

The Reduction of Internal Phosphorus Loading Using Alum in Spring Lake, Michigan

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ABSTRACT

The release of P from lake sediments, which occurs as a part of internal loading, may contribute a significant portion of the total P load to a lake. Phosphorus release rates from sediments in Spring Lake, Michigan, and the degree to which alum reduces P release from these sediments, were investigated during the summer of 2003. Triplicate sediment cores were sampled from four sites in the lake, and exposed to one of four treatments in the laboratory: (i) aerobic water column/alum, (ii) aerobic water column/no alum, (iii) anaerobic water column/alum, or (iv) anaerobic water column/no alum. Total P (TP) release rates were virtually undetectable in the alum treatments (both aerobic and anaerobic). Low, but detectable, release rates were measured in the aerobic/no alum treatment. The highest release rates were measured in the anaerobic/no alum treatments, and ranged from 1.6 to 29.5 mg P m⁻² d⁻¹ depending on how the calculations were derived. These fluxes translated to mean internal loads that ranged between 2.7 (low range) and 6.4 (high range) Mg yr⁻¹ when extrapolated to a whole-lake basis. Internal P loads accounted for between 55 and 65% of the total P load to Spring Lake. Although alum is a potentially effective means of reducing the sediment source of P, there is considerable uncertainty in how long an alum treatment would remain effective in this system given the current rates of external loading and the lack of information on wind-wave action and bioturbation in Spring Lake.

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: (i) release at the sediment-water interface during periods of anoxia or hypoxia, and the subsequent diffusion of dissolved phosphate into the water column; and (ii) 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).

Mineral associations play an important role in the release of P during anoxic or anaerobic conditions. Phosphorus associated with iron minerals can become soluble in the absence of oxygen while the P fraction associated with calcium-based minerals may remain stable (Mortimer, 1971). Phosphorus release rates have been found to be closely correlated to the iron-bound fraction in sediment (Petticrew and Arocena, 2001).

Historically, field measurements of P concentration in lakes have concentrated on the "external" loading of

P. This is the contribution of P from point and nonpoint sources flowing into a waterbody. The contribution of P being released from the sediments, or the internal load, while acknowledged to be of potential importance, is measured less often. However, 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, the most common practices include chemical treatment, oxidation, and dredging (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.

Previous studies showed that the effectiveness of alum application depends on a number of factors. For example, Welch and Cooke (1999) reported that alum application reduced internal loading in seven of seven dimictic lakes by an average of 80% during a period of 4 to 21 yr (avg. length of effectiveness: 13 yr). However, they also found that internal loading was reduced in only six of nine polymictic lakes, with reductions averaging 67% and remaining effective for an average of 10 yr. They speculated that differences in macrophyte density (which can physically interfere with floc distribution), rates of plant senescence, and/or resuspension of sediments by bioturbation may have been responsible for the different results both among and within lake types.

Studies on hypereutrophic lakes in Florida indicated that internal loading could contribute a significant amount of bioavailable P in these lakes (Moore et al., 1998; Steinman et al., 1999). The source of P in these cases was the top layer of sediment. If P is not tightly bound to sediment, it becomes available to the water column on resuspension of the surface sediments or simply by gradient flux under the appropriate conditions of temperature, pH, dissolved oxygen, and ambient surface water P concentration. If there is a similar significant internal loading source of P in Spring Lake, reductions in external P loads alone likely will be insufficient to reduce P levels in the lake water, at least for the foresee-

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Abbreviations: DO, dissolved oxygen; SRP, soluble reactive phosphorus; TP, total phosphorus.

able future. Although there is general consensus that internal load will eventually decline following external load reduction, the time required may be long and rates may actually increase temporarily (Ahlgren, 1988; Sas, 1989; Chapra and Canale, 1991; Søndergaard et al., 1993; Welch and Cooke, 1995).

Spring Lake faces some of the most critical water quality challenges in west Michigan. The TP concentrations in Spring Lake are usually far in excess of water quality standards. For example, the USEPA has set a surface TP water quality goal of 0.015 mg L^{-1} for the west Michigan ecoregion (USEPA, 2000). However, during ice-free periods from 1999 through 2002, surface TP concentrations in Spring Lake averaged 0.100 mg L^{-1} (range: $0.006\text{--}0.631 \text{ mg L}^{-1}$).

The goals of this project were to measure whether internal loading of P from the sediment to surface water is a significant source of P to Spring Lake, and if alum application to the sediment surface was effective at controlling P release.

MATERIALS AND METHODS

Site Description

Spring Lake is located in west-central Michigan and drains to the Grand River, approximately 1 km east of Lake Michigan (Fig. 1). This drowned river mouth lake has a surface area of 5.25 km^2 , with mean and maximum depths of 6 and 13 m, respectively. Water residence time in the lake is approximately 5 mo in the winter and 11 mo in the summer. The lake pH is generally circumneutral (Lauber, 1999), and chlorophyll *a* concentrations during the ice-free period of 1999 to 2002 averaged $9 \mu\text{g L}^{-1}$ (range: $0\text{--}121 \mu\text{g L}^{-1}$) (2003, unpublished data). The Spring Lake watershed covers 134 km^2 , with forest/undeveloped (57%), urban (19%), agriculture (18%), and wetland (6%) the major land use/land cover categories. The lake's shoreline is densely populated with primary residences.

