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Internal Phosphorus Loading in Spring Lake: Year 1

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Executive Summary

The rate of phosphorus release from sediments, and the degree to which alum reduces phosphorus release from sediments, was investigated in Spring Lake during the summer of 2003. Triplicate cores were sampled from 4 sites in the lake, and exposed to one of four treatments in the laboratory: 1) oxygen/alum; 2) oxygen/ no alum; 3) nitrogen/alum; or 4) nitrogen/no alum. Both soluble reactive phosphorus (SRP) and total phosphorus (TP) release rates were virtually undetectable in the alum treatments (both with and without oxygen). Low, but detectable, release rates were measured in the oxygen/no alum treatment. The highest release rates were measured in the nitrogen/no alum treatments; these rates translated to an internal load that ranged between 2.8 (low range) to 7.7 (high range) tons/year when extrapolated to a whole-lake basis. Internal phosphorus loads were approximately double that of previously estimated external phosphorus loads, and accounted for between 56 and 66% of the total phosphorus load to Spring Lake.

Uncertainties in our estimates are discussed, including spatial heterogeneity of sediment type, calculation of percent anoxia in Spring Lake, extrapolation of laboratory release rates to the whole lake, and external load estimates. We conclude that internal loading is a significant source of phosphorus to Spring Lake, and that alum is a potentially effective means of reducing this source. However, it is unknown how long an alum treatment would remain effective in this system. We recommend: 1) additional laboratory studies to obtain an estimate of how long an alum treatment would remain effective; 2) a pilot field study; and 3) continued efforts to reduce external loading to Spring Lake.

1.0 Introduction

1.1 Background

Internal loading of phosphorus refers to the release of phosphorus from lake sediments. This phosphorus pool accumulates when external loading of phosphorus (from the watershed and atmosphere) is high. 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 release can occur via two different mechanisms (Selig 2003):

- release at the sediment-water interface during periods of anoxia or hypoxia (no or very low levels of dissolved oxygen), and the subsequent diffusion of dissolved phosphate into the water column

- resuspension of bottom sediment, whereby phosphate in the pore water can be released into the water column or phosphorus adsorbed to sediment particles can desorb into the water column

Mineral associations play an important role in the release of phosphorus during anoxic conditions. Phosphorus associated with iron minerals can become soluble in the absence of oxygen while the 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 phosphorus concentration in watersheds have concentrated on the "external" loading of phosphorus. This is the contribution of phosphorus from point and nonpoint sources currently flowing into a waterbody. The contribution of phosphorus being released from the sediments, or the internal load, often

is overlooked. However, in highly eutrophic lakes, internal loading can account for a substantial amount of the total phosphorus load. 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 phosphorus from sediments (Bjork 1985, Graneli 1999, Steinman et al. 1999).

Although many sediment management technologies exist to deal with internal loading, the most common ones include chemical treatment, oxidation, and dredging (Cooke et al. 1993). Chemical applications are intended to bind the phosphorus, and usually include aluminum sulfate (alum), lime, or iron (Cooke et al. 1993). Alum is particularly effective due its dual mode of action for phosphorus removal. Alum reacts with soluble phosphorus to form an insoluble precipitate (Stumm and Morgan 1996) as follows:

$$Al_2(SO_4)_3 \cdot 14H_2O + 2PO_4^{3-} \rightarrow 2AlPO_4 + 3SO_4^{2-} + 14H_2O \qquad (K_{sp} = 6.3 \text{ X } 10^{-19})$$
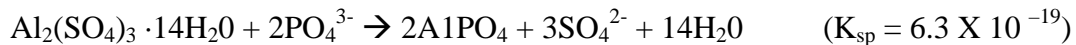
In addition, alum will form an insoluble aluminum hydroxide floc at pH 6 to 8, which has a high capacity to adsorb large amounts of inorganic phosphorus (Kennedy and Cooke 1982). By these two mechanisms, an alum application can irreversibly bind phosphorus and inhibit diffusive flux from sediments.

Previous studies showed that on average, alum application reduces internal loading by approximately 70% and its effectiveness lasts about 8-10 years (Welch and Cooke 1995). However, these numbers vary based on phosphorus concentrations, limnological conditions, and sediment characteristics.

Recent research (Moore et al. 1998, Steinman et al. 1999) on two hypereutrophic lakes in Florida indicated that there could be a significant contribution of bioavailable

phosphorus in the lakes arising from internal loading. The source of phosphorus in these cases was the top layer of sediment. If phosphorus is not tightly bound to sediment, it becomes available to the surface waters upon resuspension of the sediment or simply by gradient flux under the correct conditions of temperature, pH, dissolved oxygen, and ambient surface water phosphorus concentration. If there is a similar significant internal loading source of phosphorus in Spring Lake, reductions in external P loads alone likely will be insufficient to reduce phosphorus levels in the lake water, at least for the foreseeable 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. Total phosphorus concentrations (TP) in Spring Lake are usually far in excess of water quality standards. For example, the USEPA has set a TP water quality goal of 15 ppb for the west Michigan ecoregion (USEPA 2000). However, during ice-free periods from 1999 through 2002, TP concentrations in Spring Lake averaged 100 ppb, and ranged from 6 to 631 ppb (Progressive AE 2002), far in excess of USEPA standards. The goal of this project is to measure whether internal loading of phosphorus from the sediment to surface water is a significant source of phosphorus to Spring Lake. In order to accomplish this goal, internal loading of phosphorus was measured from 4 sites in Spring Lake during the summer of 2003.

