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To cite this article: Alan D. Steinman, Michael C. Hassett, Maggie Oudsema & Richard Rediske (2018) Alum efficacy 11 years following treatment: phosphorus and macroinvertebrates, Lake and Reservoir Management, 34:2, 167-181, DOI: [10.1080/10402381.2017.1402834](https://doi.org/10.1080/10402381.2017.1402834)

To link to this article: <https://doi.org/10.1080/10402381.2017.1402834>



Published online: 02 Jan 2018.



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## Alum efficacy 11 years following treatment: phosphorus and macroinvertebrates

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### ABSTRACT

Steinman AD, Hassett MC, Oudsema M, Rediske R. 2018. Alum efficacy 11 years following treatment: phosphorus and macroinvertebrates. *Lake Reserv Manage.* 34:167–181.

Internal phosphorus loading and benthic macroinvertebrate community structure were analyzed at 4 sites in Spring Lake, Michigan, ~11 yr following an alum treatment. Phosphorus (P) release rates, benthic macroinvertebrate community structure, sediment chemistry, and water quality variables (total dissolved solids, pH, dissolved oxygen, water clarity) were compared to measurements taken previously (2003/2004: pre-alum application, 2006: 8 mo post-alum application, and 2010: 5 yr post-alum application) at the same sites and using comparable methods. Total phosphorus (TP) concentrations in surface water samples from 2016 (38–45  $\mu\text{g/L}$ ) were similar to those measured in 2006 and 2010 (20–80  $\mu\text{g/L}$ ) at all sites; however, 2016 TP concentrations in the near-bottom water at the 2 deeper sites were elevated (~250 and 1,000  $\mu\text{g/L}$ , respectively) compared to TP concentrations of <60  $\mu\text{g/L}$  in 2006 and 2010, suggesting internal loading may be increasing, at least at these 2 sites. In contrast, maximum P release rates from the 2016 sediments were similar to or lower than 2010 rates, and an order of magnitude lower than before alum was applied. Phosphorus content in the sediment was fractionated; loosely sorbed sediment SRP concentrations were very low at all sites. Macroinvertebrate community was similar in density and composition to the 2010 results. These results are suggestive, but not conclusive, that internal P loading is increasing in parts of Spring Lake. Alum application can serve as an effective short-term solution to the longer-term problem of internal P loading, but its effectiveness is critically tied to concurrent reductions in external P loading.

### KEYWORDS


Alum treatment; internal phosphorus loading; macroinvertebrates; west Michigan

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 1990, Jeppesen et al. 2005). Phosphorus (P) release from the sediments usually occurs via (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); (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); and (3) mineralization of organic matter, with subsequent release of phosphorus into the water column (Reddy et al. 1999, Steinman et al. 2014, Huser et al. 2016). In eutrophic lakes, internal loading can account

for a substantial amount of the total P load (Moore et al. 1998, Wagner 2017). 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 counter-acting release of P from sediments (Björk 1985, Graneli 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. 2005). Chemical applications are intended to bind the P, and usually include aluminum sulfate (alum), lime, or iron (Cooke et al. 2005, Bakker et al. 2015), although lanthanum-modified bentonite (Phoslock) is gaining acceptance, especially outside of the United States (Robb et al. 2003, Spears et al. 2013, 2016; Epe et al. 2017). 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

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 Supplemental data for this article can be accessed on the [publisher's website](#)

This article was originally published with errors, which have now been corrected in the online version. Please see Correction (<http://dx.doi.org/10.1080/10402381.2020.1843208>)

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Morgan 1996). In addition, alum will form an insoluble aluminum hydroxide floc at pH 6–8, which has a high capacity to adsorb large amounts of inorganic P (Kennedy and Cooke 1982). By these 2 mechanisms, an alum application can 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 (Groves T, Progressive AE, pers. comm.). 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 55–65% of the TP entering the lake water column on an annual basis, and that an alum application of 24 mg Al/L could be effective at reducing TP release from the sediments (Steinman et al. 2004).

In the fall of 2005, an alum treatment of  $\sim 80 \text{ g Al/m}^2$ , a concentration determined by the Michigan Department of Environmental Quality, was applied by barge as a liquid slurry to the surface of Spring Lake, in locations where depths were  $\geq 4.57 \text{ m}$ , or  $\sim 48\%$  of the lake's surface area (total application was  $\sim 4.5$  million L). We measured rates of internal P loading and evaluated ecological effects of the alum application in 2006,  $\sim 8$  mo after treatment. Our results indicated that the alum treatment effectively reduced internal P loading in Spring Lake, but water column phosphorus concentrations remained relatively high and overall benthic invertebrate density had been reduced (Steinman and Ogdahl 2008). We repeated our analyses in September 2010,  $\sim 5$  yr post-treatment. We recorded the following observations at that time: (1) water column TP was still significantly lower than during 2003 (i.e., before alum was applied) but had increased from August 2006 (8 mo after alum application); (2) Chlorophyll *a* (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; and (3) maximum internal P loading rates averaged 1.68–2.81 mg P/m<sup>2</sup>/d under hypoxic 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). We repeated our analyses in 2016 using the same

or comparable methods, which allowed us to rigorously assess whether the amount of the original alum treatment was still effective, as well as the response of the benthic macroinvertebrate community,  $\sim 11$  yr after it was applied.

## Materials and methods

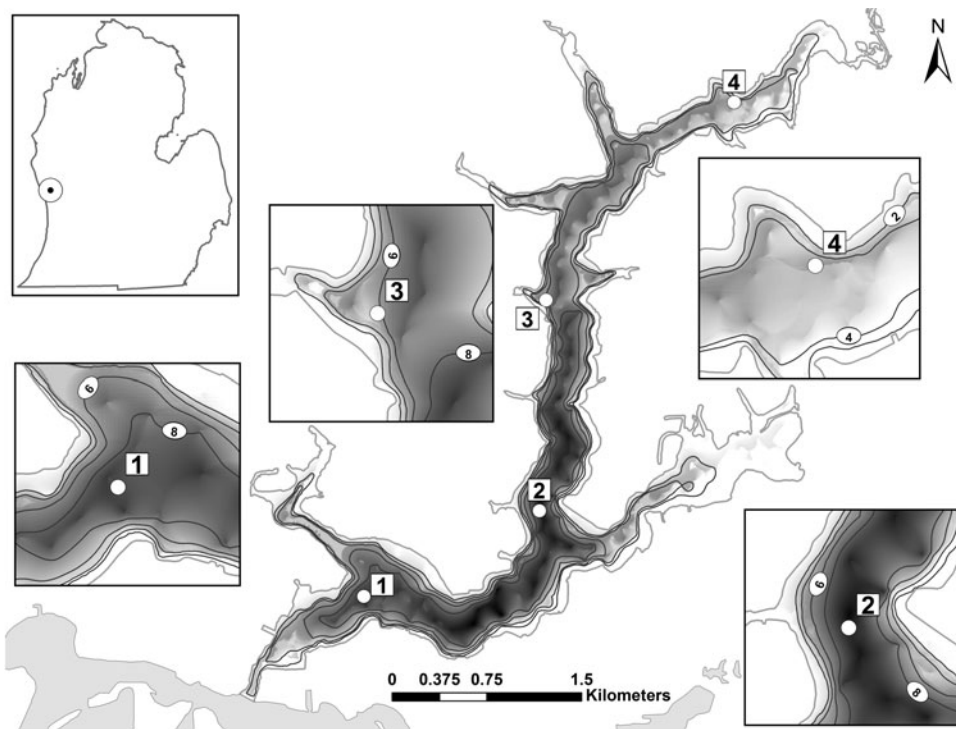
### Site description

Spring Lake is an unimpounded, drowned river mouth system, located on the western side of Michigan's lower peninsula (Fig. 1). It has a surface area of 5.25 km<sup>2</sup>, mean and maximum depths of 6 and 13 m, respectively, and a hydraulic residence time of  $\sim 150$  d in wet periods and  $\sim 330$  d in dry periods. The major tributary is Norris Creek, flowing in from the north; the lake empties into the Grand River,  $\sim 1$  km east of Lake Michigan. The watershed covers  $\sim 134$  km<sup>2</sup>, with main land use categories (2006 data) of forest (41%), residential (28%), and cropland/pasture (11%) (Steinman et al. 2015).