Field Sampling

Surface water samples and sediment cores were collected from four sites in Spring Lake (Fig. 1); sites were selected to cover different geographic regions in the lake, and also to be as close as possible to previous sampling locations (wherever practical) to take advantage of historical information. Sites 1 and 2 were sampled on 10 and 11 June 2003 and Sites 3 and 4 were sampled on 16 July 2003. At each site, vertical profiles of dissolved oxygen, pH, temperature, specific conductance, chlorophyll *a*, and total dissolved solids were measured using a Hydrolab DataSonde 4a and *in vivo* fluorometer (Hydrolab, Loveland, CO). A secchi disk was used to measure water transparency and a Li-Cor quantum sensor and data logger (LI-COR Environmental, Lincoln, NE) were used to measure incident and underwater irradiance. Water samples for nutrient analysis were collected with a van Dorn bottle at depths 1.0 m below the water surface and 1.0 m above the sediment surface, and maintained at 4°C until delivery to the laboratory.

Sediment cores were collected using a piston corer (Fisher et al., 1992). Twelve cores were collected from each site (24 per sampling date). The coring device was constructed with a graduated 0.6 m long polycarbonate core tube (7 cm i.d.), aluminum drive rods, and a PVC attachment assembly for coupling. The piston was advanced 20 cm before deployment to maintain a water layer on top of the core during collection. The corer was vertically positioned at the sediment–water

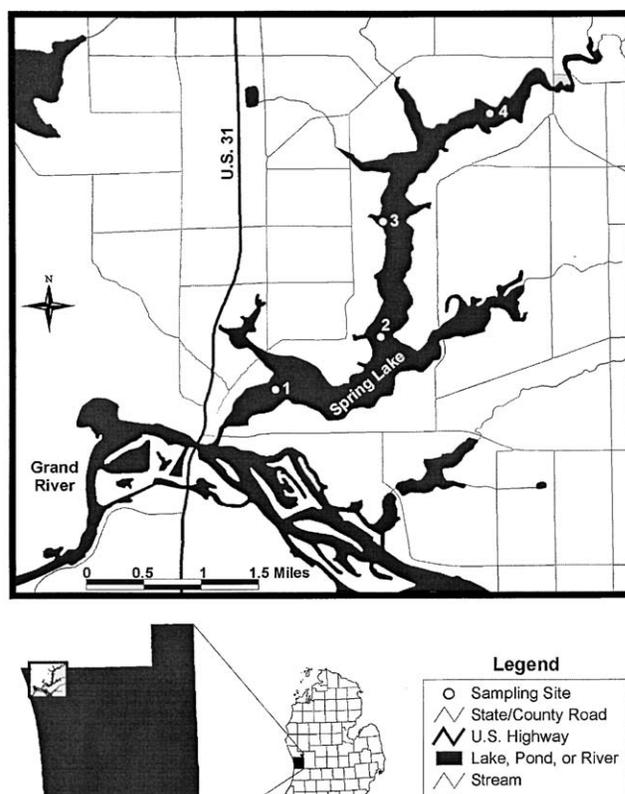


Fig. 1. Site map of Spring Lake. Bottom panel: County outline of Michigan's lower peninsula, with blow-up of Ottawa County and location of Spring Lake (in box). Top panel: Blow-up of box from lower panel, showing Spring Lake and location of four sampling sites.

interface and pushed downward with the piston cable remaining stationary. After collection, the core was brought to the surface and sealed with a rubber stopper before removal from the water, resulting in intact sediment cores that were approximately 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 transported to the laboratory in a water bath to keep temperatures near ambient.

Laboratory Set-Up and Analysis

The 24 sediment cores (12 per site) collected on each sampling trip were placed into a darkened Revco environmental growth chamber (Revco Scientific, Asheville, NC), with the temperature maintained to match ambient conditions in the field (see Table 1). The water column of the sediment cores from each site was exposed to one of four treatments (three replicates per treatment per site): (i) aerobic with alum, (ii) aerobic without alum, (iii) anaerobic with alum, and (iv) anaerobic without alum. Nitrogen (with $330 \text{ mg L}^{-1} \text{ CO}_2$) or air was bubbled into the water column of each tube to create aerobic or anaerobic conditions, respectively. Aluminum sulfate solution [$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$] was added to half of the aerobic and half of the anaerobic water column treatments at a concentration of approximately 25 mg Al L^{-1} ($\sim 6.6 \text{ g Al m}^{-2}$). At this concentration, a 1-cm deep floc formed at the water–sediment surface. The dosing concentration was based on the recommendations outlined in Cooke et al. (1993). Alum appli-

Table 1. Select limnological characteristics from surface and bottom depths at the four sampling sites in Spring Lake, MI. K_d = light attenuation coefficient. Data from Sites 1 and 2 were collected on 10 and 11 June 2003, respectively. Data from Sites 3 and 4 were collected on 16 July 2003.†