1.2 Project Objectives and Task Elements

The objective of this project was to assess the importance of internal phosphorus loading to Spring Lake. This involved four distinct task elements:

- Selection of sampling sites for coring

- Collection of cores and measurement of limnological characteristics

- Sampling and calculation of nutrient load estimates

- Provide recommendations for remediation alternatives in Spring Lake

2.0 Methods

2.1 Field methodology

Cores were collected from four sites in Spring Lake (Fig. 2.1.1); 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) in order to take advantage of historical information.

Figure 2.1.1.   Sampling sites for collection of cores for internal loading measurements.
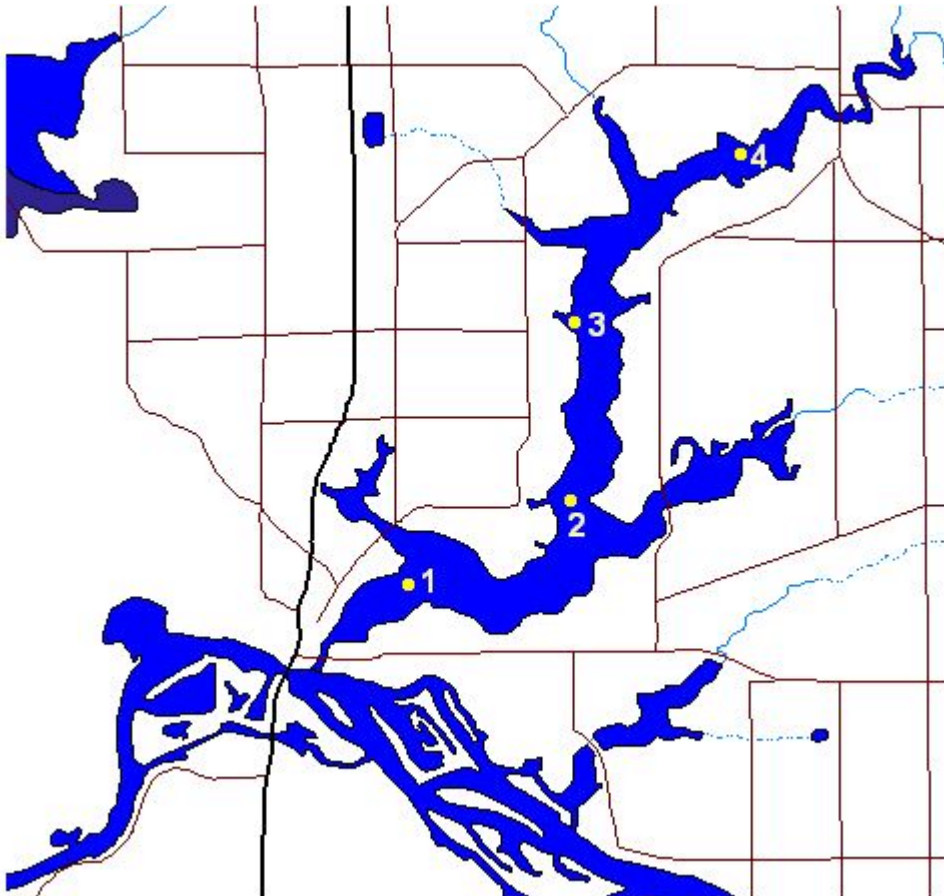
Site 1 is at the southern end of Spring Lake just downstream of where Smith Bayou enters the mainstem of Spring Lake (Fig. 2.1.1). Site 2 is upstream of the confluence of Petty's Bayou and the mainstem of the lake. Site 3 is in Dunlevy Bay. Site 4 is at the northern end of Spring Lake. Sites 1, 2, and 4 corresponded to Stations 2, 3, and 7, respectively, in Progressive AE's 2002 report.

Sites 1 and 2 were sampled on June 10 and 11, 2003 and sites 3 and 4 were sampled on July 16, 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 (Table 2.1.1). A secchi disk was used to measure water clarity and a Li-Cor quantum sensor and data logger were used to measure incident and underwater irradiance. Water samples for nutrient analysis were collected with a van Dorn bottle and maintained at 4ºC until delivery to the laboratory. Nutrient analyses were performed on a BRAN+LUEBBE Autoanalyzer following standard methods (USEPA 1983).

Table 2.1.1. Methods used for water quality analyses in Spring Lake.

Parameter	Preparation	Preservation	Holding Time (d)	Reference* or method
DO, alkalinity, pH, temp, specific conductance, chl. a, TDS	None	None	none	Hydrolab DataSonde 4a
Light transmittance	None	None	none	Li-Cor quantum sensor and Secchi disk
SRP	0.45 µm filter in field	Freeze –10°C	28	365.4*
TP	--	H_2SO_4 Cool to 4°C	28	365.4*

* USEPA (1983)

Sediment samples from Spring Lake were collected using a piston corer (Fisher et al. 1992). Twelve cores were collected from each site. 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 10 cm prior to deployment to maintain a water layer on top of the core during collection. The corer was vertically positioned at the sediment/water 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 prior to 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 maintained at ambient temperature until being transported back to the laboratory (Fig. 2.1.2).