### 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 (DO), pH, temperature, specific conductance, Chl-*a*, and total dissolved solids (TDS) were measured at the surface, middle, and bottom of the water column using a YSI 6600 sonde. Fluoroprobe measurements of Chl-*a* were validated with spectrophotometric measurements of extracted Chl-*a* (Steinman et al. 2017). Photosynthetically active radiation (PAR) profiles were measured using a LiCor Li-193 SA spherical quantum sensor. Secchi disk depth was measured at each site to estimate water clarity. Water samples for P analysis were collected with a Niskin bottle. Water for soluble reactive phosphorus (SRP) analysis was syringe-filtered immediately through 0.45  $\mu\text{m}$  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 4 Spring Lake coring sites, 3 replicate benthic samples were collected for macroinvertebrate analysis using a petite Ponar dredge. Upon collection, the benthic samples were placed in 18.93 L (5 gal)



**Figure 1.** Map of Spring Lake, showing bathymetry (m) of overall lake, and detail at each sampling location (1–4). Upper left inset shows location of Spring Lake in the lower peninsula of Michigan. Flow moves from station 4 south to station 1, and then through the outlet below station 1 into the Grand River.

buckets, covered, brought back to the lab, and washed through a 500  $\mu\text{m}$  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 4 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  $\sim$ 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 placed on ice during transit. An additional core was collected from each site for sediment chemistry analysis; the top 5 cm was removed for the analysis of TP, metals, ash-free dry mass (AFDM), and % solids in the lab (see below).

### 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 an environmental growth chamber, with the temperature maintained to match the mean ambient condition in the hypolimnion of Spring Lake at the time of collection (Table 1). The water column in 3 of the cores from each site was bubbled with  $\text{N}_2$  (with 330 ppm  $\text{CO}_2$ ) to create buffered hypoxic conditions, while the remaining 3 were bubbled with filtered air to create oxenic 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

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

Parameter	Site 1		Site 2		Site 3		Site 4	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Temp (C)	<i>17.8</i>	<i>16.6</i>	<i>17.8</i>	<i>15.3</i>	<i>24.4</i>	<i>22.7</i>	<i>24.8</i>	<i>23.6</i>
	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
	<b>23.6</b>	<b>21.7</b>	<b>23.9</b>	<b>15.4</b>	<b>23.9</b>	<b>23.6</b>	<b>24.4</b>	<b>23.7</b>
TDS (g/L)	<i>0.386</i>	<i>0.378</i>	<i>0.362</i>	<i>0.372</i>	<i>0.362</i>	<i>0.384</i>	<i>0.353</i>	<i>0.381</i>
	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
	<b>0.356</b>	<b>0.377</b>	<b>0.342</b>	<b>0.355</b>	<b>0.332</b>	<b>0.330</b>	<b>0.314</b>	<b>0.312</b>
DO (mg/L)	<i>11.3</i>	<i>6.0</i>	<i>9.3</i>	<i>0.6</i>	<i>6.1</i>	<i>1.5</i>	<i>5.4</i>	<i>4.2</i>
	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
	<b>7.4</b>	<b>0.3</b>	<b>9.0</b>	<b>0.6</b>	<b>8.0</b>	<b>6.4</b>	<b>9.7</b>	<b>8.0</b>
pH	<i>8.6</i>	<i>8.2</i>	<i>8.6</i>	<i>7.9</i>	<i>8.5</i>	<i>8.0</i>	<i>8.4</i>	<i>8.3</i>
	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
	<b>8.6</b>	<b>7.9</b>	<b>8.8</b>	<b>8.2</b>	<b>8.6</b>	<b>8.5</b>	<b>8.8</b>	<b>8.5</b>
Depth (m)		<i>8.2</i>		<i>10.1</i>		<i>6.7</i>		<i>4.9</i>
		8.8		10.9		7.0		5.5
		9.1		10.7		7.9		5.8
		<b>8.3</b>		<b>10.6</b>		<b>7.0</b>		<b>5.4</b>
Light extinction $K_d$		<i>1.44</i>		<i>1.52</i>		<i>1.72</i>		<i>2.25</i>
		1.26		1.52		1.35		2.32
		1.33		1.26		1.42		1.97
		<b>0.84</b>		<b>0.86</b>		<b>0.76</b>		<b>1.14</b>
Secchi depth (m)		<i>1.25</i>		<i>1.0</i>		<i>1.0</i>		<i>0.75</i>
		0.5		0.7		0.5		0.5
		2.0		2.0		2.0		2.0
		<b>1.1</b>		<b>0.75</b>		<b>0.75</b>		<b>0.5</b>

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  $\mu\text{m}$  membrane filter and stored at 4 C for analysis of soluble SRP. SRP and TP were analyzed on a Seal AQ2 Discrete Analyzer (USEPA 1993). SRP values below detection were calculated as one-half the detection limit of 5  $\mu\text{g/L}$ . 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. We present only the TP internal loading data; many 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, Al, Ca, Mg) analysis and AFDM. Metals were analyzed using EPA method 6010b (USEPA 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 modified by Hupfer et al. 2009). The 1.0 M  $\text{NH}_4\text{Cl}$  extraction produces the loosely sorbed P; the 0.11 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 hypoxic conditions; and finally, the 0.5 M HCl extraction produces Ca-bound P, which represents a stable mineral association. This variation from our prior fractionation scheme (Steinman and Ogdahl 2008, 2012) provided greater detail on mobile P fractions; potential implications of the change are included in the Discussion.

### Statistical analysis

Invertebrate taxa counts at each site were converted to densities (# organisms/ $\text{m}^2$ ) and averaged from replicate sediment samples. Mean invertebrate density and mean total invertebrate density for all taxa were analyzed at each site and as a lake-wide (4 sites) mean across all sampling years using either 2-tailed *t*-tests or Mann–Whitney rank sum tests. Normality assumptions were tested using Shapiro–Wilk tests. Equal variance across samples assumptions were tested using Brown–Forsythe tests. Total invertebrate density was calculated by pooling taxonomic groups within sites or lake-wide using the same methods. Significant differences were detected using  $\alpha = 0.05$ .

TP release rates under hypoxic and oxic conditions and maximum TP release rates under hypoxic conditions for each core replicate were averaged separately within each site. Mean maximum TP release rates were compared for individual sites across all 4 sampling years using 2-tailed *t*-tests or Mann–Whitney rank sum tests. P fractionation data were analyzed with a 2-way ANOVA, with site (4 levels) and redox state (2 levels) as the main factors. Normality assumptions were tested using Shapiro–Wilk tests. Equal variance assumptions were tested using Brown–Forsythe tests. Data failing to meet assumptions of normality or variance were transformed with logarithmic, square root, reciprocal, or Box–Cox transformations. Significant differences were detected using  $\alpha = 0.05$ .