Parameter	Site 1		Site 2		Site 3		Site 4	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Temp., °C	17.8	16.6	17.8	15.3	24.4	22.7	24.8	23.6
DO, mg L ⁻¹	11.3	6.0	9.3	0.6	6.1	1.5	5.4	4.2
Chl <i>a</i> , µg L ⁻¹	23.9	6.2	21.7	3.3	5.3	3.8	3.6	4.9
Specific conductance, µS cm ⁻¹	602	590	566	581	565	601	552	596
SRP, mg L ⁻¹	<0.01	<0.01	<0.01	0.04	0.03	0.04	0.04	0.03
TP, mg L ⁻¹	0.06	0.04	0.11	0.08	0.10	0.08	0.12	0.08
TDS, g L ⁻¹	0.386	0.378	0.362	0.372	0.362	0.384	0.353	0.381
pH	8.6	8.2	8.6	7.9	8.5	8.0	8.4	8.3
K_d		1.439		1.525		1.721		2.247
Secchi depth, m		1.25		1.0		1.0		0.75
Depth, m		8.2		10.1		6.7		4.9

† DO, dissolved oxygen; SRP, soluble reactive phosphorus; TDS, total dissolved solids; TP, total phosphorus.

cation was considered time zero. Alum was obtained from General Chemical Corporation (River Rouge, MI).

Internal load estimates were made using the methodology outlined in Moore et al. (1998), with minor modifications. Briefly, a 30-mL water sample was removed by syringe through the sampling port of each tube core at 2, 4, 8, and 16 h, and 1, 2, 4, 8, 12, 16, 20, and 28 d (Day 28 only for Sites 3 and 4) after time zero, and replaced with an equal volume of filtered lake water. A 20-mL subsample was immediately refrigerated for analysis of TP. The soluble reactive phosphorus (SRP) was measured as part of this study but these data are not reported because release rates showed indications of potential interferences in SRP measurement (cf. Nürnberg, 1984).

Flux calculations were based on the increase in water column concentrations of TP. Calculations were based on three different time periods to reflect: (i) the maximum release rates (linear portion of the curve), (ii) moderate release rates, and (iii) minimum release rates. These different rates allowed us to capture the full range of potential internal loading rates, and gain a better understanding of the possible uncertainties in estimating internal loading in Spring Lake. Phosphorus flux was calculated using the following equation:

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

where, P_{flux} is the net P flux or retention per unit surface area of sediments (mg P m⁻² d⁻¹), C_t is the P concentration in the water column at time t , C_0 is the P concentration in the water column at time 0, V is the volume of water in the water column, and A is the area of the sediment surface.

Internal load at a specific site was calculated by scaling up the mean P flux from the ambient (i.e., anaerobic/no alum) treatment condition as calculated in Eq. [1] to the entire lake area and multiplying by the percentage of time during the year that the lake was estimated to have DO concentrations <1 mg L⁻¹ (see below).

Following the incubations, cores were centrifuged to remove excess porewater and the top 10 cm of each core was sequentially fractionated (Moore and Reddy, 1994) to determine the fraction of P bound to Fe/Al and Ca/Mg in the sediments. Residual sediment was shaken for 17 h with 0.1 M NaOH and centrifuged, and the porewater was then filtered and analyzed for SRP. This fraction represents the Al- and Fe-bound P. After this extraction, the residual sediment was extracted for 24 h with 0.5 M HCl and centrifuged, and the porewater was filtered and analyzed for SRP. This fraction represents the Ca- and Mg-bound P.

Phosphorus analyses were performed on a BRAN+LUEBBE Autoanalyzer (Bran+Luebbe, Delavan, WI) by the automated ascorbic acid method (USEPA, 1983). Sediment extracts were neutralized before analysis.

Statistical Analysis

Phosphorus release rates were calculated for individual cores and treatments compared ($n = 3$) within each site using analysis of variance. Tukey's post-hoc multiple comparison test was used to determine if mean release rates from individual treatments were significantly different from one another. Phosphorus concentrations of the chemically fractionated sediment cores also were analyzed by analysis of variance to detect statistically significant differences among sites and treatment conditions. All statistical analyses were conducted using SAS (version 8).

RESULTS

Field Results

Sites 1 and 2 were deeper, and had greater surface dissolved oxygen (DO) and chlorophyll *a* concentrations than Sites 3 and 4 (Fig. 2, Table 1). Temperatures were relatively constant throughout the water columns at all sites (Fig. 2). Concentrations of DO declined with depth at all sites but only Site 2 had concentrations <1 mg L⁻¹ during the sampling dates (Fig. 2). Chlorophyll *a* concentrations exhibited subsurface maxima approaching 30 µg L⁻¹ at Sites 1 and 2 (Fig. 2), but were <10 µg L⁻¹ at the shallower Sites 3 and 4 (Fig. 2, Table 1). Despite the greater chlorophyll concentrations at Sites 1 and 2, these sites had greater water transparency than Sites 3 and 4 based on light extinction coefficients and Secchi depths (Table 1).

The SRP concentrations were lower at Sites 1 and 2 than at Sites 3 and 4, ranging from below detection to 0.04 mg L⁻¹ (Table 1). The TP concentrations were greater at the surface than bottom depths at all sites (total range 0.04–0.12 mg L⁻¹), and were approximately 50% lower at Site 1 compared with the other sites (Table 1).