Fig. 2.1.2. Photograph of stoppered tubes (tubes on right with collected cores) seated in holding racks, which are placed in tubs to maintain ambient temperature.

2.2. Laboratory Methodology

The 24 cores (twelve per site) collected on each sampling trip were placed into a Revco environmental growth chamber, with the temperature maintained to match ambient conditions in the field. Cores were exposed to one of four treatments (three replicates per treatment per site):

- oxygen (aerobic) with alum

- oxygen (aerobic) without alum

- nitrogen (anaerobic) with alum

- nitrogen (anaerobic) without alum

Nitrogen (with 330 ppm CO_2) or oxygen was bubbled into the water column of each tube to create aerobic or anaerobic conditions, respectively. Approximately 545 mg of alum (as aluminum sulfate solution) was placed in half of the oxygen and half of the nitrogen treatments and allowed to settle, forming a floc at the water-sediment surface (Fig. 2.2.1). This was considered time zero. Alum was obtained from General Chemical Corporation (River Rouge, MI).

Figure 2.2.1. Schematic of experimental set-up. Core tubes consisted of a 25-cm overlying water layer and a 20-cm sediment core. Half of the tubes received alum (e.g. left tube). See text for additional details.
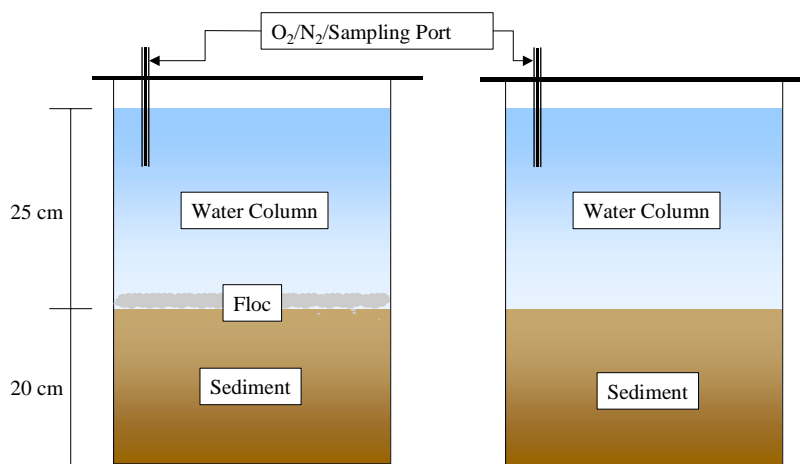
Internal load estimates were made using the methodology outlined in Moore et al. (1998), with minor modifications. Briefly, a 30 mL water sample was removed by syringe through the sampling port of each tube core at 2 h, 4 h, 8 h, 16 h, 1 d, 2 d, 4 d, 8d, 12 d, 16 d, 20 d, and 28 d (day 28 only for Sites 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, and within 2-12 h of collection a 10 mL

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subsample was filtered through a 0.45 µm membrane filter and immediately frozen for future SRP analysis using the methods described above (Table 2.1.1).

Flux calculations were based on the increase in water column TP and SRP. Calculations were based on three different time periods to reflect: 1) the maximum release rates (linear portion of the curve); 2) moderate release rates; and 3) 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:

$$P_{flux} = (C_0 - C_t) * V/A, \hspace{3cm} (1)$$

where, P_{flux} is the net P flux or retention per unit surface area of sediments, C_0 is the P concentration in the water column at time 0, C_t is the P concentration in the water column at time t, V is the volume of water in the water column, and A is the surface area of the sediments.

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

2.3. Statistical Analysis

Phosphorus release rates were calculated for individual cores and treatments compared (n = 3) within each site using analysis of variance. Data were not transformed prior to analysis. Tukey's post-hoc multiple comparison test was used to determine if mean release rates from individual treatments were significantly different from one another. P concentrations of the chemically-fractionated sediment cores also were analyzed by one-way analysis of variance to detect statistically significant differences among sites and treatment conditions. All statistical analyses were conducted using SAS (version 8).

3.0 Results

3.1 Field results

Site 1: This site was relatively deep (8.23 m) with a Secchi depth of 1.25 m. Temperature was relatively constant through the water column, whereas dissolved oxygen concentration dropped from 11.31 ppm at the surface to 6.0 ppm at the bottom (Fig. 3.1.1). Chlorophyll a values exhibited a subsurface maximum at 2m (28.3 ppb) and declined to 6.2 ppb at the bottom (Fig. 3.1.1).