## Results

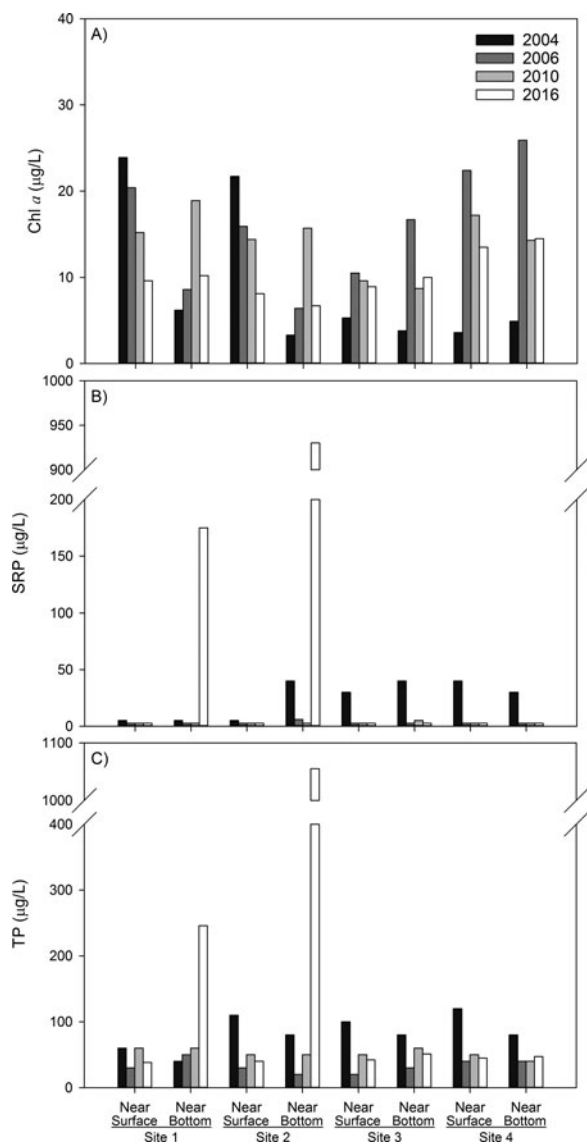
### Lake water quality

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. Surface DO ranged between 7.4 and 9.7 mg/L at all sites (Table 1); 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 aluminum is no longer effectively binding P.

Light extinction coefficients were lower than those measured in prior years; 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), although interpretation of these relatively infrequent observations should be done with caution. 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 or suspended solids. Values of pH generally were more alkaline than in prior years, with some sites increasing by 0.6 to 0.8 units (Table 1).

Chl-*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 2006 or 2010 (Fig. 2). SRP concentrations from near-surface were below detection at all sites (Fig. 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 (Fig. 2). Moderately high TP concentrations ( $\sim 40$ – $50 \mu\text{g/L}$ ) 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 (Fig. 2). Mean surface water SRP and TP concentrations in 2016 remained similar to, or lower than, surface water concentrations from 2006 and 2010 (Fig. 2). In addition, bottom-water concentrations at sites 3 and 4 in 2016 were very similar to what we measured in 2006 and 2010 (Fig. 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



**Figure 2.** a) Chlorophyll *a*, b) SRP, and c) TP concentrations from samples collected at the 4 sites in Spring Lake in 2004 (pre-alum), 2006, 2010, and 2016. Note that for SRP and TP, data are presented as near surface and near bottom in the water column.

deeper sites, or may have started in prior years, given that our 2016 sampling date was later in the year than 2006 or 2010, allowing for potential P accumulation in the deeper waters of Spring Lake.

### Macroinvertebrates

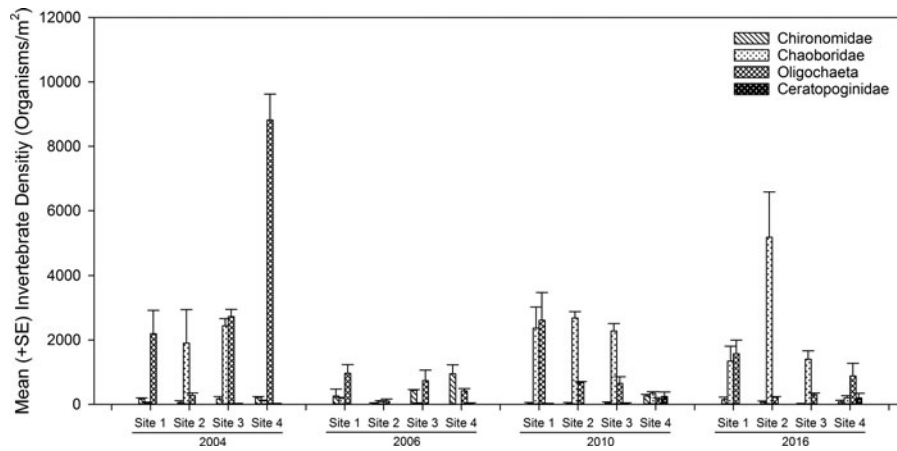
Four major groups of benthic invertebrates were identified in the Spring Lake sediments (Fig. 3). The overall pattern of invertebrate density in 2016 was similar to what was observed in 2010. Chaoborids continued to dominate the invertebrate fauna, in contrast to 2004 and 2006, when oligochaetes dominated the benthic community (Fig. 3). Chironomid and ceratopogonid

densities were both very low, similar to 2010 (Fig. 3). No one site dominated in terms of invertebrate density. In 2016, chironomids were most abundant at site 1, but overall densities were low at all 4 sites (Fig. 3 and Supplement). In prior years, site 4 had the most chironomids, although densities have been relatively low at all sites since 2004 (Fig. 3 and Supplement). Comparisons with prior years showed that chironomids were significantly lower in 2016 than in 2004 and 2006 on a lake-wide basis, and significantly lower than all other years at site 4 (Supplement). 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 the extent observed in 2016 (Fig. 3 and Supplement). In contrast to the temporal trend for chironomids, chaoborid densities significantly increased in 2016 compared to 2004 and 2006 at site 3, and on a lake-wide basis relative to 2006 (Supplement). Oligochaete density was highest at site 1 in 2016, where densities have not significantly changed over time (Fig. 3 and Supplement). Overall, densities of this group plummeted in 2006 and 2010, especially at sites 3 and 4, and in 2016 continued to be significantly lower than in 2004 on a lake-wide basis and at sites 3 and 4 (Supplement). Ceratopogonid density was low overall, similar to prior years, and they were absent entirely from sites 1, 2, and 3 (Fig. 3 and Supplement).

