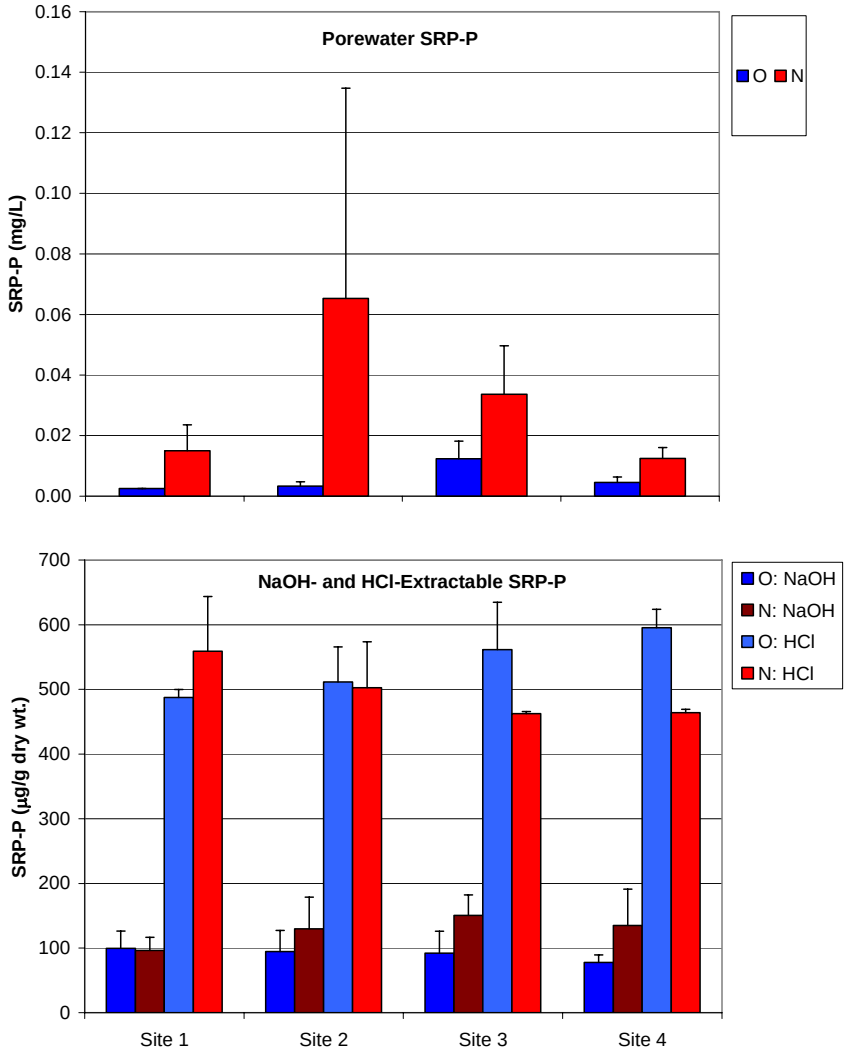
However, the interaction term between site and extraction type was highly significant (F = 11.395, P < 0.001), as the effect of site was influenced by the type of extraction; there is not a significant site effect in the NaOH fraction (P = 0.886) but there is one in the HCl fraction (P = 0.001; Fig. 7). Redox had no significant effect on extractable SRP (P = 1.00). The redox x extract was marginally significant (P = 0.092), and the site x redox x extract interactions term ws significant (F = 3.903, = 0.017).

There were distinct differences in sediment fractions of SRP between the pre-alum and post-alum sediment cores. Mean concentrations of porewater SRP were lower after the alum treatment in both the aerobic and anaerobic treatments, but these differences were not statistically significant because of the high variance in the replicates samples (Table 3). NaOH-extractable SRP declined significantly in both redox treatments but HCl-extractable SRP increased significantly in both redox treatments (Table 3).

Table 3. Comparison of mean porewater SRP (± SD) concentrations (µg/g dry wgt) from Spring Lake sediments pre- (2003) and post-alum (2006) treatment under aerobic and anaerobic conditions. P-values in bold are statistically significant at the 0.05 level; arrows indicate the direction of change (increase or decrease from 2003 to 2006.

Measurement	Pre-Alum (2003 or 2004)	Post-Alum (2006)	P-Value
Anaerobic Conditions			
Porewater SRP	0.179 ± 0.185	0.032 ± 0.024	0.176
NaOH-extractable SRP	140.984 ± 16.192	127.834 ± 22.867	**<0.001 ↓**
HCl-extractable SRP	285.571 ± 125.712	453.547 ± 135.105	**0.004 ↑**
Aerobic Conditions			
Porewater SRP	0.021 ± 0.019	0.006 ± 0.002	0.199
NaOH-extractable SRP	157.95 ± 28.834	91.010 ± 9.245	**<0.001 ↓**
HCl-extractable SRP	276.641 ± 119.310	539.001 ± 48.690	**0.001 ↑**

Figure 7. Top panel = Porewater SRP concentrations in sediment cores at the end of the incubation period. Blue bar = aerobic incubation conditions; red bar = anaerobic incubation conditions. Bottom panel = NaOH and HCl-extractable SRP concentrations from sediment cores at the end of the incubation period. Blue-toned bars = aerobic incubation conditions; red-toned bars = anaerobic incubation conditions.