Figure 3.1.1. Temperature, dissolved oxygen, and chlorophyll a values from Site 1 in Spring Lake, sampled on June 10, 2003.
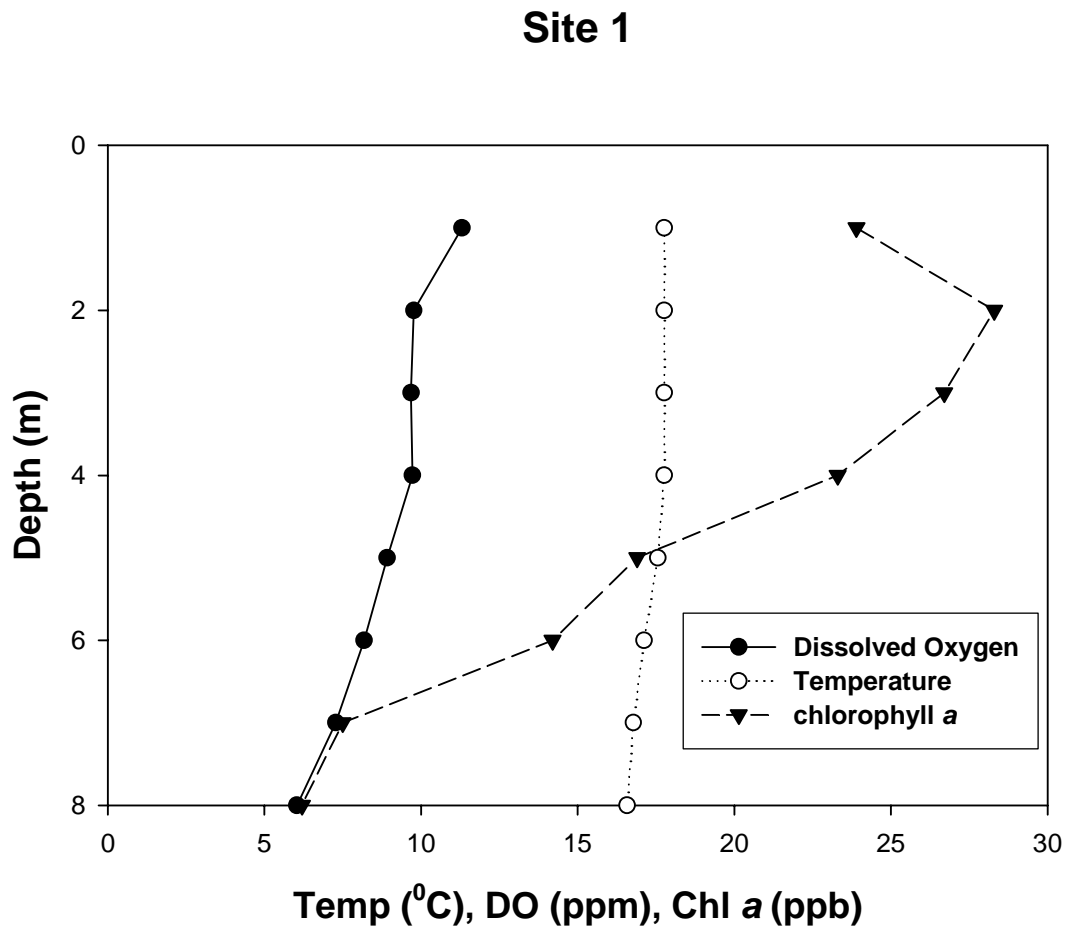
Site 1

Site 2: This site was the deepest (10.06 m) with a Secchi depth of 1.0 m. As with Site 1, temperature was relatively constant through the water column; however, this site exhibited anoxia at the bottom (Fig. 3.1.2). Chlorophyll *a* exhibited a subsurface maximum at 4 m (29.7 ppb) and declined to 3.3 ppb at the bottom (Fig. 3.1.2).

Figure 3.1.2. Temperature, dissolved oxygen, and chlorophyll a values from Site 2 in Spring Lake, sampled on June 11, 2003.

Site 2
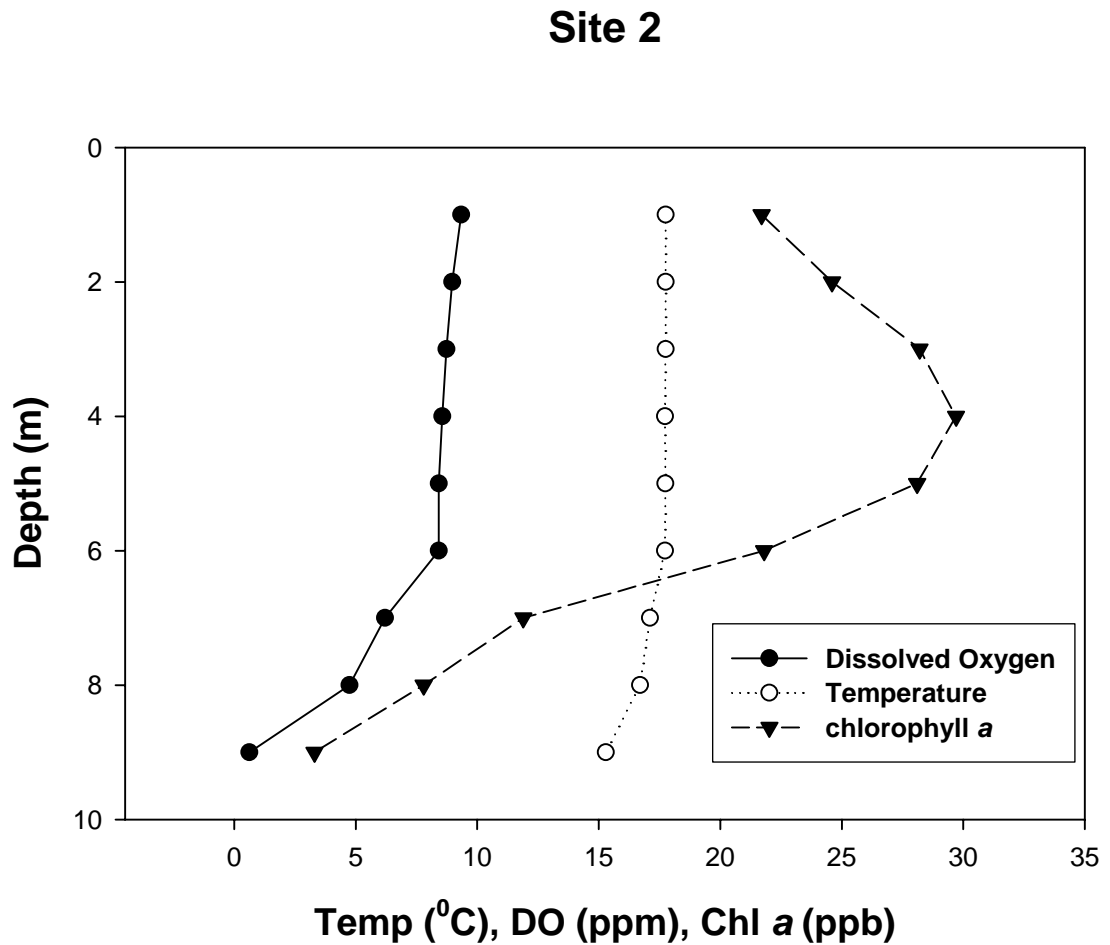
Site 3: Depth at this site was 6.71 m with a Secchi depth of 1.0 m. Temperature showed a slight decline near the bottom; both dissolved oxygen and chlorophyll *a* showed a similar pattern with relatively constant concentrations throughout most of the water column until a depth of 5 m, where both values declined considerably near the bottom sediments (Fig. 3.1.3).