To determine the frequency of anoxia in Spring Lake, historic dissolved oxygen data in Spring Lake, collected as part of Grand Valley State University's vessel education program, were analyzed. Cruises onboard the *D.J. Angus* from 1998 through 2002 resulted in a total of 864 sampling events. These data revealed that DO was <2 mg L⁻¹ between 10 and 31% of the time and <1 mg L⁻¹ between 4 and 25% of the time (Table 2). These data provide a general idea of anoxic frequency in Spring Lake,

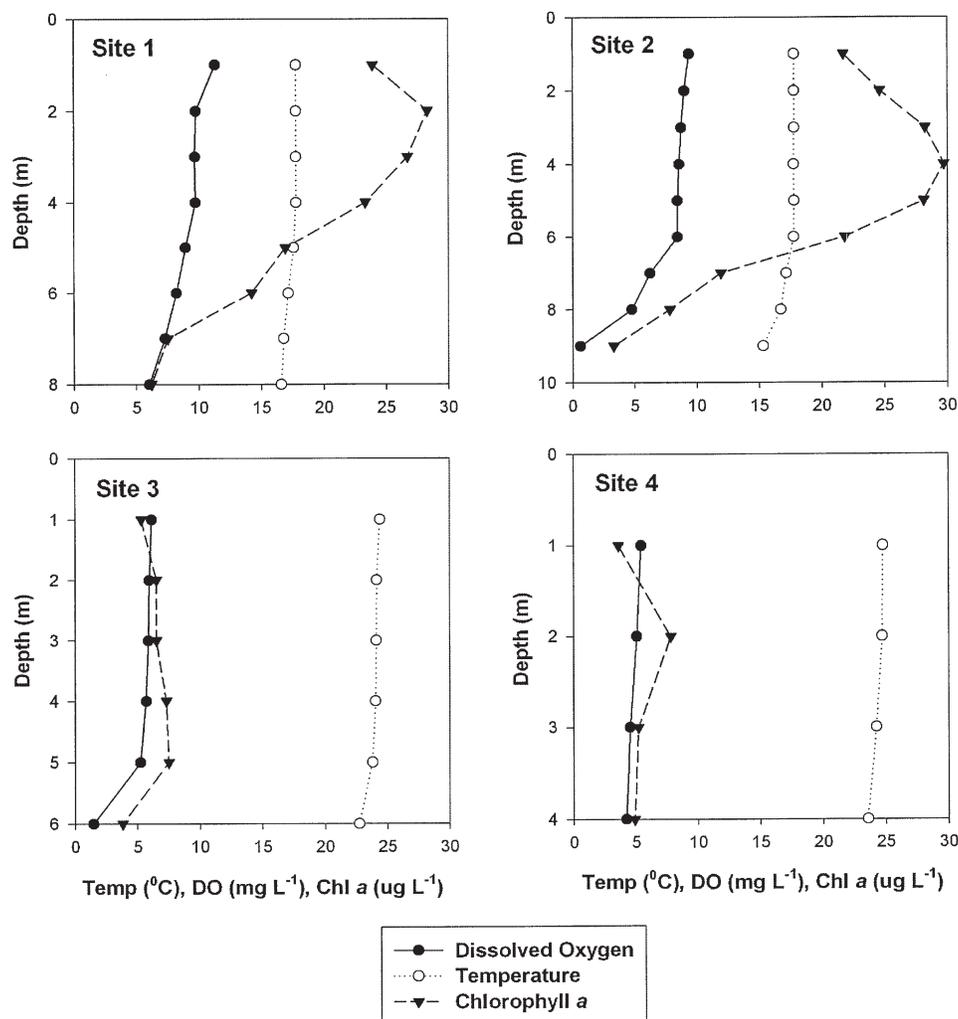


Fig. 2. Selected limnological characteristics (temperature, dissolved oxygen, and chlorophyll *a*) at Sites 1 to 4. Note different scales for the depth axis.

but they must be treated with caution. First, they were collected from only one, relatively deep station. As a consequence, they likely overestimate the percent of time low-DO concentrations exist in the lake, especially at shallower stations. Second, they are snapshots, taken only during daytime cruises. If Spring Lake exhibits diurnal cycles in anoxia, with low-DO conditions more likely at night, these data will not capture this phenomenon and therefore underestimate anoxic conditions. Finally, data were collected only from late April through early October. We assume aerobic conditions during the remainder of the year due to greater mixing of the water column and reduced metabolism in the benthos because of colder temperatures, but it is also likely that anoxia develops during periods of ice cover. If anoxic or hypoxic conditions do develop during these months, the amount of low-DO conditions in Spring Lake would be underestimated.

Laboratory Results

Total Phosphorus Release Rates

Visual inspection of the data revealed that at all sites, TP release rates were greatest in the anaerobic/no alum

treatment, followed by the aerobic/no alum treatment and then both alum treatments (aerobic and anaerobic; Fig. 3). Low, moderate, and high release rates were calculated in the different treatments from each site based on the selected start and end times. For example, in the anaerobic/no alum treatment for Site 1 (Fig. 3), the selection of Days 4 (start) to 12 (end) resulted in the calculation of the maximum TP release rate (linear phase), whereas selection of Days 1 to 12 or Days 0 to

Table 2. Percentage of time that dissolved oxygen (DO) concentrations were $<2 \text{ mg L}^{-1}$ or $<1 \text{ mg L}^{-1}$ in Spring Lake (deep hole). Data were collected from the *D.J. Angus*; period of record was 1998–2002. The DO concentrations in the nonsampled months (October–March) were assumed to be oxic.