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

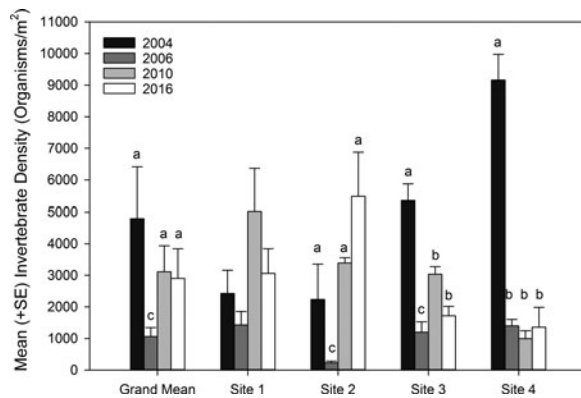
### Phosphorus release from sediment incubations

Maximum mean TP flux under hypoxic conditions ranged from 0.63 to 1.94 mg TP/m<sup>2</sup>/d, with lower rates at the 2 sites with shallow depths (Table 2). These mean rates were not statistically different from those measured in 2010, and remained significantly lower than those measured in 2003 at all sites, prior to the



**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.

alum application (Table 2). These data are consistent with the relatively low TP concentrations measured near-bottom at sites 3 and 4 ( $\sim 0.05$   $\mu\text{g/L}$ ), but contrast with the near-bottom TP concentrations at sites 1 and 2 (Fig. 2), where TP concentrations of  $\sim 250$  and  $1000$   $\mu\text{g/L}$ , respectively, suggest the presence of internal loading at these sites. There was no statistically significant difference in TP release rates between the hypoxic and oxic treatments at any of the sites ( $P > 0.05$ ), although the difference at site 2 was marginally significant ( $P = 0.086$ ; data not shown).



**Figure 4.** Mean ( $\pm$  SE) total invertebrate densities in Spring Lake in 2004, 2006, 2010, and 2016. Different letters within a site indicate statistically significant differences among years.

**Table 2.** Maximum TP release rate (hypoxic conditions) from sediment cores. Units in  $\text{mgP/m}^2/\text{d}$ . Different letters within a row signify significant difference among years at  $P < 0.05$ .

Site	2003	2006	2010	2016
1	$29.54 \pm 0.95^a$	$0.33 \pm 0.31^c$	$2.81 \pm 1.02^b$	$1.94 \pm 0.69^b$
2	$17.33 \pm 4.89^a$	$0.88 \pm 1.52^b$	$1.68 \pm 0.53^b$	$1.62 \pm 0.37^b$
3	$13.33 \pm 8.36^a$	$0.49 \pm 0.55^b$	$2.33 \pm 2.46^b$	$0.81 \pm 0.32^b$
4	$11.67 \pm 4.08^a$	$-0.05 \pm 0.09^c$	$2.25 \pm 1.40^b$	$0.63 \pm 0.24^b$

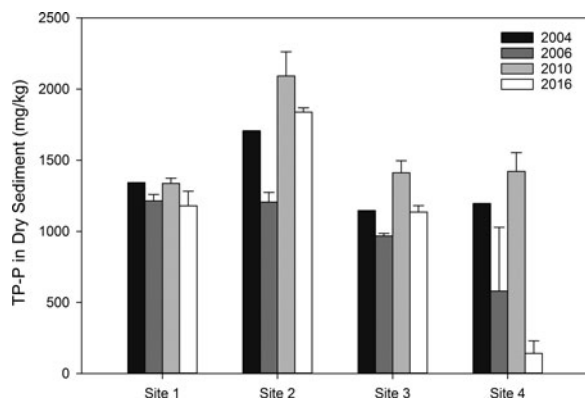
The maximum mean TP concentration measured in the overlying water column under hypoxic conditions increased 155% and 64% at sites between 2016 and 2010 at sites 2 and 4 but declined 15% and 9% at sites 1 and 3 (Table 3). All the maximum mean concentrations were still well below those measured from pre-alum sediment cores, despite more than doubling at site 2. Direct comparisons of 2010 and 2016 data with 2003 and 2006 should be made with caution, as the 2003/2006 sampling dates took place earlier in the year than in 2010/2016, and might be expected to yield lower values.

Sediment TP in 2016 (as a function of dry weight) prior to incubation ranged from 77 (site 4) to 1837 (site 2)  $\text{mg/kg}$  (Fig. 5). 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. Sediment AFDM data were consistent with TP concentrations, ranging from 5.6% at site 2 to 68.9% at site 4 (data not shown). We speculate that we encountered an area of high inorganic deposits at site 4, which contained less organic matter and,

**Table 3.** Maximum TP concentration released from sediment cores measured under hypoxic conditions in the laboratory from 2003 (pre-alum), 2006, 2010, and 2016. Note that sampling times varied among years. Units in  $\mu\text{g/L}$ .

Site (sampling date)	2003 (10/11 Jun: sites 1 & 2) (16 Jul: sites 3 & 4)	2006 (1 Aug)	2010 (9 Sep)	2016 (16 Sep)
1	1420	30	260	220
2	850	110	220	560
3	610	60	220	200
4	770	20	110	180





**Figure 5.** TP concentration (mg/kg) in dry sediment collected in 2004, 2006, 2010, and 2016. To facilitate comparisons among years, the data shown represent post-anoxic incubation conditions.

therefore, lower TP concentrations. We believe this is an isolated area given that we have not encountered sediment of this nature previously, but more spatially intensive sampling would be needed to have greater confidence in this belief.

Sediment fractionation revealed the following trends (Fig. 6): (1) the  $\text{NH}_4\text{Cl}$ -extractable SRP fraction (loosely bound P) was very low at all sites, with significantly lower amounts at site 4, although it is unlikely this difference had any ecological impact given the very low overall concentrations (Fig. 6); (2) site had a significant effect for both the BD- and NaOH-extractable SRP fractions, with site 2 having the largest amounts and site 4 having the smallest amounts of these fractions; in contrast, site had no significant effect on the HCl-extractable SRP fraction (Fig. 6); and (3) the oxidation state had no significant impact on any fraction (Fig 6).

As was the case in prior years, calcium was the most abundant metal at all sites (Fig. 7). Aluminum concentrations declined between 2010 and 2016, with the decline most dramatic at site 4 (Fig. 7). 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. 7).

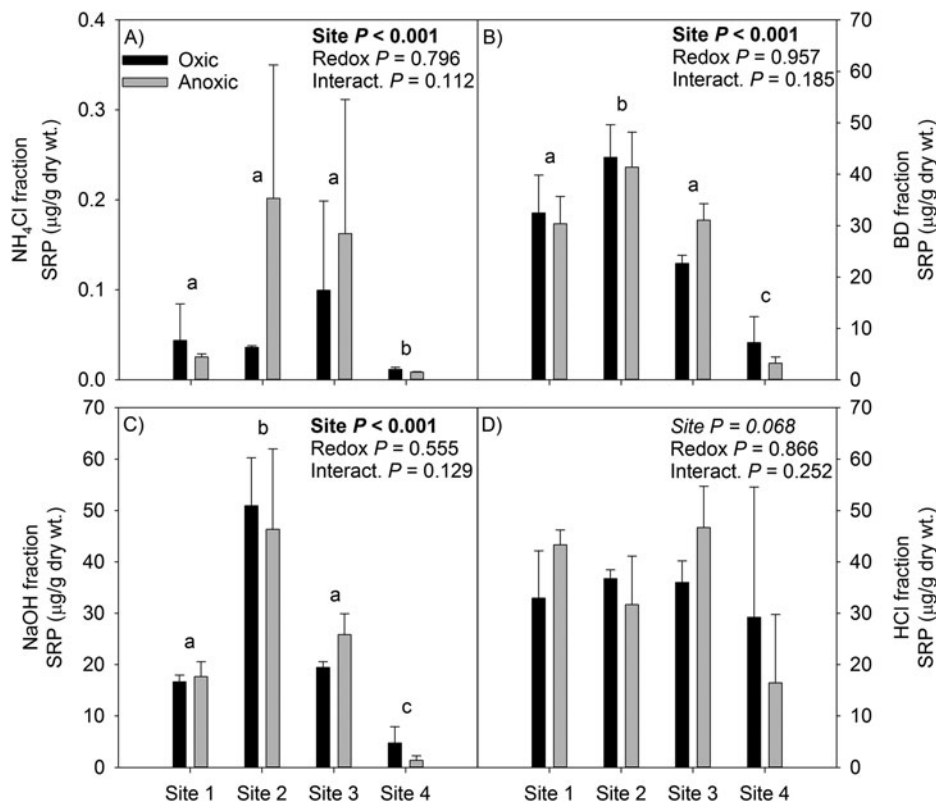
## Discussion

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, Nürnberg and LaZerte 2004, 2016; Matisoff et al. 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, especially as it relates to harmful algal blooms, includes aesthetic issues and potential human health concerns (Codd et al. 1999, Zhao et al. 2016), often prompting management strategies in lakes where rates are high.