Figure 3.1.3. Temperature, dissolved oxygen, and chlorophyll a values from Site 3 in Spring Lake, sampled on July 16, 2003.

Site 3
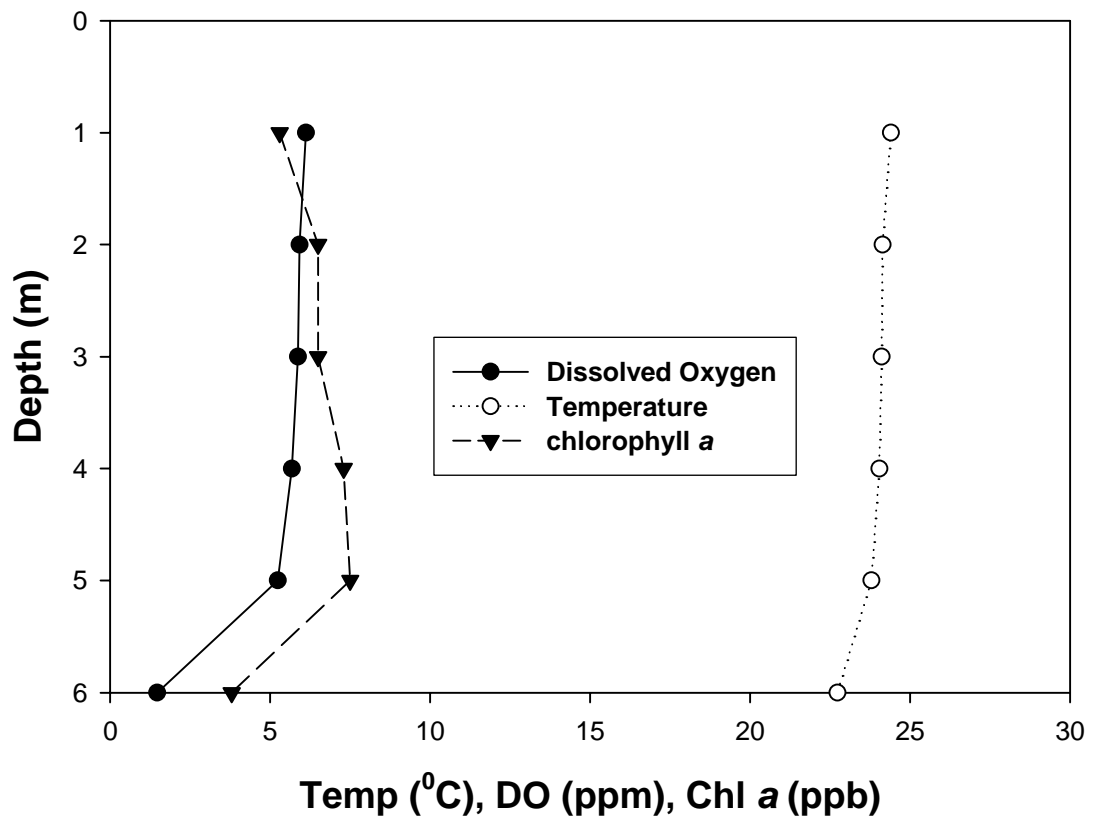
Site 4: Depth at this site was only 4.88 m and clarity was relatively poor (secchi depth: 0.75 m). Temperature showed a slight decline near the bottom; dissolved oxygen remained between 4.2 and 5.4 ppm throughout the water column, whereas chlorophyll *a* had a subsurface maximum at 2 m (7.8 ppb) and was lower near the surface than near the bottom (Fig. 3.1.4).

Figure 3.1.4. Temperature, dissolved oxygen, and chlorophyll a values from Site 4 in Spring Lake, sampled on July 16, 2003.