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). This process has both

ecological and societal implications. Even when external loading rates are relatively low, high diffusive flux rates can help trigger or sustain algal blooms. Costly attempts to reduce external loading (via best management practices) may not have the desired results in improving water quality if internal loading is not addressed.

Prior studies have shown that alum treatments usually have short-term benefits (Cooke et al. 1993, Welch and Schrieve 1994, Welch and Cooke 1999), but 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) the morphometry of the lake, which influences the likelihood that the alum will be resuspended by wind-wave action and/or shift to no longer cover the sediments uniformly (Welch and Cooke 1995, 1999); 2) the amount of alum added to the sediment, to ensure there is sufficient aluminum to bind the P, but not more than necessary because of financial or environmental concerns (Rydin and Welch 1999; Lewandowski et al. 2003); 3) activity from bottom-dwelling animals (i.e., bioturbation) in the sediments, which can redistribute and bury the alum, reducing its efficacy, and enhance P flux from the sediments due to particle mixing and alteration of the redox conditions (Van Rees et al. 1996, Matisoff and Wang 1998); 4) the presence of macrophytes, which can intercept the alum floc and prevent a uniform cover forming over the sediment, and also release P from tissue during senescence (Welch and Schrieve 1994, Welch and Cooke 1999); 5) water column pH, as circumneutral waters (pH 6-8) are optimal for creating an alum floc (Rydin and Welch 1998, Lewandowski et al. 2003); 6) the rate of sedimentation in the water column because new organic matter that settles over the alum can reduce its ability to bind P (Lewandowski et al. 2003); 7) shallow areas not treated by alum and areas where frequent mixing occurs, which have been reported as significant contributors to internal loading (Søndergaard et al. 1999, Nixdorf and

Deneke 1995); and 8) the degree to which external loads have been reduced following the alum treatment, as continued inputs of high phosphorus will fuel the production of new biomass, which becomes the basis for future internal loads to the system (Carpenter 2005).

The phosphorus data from our snapshots samples in Spring Lake showed significant declines in 2006 compared to 2003, which was presumably related to the alum treatment (see below). However, the light and chlorophyll data did not reveal a marked improvement in water quality between 2003 and 2006. The substantial algal biomass in the 2006 Spring Lake samples suggests that 1) even though TP was reduced, there is still sufficient phosphorus in the water column (20-50 µg/L) to stimulate algal growth; and 2) external loading may still be inputting sufficient phosphorus to offset, at least to some degree, the benefits of the alum treatment. Nonpoint sources of phosphorus, such as tributaries, storm drain runoff, septic systems, waterfowl, fertilizer application, and atmospheric deposition are likely still contributing significant amounts of phosphorus to Spring Lake. Lauber (1999) identified tributary inflow, septage, and lawn fertilizer as the three major sources of external loading to Spring Lake.

Benthic invertebrate community composition is an effective metric for assessing environmental conditions in streams (Barbour et al. 1999) and lakes (Canfield et al. 1996). Although genus- and species-level information is preferable for bioassessment work, family-level information has value (cf. King and Richardson 2002). In general, oligochaetes tend to be more tolerant of nutrient-enriched conditions, especially compared to chironomids, which are more sensitive to nutrient enrichment (cf. Wiederholm 1980), although this generality is dependent on the specific taxa comprising each family. In Spring Lake, the invertebrate data showed a general pattern of an increase in mean density of Chironomidae, and a decline in the mean densities of Chaoboridae and Oligochaeta between 2004 and 2006. These data are

consistent with the other data suggesting that the alum treatment improved environmental conditions, at least with respect to nutrients. However, overall density of chironomids was still low; for example, mean chironomid density in Muskegon Lake ranged from 632 to 909 individuals/m^2 (Carter et al. 2006), whereas sites 1 and 2 in Spring Lake had mean chironomid densities of 260 and 43 individuals/m^2, respectively.

Relatively few published studies have examined the influence of alum on benthic invertebrate populations. In Newman Lake, WA, low dissolved oxygen concentrations had created an environment where chaoborids did well but both chironomids and oligochaetes did poorly. An alum application resulted in a doubling of chaoborid density, which was attributed to a change in trophic structure resulting in more food resources, but there was no affect on chironomid or oligochaete populations (Doke et al. 1995). In Morey Lake, VT, an alum addition resulted in a significant decline in invertebrate species density and richness the year after application, but recovery to pre-treatment levels occurred within two years and significant increases above pre-treatment levels were evident after ten years (Smeltzer et al. 1999).