Year	Percentage of time	
	$<2 \text{ mg L}^{-1}$	$<1 \text{ mg L}^{-1}$
	%	
1998	30.96	24.66
1999	23.29	17.81
2000	10.14	3.56
2001	20.82	14.25
2002	25.48	24.38
Avg. (1998–2002)	22.10	16.9

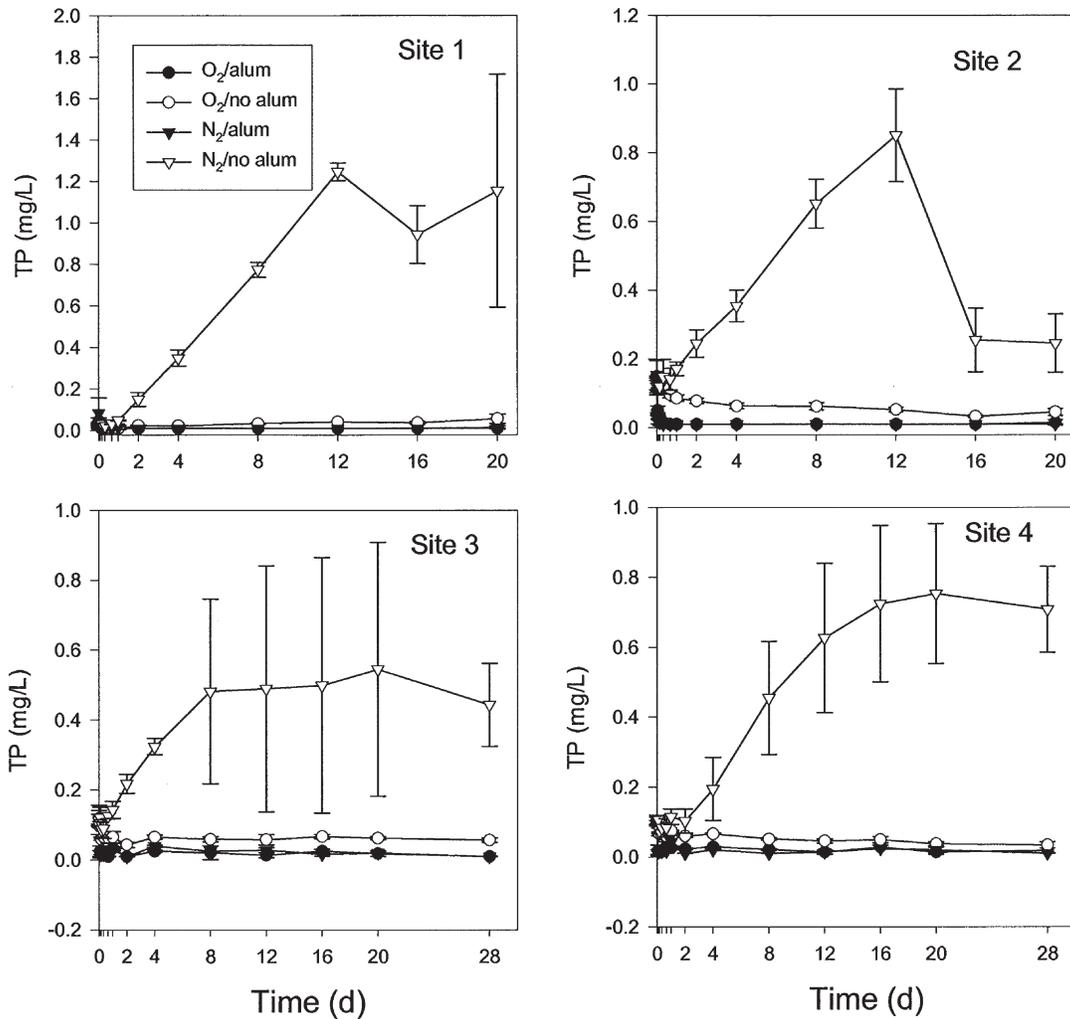


Fig. 3. Total phosphorus (TP) release rates for sediment cores from Sites 1 to 4, exposed to four different treatments. O₂ refers to aerobic treatment; N₂ refers to anaerobic treatment. Data are means (n = 3) ± 1 SD. Note different scales for the y axis.

20 resulted in the calculation of the medium or low release rates, respectively (Fig. 3).

Statistical analyses were conducted for moderate release rates, to avoid too liberal or too conservative biases. At all sites, the mean TP release rates were greatest in the anaerobic/no alum treatments compared with all other treatments, although the difference was not statistically significant at Site 3 because of high variance (Table 3). The amount of TP released was higher in the aerobic/no alum treatment compared with both alum treatments (aerobic or anaerobic; Fig. 3), but the release rates were not statistically significant (Table 3).

Within a site, “low” to “high” release rates in the an-

aerobic/no alum treatment ranged from ~10% (Site 4) to ~10-fold (Site 2; Table 4). For the anaerobic/no alum treatment, “low” TP release rates ranged from about 1.6 (Site 2) to 14.8 (Site 1) mg P m⁻² d⁻¹, whereas “high” TP release rates ranged from about 12 (Site 4) to 29.5 (Site 1) mg P m⁻² d⁻¹ (Table 4). The “high” TP release

Table 3. Mean (n = 3) release rates of TP from moderate release calculations. Data with different letters within a column (i.e., by site) are significantly different from one another.