Although prior studies have shown that chemical inactivation treatments, such as alum, usually have short-term benefits (Welch and Schriever 1994, Welch and Cooke 1999, Cooke et al. 2005, Egemose et al. 2010, Wagner et al. 2017 and references therein), the question of long-term effectiveness is less clear. Effectiveness of alum treatments generally has ranged from ~4 to 20 yr, 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 (Nixdorf and Deneke 1995, Søndergaard et al. 1999 but see Huser 2017); (8) aging (crystallization) of the  $\text{Al}(\text{OH})_3$  floc (Berkowitz et al. 2006, de Vicente et al. 2008); and (9) 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, Sharpley et al. 2013, Motew et al. 2017). A recent meta-analysis by Huser et al. (2016) found the 3 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 current study provide evidence, albeit not conclusive, that the Spring Lake alum treatment in 2005 is starting to lose its effectiveness. This conclusion is based largely on the SRP and TP data from the near-bottom depths at sites 1 and 2, where concentrations exceeded even the pre-alum P concentrations. The very high 2016 concentrations

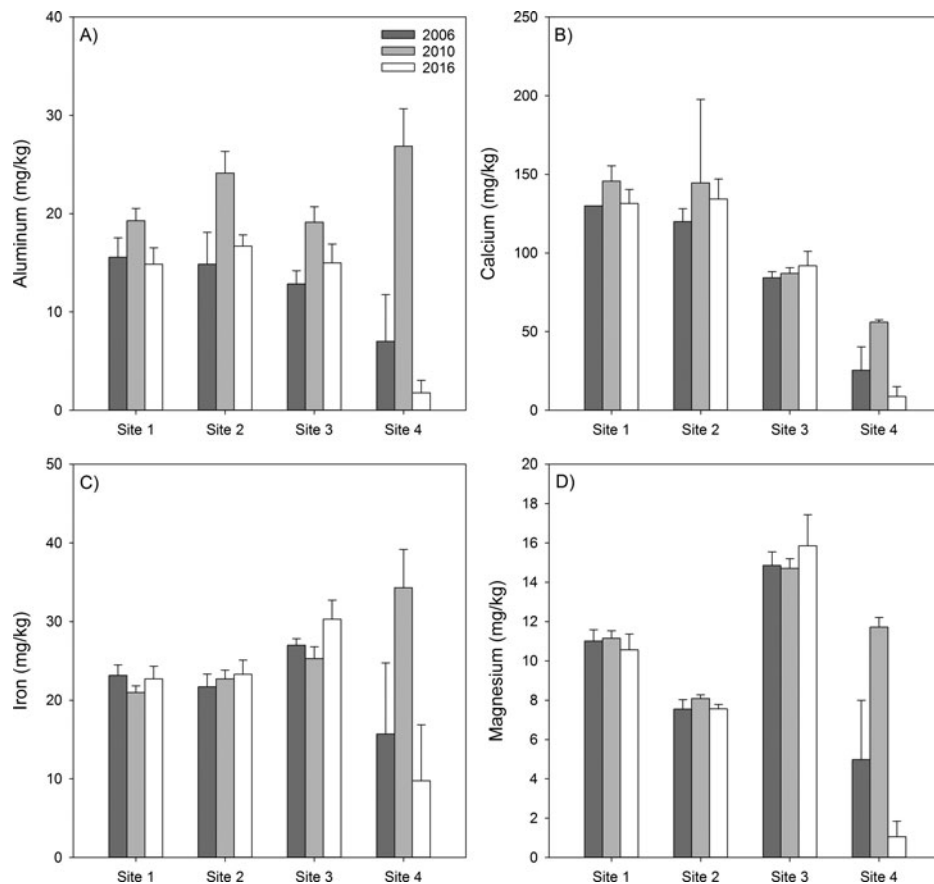


**Figure 6.** SRP concentrations from sediment fractionation shown for oxic (black bars) or hypoxic (gray bars) treatments per site. Different letters within each panel indicate statistically significant differences among sites. Note that the y-axis scale is different for panel A (NH<sub>4</sub>Cl—loosely sorbed).

coincided with very low DO concentrations in the hypolimnion, 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  $\geq 3.9$  mg/L at all near-bottom sites, so it is not surprising that P concentrations were relatively low; however, DO concentrations were  $\leq 0.5$  mg/L at the near-bottom of sites 1 and 2 in 2006, yet TP concentrations were  $< 50$   $\mu\text{g/L}$ , far less than the 250 and 1000  $\mu\text{g/L}$  measured at these sites in 2016. While this suggests that the alum in 2006 was still effective in binding P even under low DO conditions, it is possible that redox potential, which we did not measure, may have continued to decline even after oxygen was depleted; low oxygen alone may not be the best predictor of the rate of P release. Nonetheless, by 2016, the P putatively released during hypoxic conditions was no longer being sequestered by the alum, and instead was accumulating in the hypolimnetic zone. In addition to redox-related release, it is also possible that mineralization of organic matter may account for the accumulated phosphorus, which has been observed in other systems (cf. Watts 2000, Jensen et al. 2015).

The measured P release rates in 2016 were very similar to, if not lower than, those measured in 2010 at sites 1 and 2. We expected high release rates at these sites, given the elevated 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 levels at these sites were  $> 6$  mg/L, even at the near-bottom.

Another anomalous result was the lack of difference in P release rates for oxic vs. hypoxic treatments. Under oxic conditions, phosphate binds to oxidized iron ( $\text{Fe}^{3+}$ ) minerals, preventing P-rich porewater from diffusing into the water column (Mortimer 1941, 1942). However, under hypoxic conditions, the  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$ , and in the process liberates phosphate. Our prior studies in Spring Lake (Steinman et al. 2004, 2006; Steinman and Ogdahl 2008, 2012) have



**Figure 7.** 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.

clearly shown much greater P release rates, especially at sites 1 and 2, under hypoxic vs. oxic conditions, as expected. With the exception of site 4, sediment metal concentrations in 2016 were very similar to prior years, so it is unlikely that metal chemistry accounted for the similar release rates in hypoxic and oxic conditions in 2016. In addition, DO concentrations at the end of the incubations in the overlying water were sufficiently depleted ( $1.38 \pm 0.18$  mg/L) in non-oxygenated waters to promote P release, so the lack of increased internal P loading in the hypoxic treatments was not because of oxic conditions.

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, as surface Chl-*a* concentrations at these sites were  $2.5 \times$  lower than pre-alum and  $\sim$ two-thirds of concentrations measured in 2010, although still relatively high at 7–15  $\mu$ g/L. Prior studies have indicated that P release from internal loading may stimulate phytoplankton production (Nürnberg and Peters 1984, but see Cymbala et al. 2008), although other factors

control phytoplankton biomass besides P concentration, including light availability, zooplankton grazing, and hydraulic residence time (flushing). 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 2006 and 2010 (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. Given that snapshot samples of a dynamic metric such as Chl-*a* can be misleading, as concentrations change quickly, these comparisons should be viewed cautiously.