Site 4
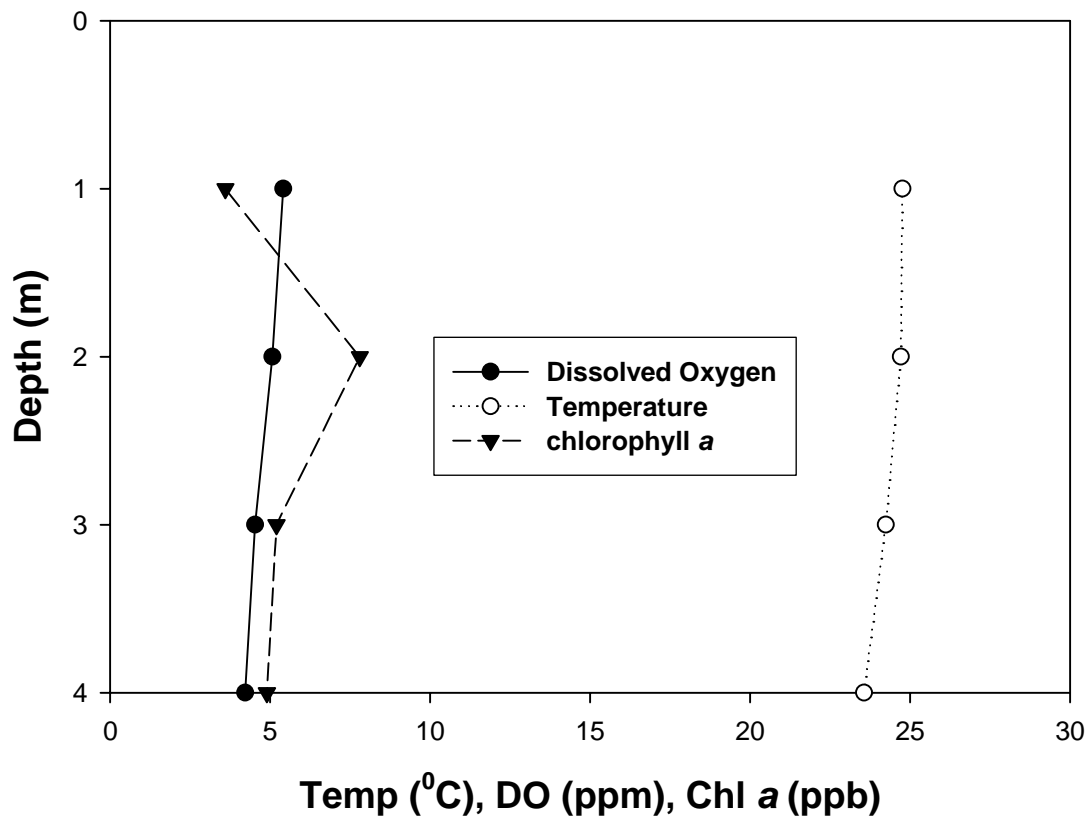
Overall patterns: Water temperatures were lower and chlorophyll concentrations were higher in June (Sites 1 and 2) than July (Sites 3 and 4). The lower temperatures reflect the earlier sampling date in the year, whereas the lower chlorophyll values in July are likely a function of sampling soon after an algicide application in Spring Lake. Distinct anoxic conditions were noted only at Site 2; it is possible that shallower sites experience anoxia less frequently than deeper sites due to greater mixing of the water column but even shallow sites can experience anoxic conditions.

Anoxic or hypoxic conditions are frequently observed in Spring Lake. Water samples have been taken from onboard the *D.J. Angus*, a research vessel owned and operated by AWRI, over the previous decade. A representative graph of these data from 1998 is shown in Fig. 3.1.5.

Figure 3.1.5. Dissolved oxygen (mg/L = ppm) concentration (blue line) from the "deep hole" station in Spring Lake during the 1998 field season of the *D.J. Angus*.
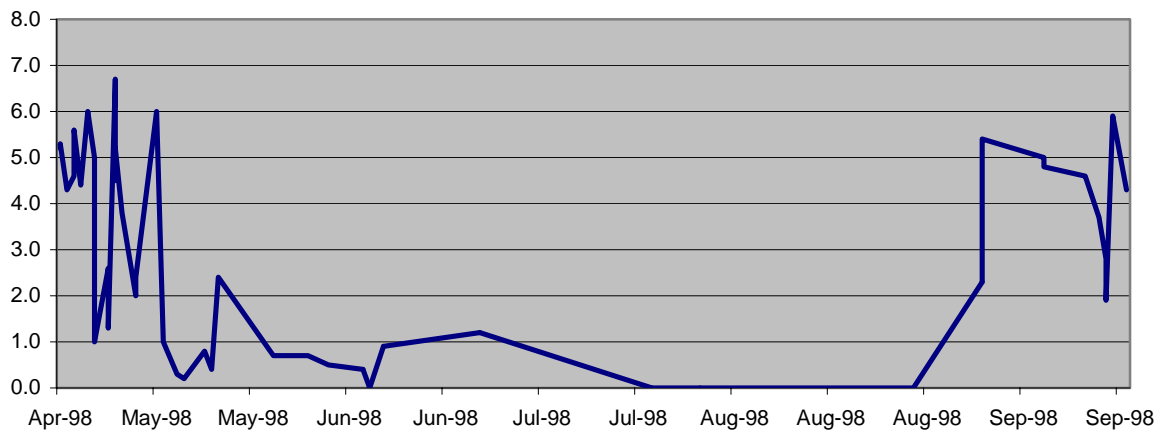
Data collected from cruises onboard the *D.J. Angus* from 1998 through 2002 were analyzed; a total of 864 sampling events were tallied (Table 3.1.1).