Treatment	Site 1	Site 2	Site 3	Site 4
	mg P m ⁻² d ⁻¹			
Aerobic/no alum	0.40 a	-2.00 a	0.16 a	-1.04 a
Aerobic/alum	-0.85 a	-3.06 a	0.34 a	-1.65 a
Anaerobic/no alum	26.71 b	16.02 b	9.04 a	10.64 b
Anaerobic/alum	-1.64 a	-3.29 a	0.15 a	-1.48 a

Table 4. Low, medium, and high release rates for total phosphorus (TP) from the anaerobic/no alum treatment for the four sampling sites.

Site	Category	Days used in calculation	TP release rate
Site 1	low release rate	Day 0-20	14.82 ± 7.40
	medium release rate	Day 0-12	26.71 ± 1.06
	high release rate	Day 4-12	29.54 ± 0.95
Site 2	low release rate	Day 0-20	1.64 ± 1.44
	medium release rate	Day 0-12	16.02 ± 2.54
	high release rate	Day 4-12	17.33 ± 4.89
Site 3	low release rate	Day 0-28	3.10 ± 1.01
	medium release rate	Hour 4-Day 16	9.04 ± 7.58
	high release rate	Hour 4-Day 8	13.33 ± 8.36
Site 4	low release rate	Day 0-16	10.64 ± 3.14
	medium release rate	Day 0-16	10.64 ± 3.14
	high release rate	Day 2-16	11.67 ± 4.08

Table 5. Internal and external total phosphorus (TP) load estimates (Mg yr^{-1}). Internal TP load estimates are based on data from this study. Grand means are the unweighted averages from each site. External TP load estimates are based on data from Lauber (1999).

Category	Internal TP load					External TP load
	Site 1	Site 2	Site 3	Site 4	Grand mean	
	Mg yr^{-1}					
Low	5.29	0.59	1.11	3.80	2.7	2.2 (45%)
Medium	9.53	5.72	3.23	3.80	5.8	3.1 (35%)
High	10.55	6.19	4.76	4.17	6.4	4.7 (42%)

rates were greater at Sites 1 and 2 than at Sites 3 and 4 (Table 4).

The maximum mean concentrations of TP measured in the water column above the sediment cores were 1.25 mg L^{-1} in Site 1 (Day 12), 0.85 mg L^{-1} in Site 2 (Day 12), 0.55 mg L^{-1} in Site 3 (Day 20), and 0.75 mg L^{-1} in Site 4 (Day 20) (Fig. 3). These concentrations are approximately an order of magnitude greater than what was measured in the water column of Spring Lake (Table 1).

Internal Load Calculations

Internal TP loads were estimated from the anaerobic/no alum treatment. This treatment reflected the condition when P release was most likely to occur in nature. Internal P loads varied approximately 2.5-fold from the mean in the low range to the mean in the high range (Table 5). Hence, the portion of the curve used to estimate P release rates clearly has a significant impact on calculating the internal load in Spring Lake. Overall, the estimated internal P load to Spring Lake ranged from a low of 0.6 Mg yr^{-1} at Site 2 to a high of 10.6 Mg yr^{-1} at Site 1. The mean internal P loads were 2.7, 6.2, and 6.4 Mg yr^{-1} under the low, medium, and high categories, respectively (Table 5).

Internal vs. External Phosphorus Loads

Estimated TP external loads to Spring Lake were available for 1997 and 1998 (Lauber, 1999). These calculations included loading estimates from tributaries (measured monthly), atmosphere (literature values from Gull Lake, MI), stormwater (measured precipitation and published coefficient on P concentration), septic systems (resident survey for number of systems and published coefficient on P concentration), waterfowl (survey of duck [*Anas* sp.] counts and literature value of goose [*Anser* sp.] excretion rate, droppings per day, and P content of droppings; Manny et al., 1975), and lawn fertilizer (resident survey of fertilizer use and literature value of P content of commercial fertilizer). Error estimates from water budgets were used to generate seasonal low and high estimates (Lauber, 1999). Estimated external TP loads ranged from 2.2 to 4.7 Mg yr^{-1} (Table 5), with the three largest sources being tributary loading (67%), septic systems (17%), and lawn fertilizer (10%) (Lauber, 1999). Comparisons of internal and external TP load estimates show that internal loading accounted for somewhere between one-half and two-thirds of the TP load to Spring Lake (Table 5).