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, Johnson 1998, Bonada et al. 2006). 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; their relatively

narrow range of mobility, range of sensitivities to contaminants, and 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, densities at sites 3 and 4 were still significantly lower than in 2004, prior to the alum treatment. 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. 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 yr and significant increases above pre-treatment levels were evident after 10 yr.

Macroinvertebrate community composition in 2016 also was very similar to that observed in 2010. 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 (Narf 1990, Doke et al. 1995) and attributed to a change in increased rotifer populations as water quality conditions improved (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. Although ceratopogonid density was significantly lower at site 3 in 2016 compared to 2010, the very low absolute densities in both years likely resulted in minimal ecological impact. Chironomids and ceratopogonids are generally considered pollution-tolerant organisms, although there is variation within species; the low densities of these groups in Spring Lake may be indicative of alum's continued benefits. However, there is considerable variation in pollution tolerance among species (Steinman and Ogdahl 2012), and our level of taxonomic resolution was too coarse to examine changes at that level.

Sediment fractionation revealed very low amounts of the  $\text{NH}_4\text{Cl}$ -extractable SRP fraction (loosely sorbed) in Spring Lake, regardless of site. In 2016, we altered

our fractionation scheme to include 4 fractions. In particular, we were interested in the amount of loosely sorbed (highly bioavailable) P in the sediment, which we had not measured previously, as any future calculations of possible alum reapplication rates should focus on the readily available P in the sediment (loosely sorbed and redox sensitive) instead of simply total P (Pilgrim et al. 2007). Although loosely sorbed P was in very low amounts, the redox sensitive (BD) fraction was more substantial at all sites, providing potential sorption sites for P under oxic conditions but serving as source sites during hypoxia. 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, Welch et al. 2017). This fraction's greater abundance at site 2 suggests possible focusing of alum-bound P at this site compared to the other sites; this location had the greatest water depth and would have the greatest water column stability. While still relatively abundant, the HCl-extractable SRP fraction was lower in 2016 than in prior years. Given the relatively high Ca concentrations in the sediment, one would expect HCl-extractable P fraction to have remained high; previously, we speculated the P that was loosely bound to the alum floc may have become exchanged with soluble Ca, thereby causing the increases we measured in 2006 and 2010 (Steinman and Ogdahl 2008, 2012). There is no evidence of that in 2016, however. It is possible that the change in extraction methodology may have resulted in less efficient extraction of Ca-P 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 vs. 24 hr in previous years. In addition, the NaOH molarity was 0.1 M in 2006 and 2010 vs. 1 M 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.

The external load to Spring Lake, based on data from Lauber (1999), was estimated to vary between 2.2 (dry years) and 4.7 (wet years) Mg/yr (metric ton/yr), accounting for 35–45% of the (pre-alum) total load in Spring Lake (Steinman et al. 2004). Internal P loading, based on sediment P release incubations in the laboratory, has declined about 10-fold between 2003 and 2016 (Table 2). In addition, land use change analyses revealed that between 1978 and 2006 the amount of residential land and mean impervious surface area in the watershed have each approximately doubled, with

most of that change immediately adjacent to the lake, contributing to greater surface runoff (Steinman et al. 2015). Hence, the role of external loading relative to internal loading to Spring Lake has almost certainly increased in magnitude since the alum treatment, suggesting nutrient management needs to focus on both external and internal loading.

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, at least in the deeper portions of the lake; 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. The data are suggestive that the alum treatment is losing its efficacy; if so, possible reasons include (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 that is being made available from internal or external sources.

We acknowledge that our results also are conflated by sampling during different periods in each of the 4 yr; for example, the high hypolimnetic P concentrations in the deeper sites in 2016 may have been due to our later sampling date that year (mid-Sep), allowing P to accumulate. However, our 2010 measurements, taken just a week earlier than in 2016, revealed far more modest P concentrations. Of course, different weather and stratification patterns among years also may account for these differences. Regardless of mechanism, the overall TP and Chl-*a* concentrations in the water column of Spring Lake remain high, and suggest the continued need for water quality improvements in Spring Lake. Recommendations for the type and placement of Best Management Practices (BMPs) in the watershed have been previously identified. Modeling results indicated that if infiltration BMPs, filtration BMPs, regional storage areas, and site-specific BMPs held on publicly held lands were fully implemented, TP and TSS loads would be reduced by 15% and 17%, respectively (Steinman et al. 2015).

Our current results illustrate what has been cautioned in previous studies (Steinman et al. 2006, 2015; Steinman and Ogdahl 2008, 2012): alum application is a short-term solution to the longer-term problem

of internal P loading and its long-term effectiveness is critically tied to concurrent reductions in external P loading (but see Brattebo et al. 2017).

## Acknowledgments

Brian Scull, Kurt Thompson, Emily Kindervater, and Kim Oldenborg provided field and laboratory support. Funding was provided by the Spring Lake – Lake Board. We are grateful to Tony Groves and Pam Tynning for their collaborative spirit, and especially to Ken Wagner, Gertrud Nürnberg, and an anonymous reviewer whose comments greatly improved the manuscript.

## References

- Bakker ES, Van Donk E, Immers AK. 2015. Lake restoration by in-lake iron addition: a synopsis of iron impact on aquatic organisms and shallow lake ecosystems. *Aquat Ecol.* 50:121–135.
- Berkowitz J, Anderson MA, Amrhein C. 2006. Influence of aging on phosphorus sorption to alum floc in lake water. *Water Res.* 40:911–916.
- Björk S. 1985. Lake restoration techniques. In: *Lake pollution and recovery*. Rome, Italy: Internat Congress European Water Poll Cont Assn. p. 293–301.
- Bonada N, Prat N, Resh VH, Statzner B. 2006. Developments in aquatic insect biomonitoring: a comparative analysis of recent approaches. *Annu Rev Entomol.* 51:495–523.
- Boström B, Janson M, Forsberg C. 1982. Phosphorus release from lake sediments. *Arch Hydrobiol Beih Ergeb Limnol.* 18:5–59.
- Brattebo SK, Welch EB, Gibbons HL, Burghdoff MK, Williams GN, Oden JL. 2017. Effectiveness of alum in a hypereutrophic lake with substantial external loading. *Lake Reserv Manage.* 33:108–118.
- Carpenter SR. 2005. Eutrophication of aquatic ecosystems: bistability and soil phosphorus. *Proc Natl Acad Sci.* 102:10002–10005.
- Codd GA, Bell SG, Kaya K, Ward CJ, Beattie KA, Metcalf JS. 1999. Cyanobacterial toxins, exposure routes and human health. *Eur J Phycol.* 34:405–415.
- Cook DG, Johnson MG. 1974. Benthic macroinvertebrates of the St. Lawrence Great Lakes. *J Fish Res Bd Can.* 31:763–782.
- Cooke GD, Welch EB, Peterson SA, Nichols SA. 2005. *Restoration and management of lakes and reservoirs*. 3rd ed. Boca Raton (FL): Taylor & Francis.
- Cymbala J, Ogdahl M, Steinman AD. 2008. Phytoplankton response to light and internal phosphorus loading from sediment release. *Freshwat Biol.* 53:2530–2542.
- Cyr H, McCabe SK, Nürnberg GK. 2009. Phosphorus sorption experiments and the potential for internal phosphorus loading in littoral areas of a stratified lake. *Water Res.* 43:1654–1666.
- de Vicente I, Huang P, Anderson FØ, Jensen HS. 2008. Phosphate adsorption by fresh and aged aluminum hydroxide.