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Table 3.1.1. Percent of time that dissolved oxygen concentrations were less than 2 ppm or less than 1 ppm in Spring Lake (deep hole). Data were collected from the D.J. Angus; period of record was 1998 – 2002. DO concentrations in the non-sampled months (Oct – March) were assumed to be oxic.

Year	Percent of Time	
	< 2 ppm	< 1 ppm
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
Total (1998 – 2002)	22.10	16.9

These data provide a general idea of anoxic frequency in Spring Lake, 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 diel 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; although we assume oxic conditions during the remainder of the year due to greater mixing of the water column and reduced respiration in the benthos, this assumption remains unvalidated. If anoxic or hypoxic conditions do develop during these months, we have again underestimated the amount of low-DO conditions in Spring Lake. Although these data are imperfect, they do provide a relatively comprehensive

data set, and allow us to make some first-order estimates about phosphorus release from the sediments in Spring Lake (Section 3.2).

Additional field data were collected from each station, to help characterize the limnological conditions at each site. These data are included in Appendix A.

3.2. Laboratory results

Soluble Reactive Phosphorus (SRP). SRP release rates were very low in both alum treatments (with and without oxygen) and also low in the O_2/ no alum treatment, but were distinct and measurable in the N_2/no alum treatment (Figs. 3.1.1 – 3.1.4). Because release rates varied over the 20 or 28-d experimental period, it was possible to calculate low, moderate, and high rates from each site, depending on the selected start and end times. For example, in the N_2/no alum treatment for Site 1 (Fig. 3.2.1), the selection of days 12 (start) to 20 (end) resulted in the calculation of the maximum SRP release rate (linear phase), whereas selection of days 2 to 20 or days 0 to 20 resulted in the calculation of the medium or low release rates, respectively (Fig. 3.2.1). A similar approach was used for all sites, and for both SRP and total phosphorus (TP).

Within a site, release rates ranged from approximately 2.5-fold (Site 4) to approximately 15-fold (Sites 2 and 3; Table 3.2.1). "Low" release rates ranged from about 1 to 5 mg P/m^2/d, whereas high release rates ranged from about 12 to 32 mg P/m^2/d. The high release rates were greater at Sites 1 and 2 than at Sites 3 and 4 (Table 3.2.1). Statistical analysis of moderate release rates revealed that at all sites, the SRP release rate from the N_2/no alum was significantly greater than all other treatments, and there was no significant difference among the other three treatments (Appendix B).