Sediment Phosphorus Forms

Mean NaOH-extractable inorganic P (NaOH-P_i) concentrations (i.e., Fe/Al-bound P) from the sediment cores ranged from approximately 123 to 200 mg kg^{-1} dry weight (Fig. 4). There were no statistically significant differences among sampling location, redox state (aerobic vs. anaerobic), or alum treatment (present vs. absent) for the NaOH-P_i fraction. Mean HCl-extractable P (HCl-P_i) concentrations (i.e., Ca/Mg-bound P) were more variable than NaOH-P_i , ranging from 126 to 513 mg kg^{-1} dry weight (Fig. 4). With the exception of

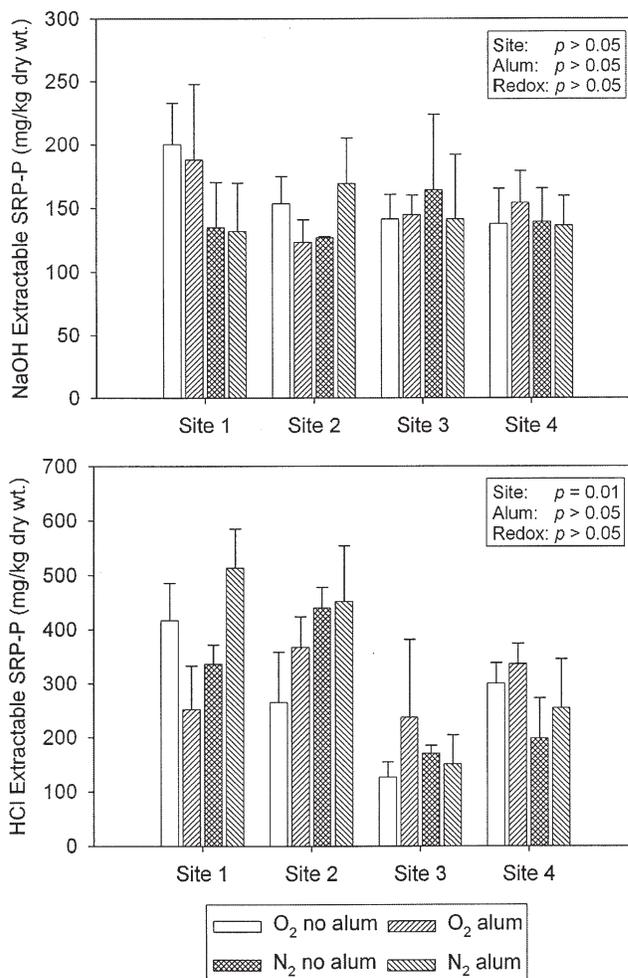


Fig. 4. Top panel: concentration of NaOH-P_i (Fe/Al-bound P) in Spring Lake sediments. Bottom panel: Concentration of HCl-P_i (Ca/Mg-bound P) in Spring Lake sediments. O_2 = aerobic treatment; N_2 = anaerobic treatment; T = alum; C = control. Data are means ($n = 3$) ± 1 SD. Results from the ANOVA are presented in upper right corner of each panel.

Station 3, the HCl-P_i concentrations were greater than NaOH-P_i concentrations. A statistically significant difference between sites was noted ($p = 0.01$) for HCl-P_i, with Stations 3 and 4 being significantly lower than Stations 1 and 2. As with the NaOH-P_i, no statistically significant differences were observed with respect to redox or alum treatments for the HCl-P_i.

There was no statistically significant relationship between the NaOH-P_i and TP flux ($R = 0.01$; $p > 0.05$). Similarly, no statistically significant relationship existed between the HCl-P_i and TP flux ($R = 0.06$; $p > 0.05$).

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; Søndergaard et al., 2001; Nürnberg and LaZerte, 2004). This process has both ecological and societal implications; internal loading rates can be sufficiently great that reductions in external loading fail to improve water quality. If these reductions in external loading require the investment of money and create expectations of success, the resulting disappointment (or worse) from stakeholders at the failure to improve lake conditions can set back future restoration activities and harm the reputation and credibility of natural resource managers.

The P release rates from Spring Lake were in the same range as those measured in eutrophic systems (6–18 mg m⁻² d⁻¹; Nürnberg and LaZerte, 2004), and even approached some of the highest recorded release rates (30–60 mg m⁻² d⁻¹; Nürnberg, 1988). These results strongly suggest that internal P loading is a significant source of P in Spring Lake, potentially accounting for somewhere between 55 to 65% of the total P load to the system. However, a number of assumptions were built into these calculations, which are evaluated below.

First, it was assumed that release rates from sediments in the core tubes were representative of sediments and conditions in Spring Lake. The sampling strategy was designed to cover as much of the geographic range in Spring Lake as possible. Indeed, this study revealed that there was spatial variability in P release rates in Spring Lake; in general, P release rates were higher at Sites 1 and 2 than at Sites 3 and 4. It does not appear that this difference was due to sediment chemistry, as the Fe-bound P sediment fractions were similar among all sites. Although the Ca-bound P sediment fraction was higher at Sites 1 and 2, if anything this should account for lower, not higher, P release rates. Since our sampling approach introduced no systematic bias, we have no reason to believe our results are not spatially representative of Spring Lake as a whole.

The second major assumption in our calculations was that the measured P release rates applied whenever DO concentrations were <1 mg L⁻¹. Under aerobic conditions, oxidized iron will remain bound to P in the sediments but when conditions become anaerobic, the reduced form of iron becomes more soluble, and the P is released (Mortimer, 1941, 1942). In addition, biological

processes (e.g., bacterial activity, mineralization processes, and bioturbation), chemical parameters (e.g., pH, alkalinity, and nitrate), and physical factors (e.g., resuspension and sediment mixing) also will influence P release rates (Boström et al., 1982; Søndergaard et al., 1992; Petterson, 1998). We used a 1 mg L⁻¹ threshold for DO (cf. Mortimer, 1971; Nürnberg, 1995); this was an operational threshold, as our datasonde was actually located approximately 1.0 m above the sediment–water interface, and it is likely that conditions were even more reduced below this depth.