Our comparisons of field data between 2003/2004 and 2006 must be viewed with caution for several reasons: 1) the 2003 data were collected earlier in the summer than the 2006 data, which will directly influence parameters such as temperature, and indirectly influence other parameters such as chlorophyll *a* and dissolved oxygen; 2) as snapshots, these one-time samples (of physical and chemical conditions) may not be representative of ambient conditions, as antecedent events (e.g., storms) may have a strong, but ephemeral, influence on the data; 3) the chlorophyll data may be confounded by the use of two different datasondes in 2003 vs 2006; and 4) it may take many years of monitoring to detect significant changes in the populations of longer-lived organisms, such as benthic invertebrates (cf. Smeltzer el al. 1999).

The 2006 TP release rates under anaerobic conditions were substantially lower than those measured in 2003, and were in the same general range as those measured in oligotrophic systems (Nürnberg and LaZerte 2004). This provides evidence that the alum treatment effectively reduced diffusive flux of phosphorus from the sediments. Release rates under aerobic conditions remained low, and were similar to the 2003 rates, suggesting that redox-based biogeochemical reactions strongly affect phosphorus dynamics in Spring Lake.

The differential response of the sediment fractions was instructive, although the data were counterintuitive. The NaOH-extractable SRP declined after the alum treatment. Because this fraction contains the Al- and Fe-bound phosphorus, one might expect this fraction to increase after an alum application. Increases in the NaOH-extractable P fraction after alum dosing have been observed in other lakes (Rydin and Welch 1999, Reitzel et al. 2005). However, this was not the case in Spring Lake. At the pH of Spring Lake water, alum will dissociate to give trivalent Al^{3+} ions, which hydrolyze rapidly to form soluble monomeric and polymeric species and an amorphous $Al(OH)_3$ floc. The monomeric species can precipitate soluble P as $Al(PO_4)$, whereas the floc can remove soluble and particulate forms of P by adsorption or physical entrapment (Bottero et al. 1980, Galarneau and Gehr 1997, Omoike and Valoon 1999). One possible explanation for our results is that the P that was loosely bound to the alum floc may have become exchanged with soluble calcium, thereby accounting for the increase in the HCl-extractable SRP.

As noted in previous studies (Steinman et al. 2004, 2006a), our analyses make several assumptions that need to be caveated. It was assumed that release rates from sediments in the core tubes were representative of sediments and conditions in Spring Lake. Our sampling strategy was designed to cover as much of the geographic range in Spring Lake as possible,

given the study's constraints. However, there is likely considerable sediment variation throughout the lake; sampling only one site per region of the lake does not allow us to estimate the importance of this variation.

The second assumption was that the incubation conditions were representative of natural conditions. Although the laboratory conditions mimicked the ambient temperature and light regime as closely as feasible, the hydrodynamics in the core tubes clearly were different than in nature. It is likely that the laboratory set-up for the anaerobic water column represented an optimal situation for release of P (constant anaerobic conditions) compared to natural conditions. Hence, our estimates of internal loading are likely higher than what is occurring in nature.

These caveats apply equally to all the analyses we have conducted in Spring Lake, so the relative comparisons across years remain valid. Our data indicate that the Spring Lake alum treatment has resulted in reduced phosphorus concentrations, marginal reductions in invertebrate populations, and reduced rates of internal loading. However, chlorophyll *a* levels have not declined, based on our snapshot samples. It is important to determine the species composition of the phytoplankton (which was not part of this study)—the relatively high chlorophyll levels may be ecologically or socially acceptable if the species are not potentially harmful.

Nonetheless, reducing the lake chlorophyll concentration is an understandable goal, and these data suggest that phosphorus continues to be a problem in Spring Lake. Hence, new approaches will be needed to reduce the external phosphorus loads entering this system. As noted by Steinman et al. (2006a), alum application is a short-term solution to the longer-term problem of internal P loading. Welch and Cooke (1999) concluded that a reasonable expectation of longevity of benefits from alum treatments is 10-15 years. However, impacts associated with nonpoint sources of P in impaired lakes can last for hundreds or thousands of years (Carpenter

2005). Hence, it is critical that we address the underlying reasons for impaired water quality. External load reduction must complement any chemical addition (Hansson et al. 1998) regardless of the long-term effectiveness of alum treatment. Reducing stormwater discharge, conversion of septic systems to sewers, use of low- or no-P fertilizer, and implementation of other best management practices should be emphasized and implemented wherever possible in the Spring Lake watershed (Walsh et al. 2005, Steinman et al. 2006b).

ACKNOWLEDGEMENTS

We are grateful to Scott Kendall, Jennifer Cymbola, and Kelly Wessell for their help with field and/or laboratory sampling, Gail Smythe for assistance with laboratory analysis, and Rick Rediske for assistance with data analysis and reporting. We are grateful to Tony Groves and Pam Tyning for their collaborative spirit and to the Spring Lake – Lake Board for funding.

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