- Consequences for lake restoration. *Environ Sci Technol.* 42:6650–6655.
- Dixit SS, Smol JP, Charles DF. 1992. Diatoms: powerful indicators of environmental change. *Environ Sci Technol.* 6:22–33.
- Doke JL, Funk WH, Juul STJ, Moore BC. 1995. Habitat availability and benthic invertebrate population changes following alum and hypolimnetic oxygenation in Newman Lake, Washington. *J Freshwat Ecol.* 10:87–102.
- Egemose S, Reitzel K, Andersen FØ, Flindt MR. 2010. Chemical lake restoration products: sediment stability and phosphorus dynamics. *Environ Sci Technol.* 44:985–991.
- Epe TS, Finsterle K, Yasseri S. 2017. Nine sources of phosphorus management with lanthanum modified bentonite (Phoslock) in a eutrophic, shallow swimming lake in Germany. *Lake Reserv Manage.* 33:119–129.
- Fisher MM, Brenner M, Reddy KR. 1992. A simple, inexpensive piston corer for collecting undisturbed sediment/water interface profiles. *J Paleolimnol.* 7:157–161.
- Graneli W. 1999. Internal phosphorus loading in Lake Ringsjön. *Hydrobiologia* 404:19–26.
- Hansson L-A, Annadotter H, Bergman E, Hamrin SF, Jeppesen E, Kairesalo T, Luokkanen E, Nilsson P-Å, Søndergaard M, Strand J. 1998. Biomanipulation as an application of food chain theory: constraints, synthesis and recommendations for temperate lakes. *Ecosystems.* 1:558–574.
- Hilsenhoff WL. 1987. An improved biotic index of organic stream pollution. *Great Lakes Entomol.* 20:31–39.
- Hupfer M, Zak D, Roßberg R, Herzog C, Pöthig R. 2009. Evaluation of a well-established sequential phosphorus fractionation technique for use in calcite-rich lake sediments: identification and prevention of artifacts due to apatite formation. *Limnol Oceanogr: Methods.* 7:399–410.
- Huser BJ. 2017. Aluminum application to restore water quality in eutrophic lakes: maximizing binding efficiency between aluminum and phosphorus. *Lake Reserv Manage.* 33:143–151.
- Huser BJ, Egemose S, Harper H, Hupfer M, Jensen H, Pilgrim KM, Reitzel K, Rydin E, Futter M. 2016. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Res.* 97:122–132.
- Jensen HS, Reitzel K, Egemose S. 2015. Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia.* 751:189–199.
- Jeppesen E, Søndergaard M, Jensen JP, Havens KE, Anneville O, Carvalho L, Coveney MF, Deneke R, Dokulil MT, Foy BOB, et al. 2005. Lake responses to reduced nutrient loading – an analysis of contemporary long-term data from 35 case studies. *Freshwat Biol.* 50:1747–1771.
- Johnson RK. 1998. Spatio-temporal variability of temperate lake macroinvertebrate communities: detection of impact. *Ecol Appl.* 8:61–70.
- Karr JR. 1993. Defining and assessing ecological integrity: beyond water quality. *Environ Toxicol Chem.* 12:1521–1531.
- Kennedy RH, Cooke DG. 1982. Control of lake phosphorus with aluminum sulfate. Dose determination and application techniques. *Water Res Bull.* 18:389–395.
- Lauber TEL. 1999. Can the Big Bayou be saved? Water quality assessment and management recommendations for Spring Lake Watershed, Ottawa and Muskegon Counties, Michigan. MS thesis. Michigan State University: East Lansing (MI).
- Lewandowski J, Schauser I, Hupfer M. 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süsser (Germany). *Water Res.* 37:3194–3204.
- Matisoff G, Kaltenberg EM, Steely RL, Hummel SK, Seo J, Gibbons KJ, Bridgeman TB, Seo Y, Behbahani M, James WF, et al. 2016. Internal loading of phosphorus in western Lake Erie. *J Great Lakes Res.* 42:771–788.
- Matisoff G, Wang X. 1998. Solute transport in sediments by freshwater infaunal bioirrigators. *Limnol Oceanogr.* 43:1487–1499.
- Matisoff G, Watson S, Guo J, Duewiger A, Steely R. 2017. Sediment and nutrient distribution and resuspension in Lake Winnipeg. *Sci Total Environ.* 575:173–186.
- Mehner T, Diekmann M, Gonsiorczyk T, Kasprzak P, Koschel R, Krienitz L, Rumpf M, Schulz M, Wauer G. 2008. Rapid recovery from eutrophication of a stratified lake by disruption of internal nutrient load. *Ecosystems.* 11:1142–1156.
- Moore PA, Reddy KR, Fisher MM. 1998. Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variations. *J Environ Qual.* 27:1428–1439.
- Mortimer CH. 1941. The exchange of dissolved substances between mud and water in lakes I. *J Ecol.* 29:280–329.
- Mortimer CH. 1942. The exchange of dissolved substances between mud and water in lakes II. *J Ecol.* 30:147–201.
- Motew M, Chen X, Booth EG, Carpenter SR, Pinkas P, Zipper SC, Loheide SP, Donner SD, Tsuruta K, Vadas PA, et al. 2017. The influence of legacy P on lake water quality in a midwestern agricultural watershed. *Ecosystems.* doi:10.1007/s10021-017-0125-0.
- Nalepa TF, Lang GA, Fanslow DL. 2000. Trends in benthic macroinvertebrate populations in southern Lake Michigan. *Verh Internat Verein Limnol.* 27:2540–2545.
- Narf RP. 1990. Interactions of Chironomidae and Chaoboridae (Diptera) with aluminum sulfate treated lake sediments. *Lake Reserv Manage.* 6:33–42.
- Nixdorf B, Deneke R. 1995. Why ‘very shallow’ lakes are more successful opposing reduced nutrient loads. *Hydrobiologia.* 342/343:269–284.
- Nogaro G, Harris A, Steinman AD. 2016. Alum application, invertebrate bioturbation and sediment characteristics interact to affect nutrient exchanges in eutrophic ecosystems. *Freshwat Sci.* 35:597–610.
- Nürnberg GK, LaZerte BD. 2004. Modeling the effect of development on internal phosphorus load in nutrient-poor lakes. *Water Resour Res.* 40:W01105. doi:10.1029/2003WR002410.