The third assumption dealt with the calculation for percentage of year that DO concentrations in Spring Lake were <1 mg L⁻¹. This extrapolation was based on data from one relatively deep site (“Deep Hole”) in Spring Lake, near Site 1. It is likely that the DO values at “Deep Hole” were lower, on average, than at other sites in Spring Lake due to its greater depth, which would result in an overestimate of anaerobic conditions (and internal loading). However, this overestimate is offset, at least to some degree, by the assumption that only oxic conditions existed between October and April (when no DO samples were taken). In fact, it is likely that anoxic conditions do occur under ice cover, at least occasionally (thereby releasing P). However, given the absence of data, a conservative approach was adopted by assuming continuous oxic conditions in the winter.

Fourth, calculations of P release rates under the moderate and especially the low ranges should be viewed with caution. Although inclusion of these rates are of value because they provide estimates of the lower and middle ranges of P flux, the inclusion of data from longer periods of incubation increase the risk that chemical or biological interference may affect the rates.

Finally, it was assumed that the incubation conditions were representative of natural conditions. Although the laboratory conditions mimicked the ambient temperature and light regime, clearly the hydrodynamics were altered. It is likely that the laboratory set-up for the anaerobic water column with no alum treatment represented an optimal situation for release of P (constant anaerobic conditions) compared with natural conditions. In addition, the P concentration of our replacement water (filtered lake water) was lower than the P concentration of the water remaining in the core tube, especially in the anaerobic/no alum treatment (which accumulated P over time). This introduction of relatively low P concentration water into the water column steepened the concentration gradient inside the core tubes, likely enhancing P release. As a consequence, these release rates should be viewed as maximum potential rates.

Given the spatial variability in P release rates among sites, it was surprising that the extractable P in the sediments was poorly related to site, redox state, or alum treatment. Previous studies have reported a reduction in the iron-bound P fraction due to the reaction with the alum layer (Kennedy and Cooke, 1982; Cooke et al., 1993). It is possible that our 10-cm deep sediment cores biased the results by introducing sufficient addi-

tional P to mask chemical changes from the alum treatment or the differences in redox conditions.

Management strategies to control internal loading usually include sediment removal and chemical applications, such as Al, Fe, or Ca salts (Cooke et al., 1993). The data from this study clearly showed that alum application was very effective at reducing internal P loading rates in our sediment cores. Irrespective of location or oxic state of the treatment, TP release rates were virtually negligible when alum was applied. Alum is particularly effective due to its dual mode of action for P removal. When added to water at pH 6 to 8, alum dissociates to give trivalent Al^{3+} ions, which undergo a series of rapid hydrolytic reactions to form soluble monomeric and polymeric species, as well as an amorphous $Al(OH)_3$ floc (Bottero et al., 1980; Omoike and Valoon, 1999). The monomeric species are capable of precipitating soluble P as $Al(PO_4)$. In addition, the amorphous $Al(OH)_3$ floc can remove soluble and particulate forms of P by adsorption and/or physical entrapment (Galarneau and Gehr, 1997). The alum floc will settle and form a layer at the sediment–water interface that has a high capacity to adsorb large amounts of inorganic P (Kennedy and Cooke, 1982).

While an alum treatment is likely to have short-term benefits, it is unclear how long an alum treatment would be effective in Spring Lake. The current study was not designed to address the question of long-term effectiveness of an alum treatment. However, prior studies have shown that effectiveness ranges from ~4 to 20 yr, and is dependent on many factors, including: (i) the morphometry of the lake, which influences the likelihood that the alum will be resuspended by wind–wave action, and no longer covers the sediments uniformly (Welch and Cooke, 1995, 1999); (ii) the amount of alum added to the sediment, to ensure there is sufficient aluminum to bind the P, but not add more than necessary because of financial or environmental concerns (Rydin and Welch, 1998; Lewandowski et al., 2003); (iii) activity from bottom-swelling animals (i.e., bioturbation) in the sediments, which can 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). In addition, bioturbation can redistribute and bury the alum, reducing its efficacy; (iv) presence of macrophytes, either by intercepting the alum floc and preventing a uniform cover over the sediment or by P release from tissue during plant senescence (Welch and Schriever, 1994; Welch and Cooke, 1999); (v) water column pH, as circumneutral waters (pH 6–8) are optimal for creating an alum floc (Rydin and Welch, 1998; Lewandowski et al., 2003); (vi) 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); and (vii) the influence of internal loading from shallow areas not treated by alum. Significant internal loading has been reported in shallow lakes and areas where frequent mixing occurs (Nixdorf and Dencke, 1995; Søndergaard et al., 1999).

A vital prerequisite for restoring lake water quality is the removal of the underlying reasons for the impair-

ment. Thus, regardless of the long-term effectiveness of an alum treatment, it is critical that external load reduction complement any chemical addition (Hansson et al., 1998). Continued efforts at reducing stormwater discharge, conversion of septic systems to sewers, use of low-P fertilizer, and implementation of other best management practices should be emphasized, along with the provision of appropriate incentives in the Spring Lake watershed.

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