- Nürnberg GK, LaZerte BD. 2016. More than 20 sources of estimated internal phosphorus loading in polymictic, eutrophic Lake Winnipeg, Manitoba. *J Great Lakes Res.* 42:18–27.
- Nürnberg G, Peters RH. 1984. Biological availability of soluble reactive phosphorus in anoxic and oxic freshwaters. *Can J Fish Aquat Sci.* 41:757–765.
- Pilgrim KM, Huser BJ, Brezonik PL. 2007. A method for comparative evaluation of whole-lake and inflow alum treatment. *Water Res.* 41:1215–1224.
- Psenner R, Dinka M, Petterson K, Pucsko R, Sager M. 1988. Fractionation of phosphorus in suspended matter and sediment. *Arch Hydrobiol Beih Ergebn Limnol.* 30: 98–103.
- Purcell AH, Bressler DW, Paul MJ, Barbour MT, Rankin ET, Carter JL, Resh VH. 2009. Assessment tools for urban catchments: developing biological indicators based on benthic macroinvertebrates. *J Am Water Resour Assoc.* 45:306–319.
- Qin L, Zeng Q, Zhang W, Li X, Steinman AD, Du X. 2016. Estimating internal P loading in a deep water reservoir of northern China using three different methods. *Environ Sci Poll Res.* 23:18512–18523.
- Reddy KR, Kadlec RH, Flaig E, Gale PM. 1999. Phosphorus retention in streams and wetlands: a review. *Crit Rev Environ Sci Tech.* 29:83–146.
- Reitzel K, Hansen J, Andersen FØ, Hansen KS, Hansen HS. 2005. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environ Sci Tech.* 39:4134–4140.
- Robb M, Greenop B, Goss Z, Douglas G, Adeney J. 2003. Application of Phoslock<sup>TM</sup>, an innovative phosphorus binding clay, to two Western Australian waterways: preliminary findings. *Hydrobiologia.* 494:237–243.
- Rydin E, Welch EB. 1998. Aluminum dose required to inactivate phosphate in lake sediments. *Water Res.* 32:2969–2976.
- Rydin E, Welch EB. 1999. Dosing alum to Wisconsin Lake sediments based on possible formation of aluminum bound phosphate. *Lake Reserv Manage.* 15:324–331.
- Sas H. 1990. Lake restoration by reduction of nutrient loading – expectations, experiences, extrapolations. *Inter Assoc Theor Appl Limnol Proc.* 24:247–251.
- Selig U. 2003. Particle size-related phosphate binding and P-release at the sediment-water interface in a shallow German lake. *Hydrobiologia.* 492:107–118.
- Sharpley A, Jarvie HP, Buda A, May L, Spears B, Kleinman P. 2013. Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. *J Environ Qual.* 42:1308–1326.
- Smeltzer E, Kirn RA, Fiske S. 1999. Long-term water quality and biological effects of alum treatment of Lake Morey, Vermont. *Lake Reserv Manage.* 15:173–184.
- Søndergaard M, Bjerring R, Jeppesen E. 2012. Persistent internal loading during summer in shallow lakes. *Hydrobiologia.* 710:95–107.
- Søndergaard M, Jensen JP, Jeppesen E. 1999. Internal phosphorus loading in shallow Danish lakes. *Hydrobiologia.* 408/409:145–152.
- Søndergaard M, Jensen JP, Jeppesen E. 2001. Retention and internal loading of phosphorus in shallow, eutrophic lakes. *The Scientific World J.* 1:427–442.
- Spears BM, Carvalho L, Perkins R, Kirika A, Paterson DM. 2012. Long-term variation and regulation of internal phosphorus loading in Loch Leven. *Hydrobiologia.* 681:23–33.
- Spears BM, Lürling M, Yasseri S, Castro-Castellon AT, Gibbs M, Meis S, McDonald C, McIntosh J, Sleep D, Van Oosterhout F. 2013. Lake responses following lanthanum-modified bentonite clay (Phoslock<sup>®</sup>) application: an analysis of water column lanthanum data from 16 case study lakes. *Water Res.* 47:5930–5942.
- Spears BM, Mackay EB, Yasseri S, Gunn IDM, Waters KE, Andrews C, Cole S, De Ville M, Kelly A, Meis S, et al. 2016. A meta-analysis of water quality and aquatic macrophyte responses in 18 lakes treated with lanthanum-modified bentonite clay (Phoslock<sup>®</sup>). *Water Res.* 97:111–121.
- Steinman AD, Isely ES, Thompson K. 2015. Stormwater runoff to an impaired lake: impacts and solutions. *Environ Monitor Assess.* 187:1–14.
- Steinman AD, Lamberti GA, Leavitt P, Uzarski DG. 2017. Biomass and pigments of benthic algae. In: Hauer R, Lamberti G, editors. *Methods in Stream Ecology* (3rd ed.). Volume 1: Ecosystem structure. Cambridge (MA): Elsevier, Academic Press. p. 223–241.
- Steinman AD, Nemeth L, Nemeth E, Rediske R. 2006. Factors influencing internal P loading in a western Michigan, drowned river-mouth lake. *J No Am Benthol Soc.* 25:304–312.
- Steinman AD, Ogdahl ME. 2008. Ecological effects after an alum treatment in Spring Lake, Michigan. *J Environ Qual.* 37:22–29.
- Steinman AD, Ogdahl ME. 2012. Macroinvertebrate response and internal phosphorus loading in a Michigan lake after alum treatment. *J Environ Qual.* 41:1540–1548.
- Steinman AD, Ogdahl ME, Weinert M, Uzarski DG. 2014. Influence of water-level fluctuation duration and magnitude on sediment-water nutrient exchange in coastal wetlands. *Aquat Ecol.* 48:143–159.
- Steinman AD, Rediske R, Reddy KR. 2004. The reduction of internal phosphorus loading using alum in Spring Lake, Michigan. *J Environ Qual.* 33:2040–2048.
- Stumm W, Morgan JJ. 1996. *Aquatic chemistry* (3rd ed.). New York (NY): John Wiley & Sons.
- [USEPA] US Environmental Protection Agency. 1993. Method for the determination of inorganic substances in environmental samples (EPA/600/R-93/100).
- [USEPA] US Environmental Protection Agency. 1996. Test methods for evaluating solid waste, physical/chemical methods, SW-846, 3rd ed., Final Update III, Revision 2, December 1996, Method 6010B. USEPA National Service Center for Environmental Publications. Available from [www.epa.gov/nscep/](http://www.epa.gov/nscep/).
- Van Rees KCJ, Reddy KR, Rao PSC. 1996. Influence of benthic organisms on solute transport in lake sediments. *Hydrobiologia.* 317:31–40.

- Wagner KJ. 2017. Preface: advances in phosphorus inactivation. *Lake Reserv Manage.* 33:103–107.
- Wagner KJ, Meringolo D, Mitchell DF, Moran E, Smith S. 2017. Aluminum treatments to control internal phosphorus loading in lakes on Cape Cod, Massachusetts. *Lake Reserv Manage.* 33:171–186.
- Wang SR, Jin XC, Zhao HC, Wu FC. 2009. Phosphorus release characteristics of different trophic lake sediments under simulative disturbing conditions. *J Hazard Mater.* 161:1551–1559.
- Watts CJ. 2000. Seasonal phosphorus release from exposed, re-inundated littoral sediments of two Australian reservoirs. *Hydrobiologia.* 431:27–39.
- Welch EB, Cooke GD. 1995. Internal phosphorus loading in shallow lakes: importance and control. *Lake Reserv Manage.* 11:273–281.
- Welch EB, Cooke GD. 1999. Effectiveness and longevity of phosphorus inactivation with alum. *Lake Reserv Manage.* 15:5–27.
- Welch EB, Gibbons HL, Brattebo SK, Corson-Rikert HA. 2017. Progressive conversion of sediment mobile phosphorus to aluminum phosphorus. *Lake Reserv Manage.* 33:205–210.
- Welch EB, Schriever GD. 1994. Alum treatment effectiveness and longevity in shallow lakes. *Hydrobiologia.* 275/276:423–431.
- Wiederholm T. 1984. Responses of aquatic insects to environmental pollution. In: Resh VH, Rosenberg DM, editors. *The ecology of aquatic insects.* New York (NY): Praeger Publishers. p. 508–557.
- Zhao Y, Xue Q, Su X, Xie L, Yan Y, Wang L, Steinman AD. 2016. First identification of the toxicity of microcystins on pancreatic islet function in humans and the involved potential biomarkers. *Environ Sci Technol.* 50:3137–3144.