Figure 3.2.1. SRP release rates for sediment cores from Site 1, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
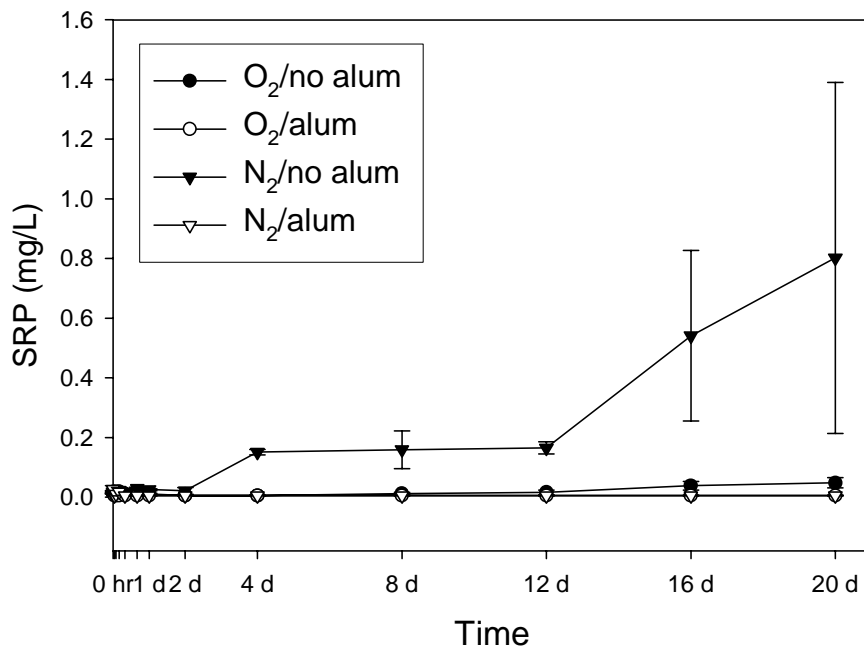
Figure 3.2.2. SRP release rates for sediment cores from Site 2, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
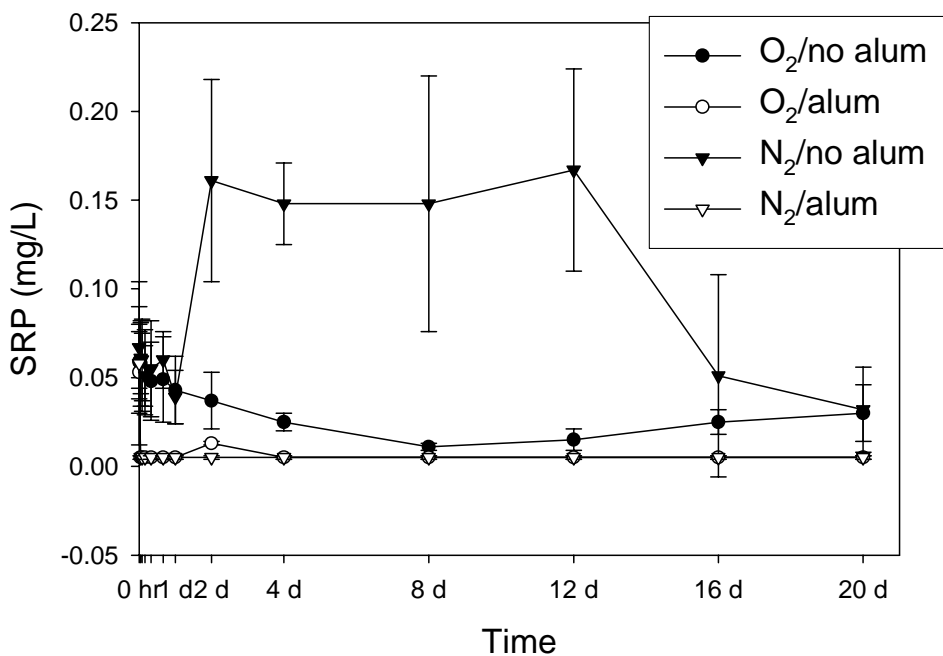
Figure 3.2.3. SRP release rates for sediment cores from Site 3, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
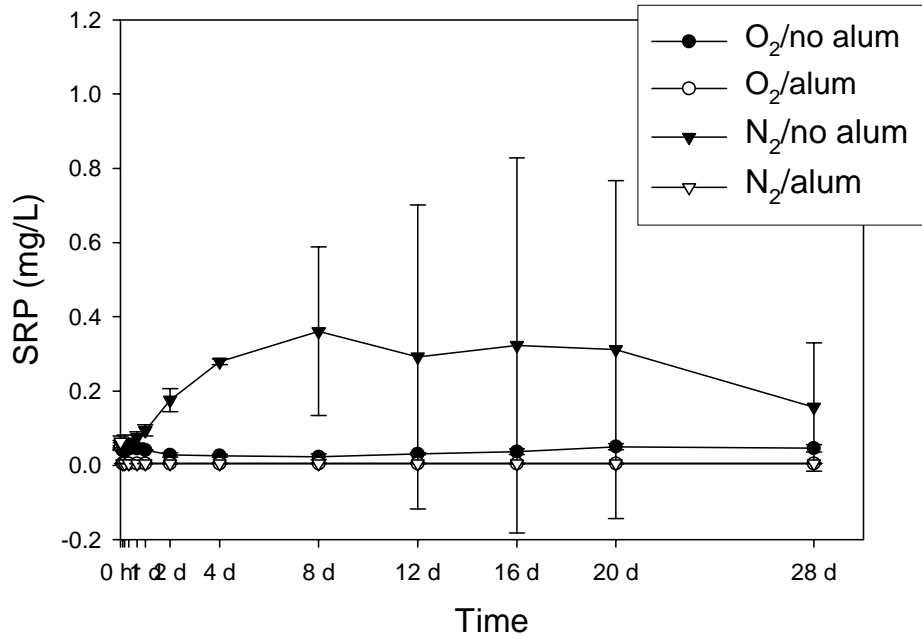
Figure 3.2.4. SRP release rates for sediment cores from Site 4, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
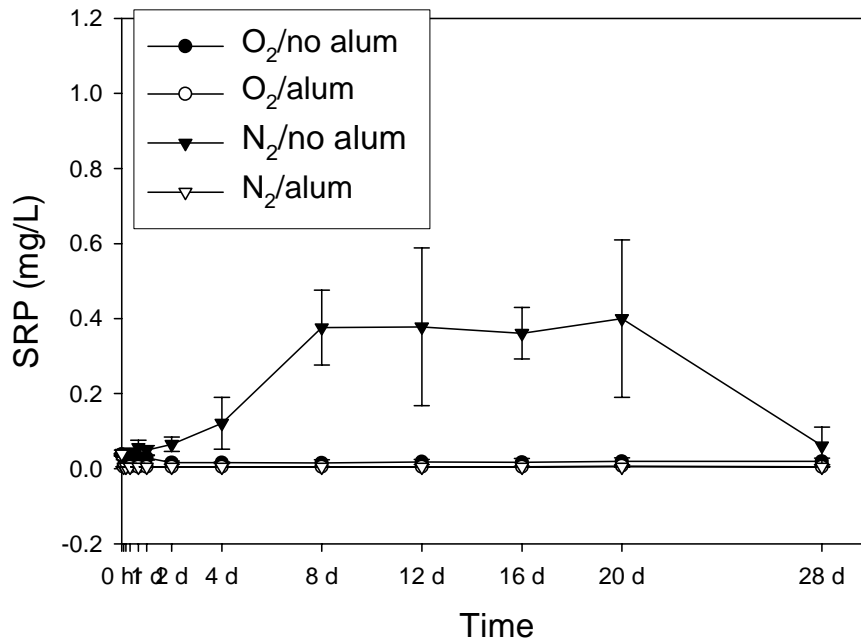
Table 3.2.1. Low, medium, and high release rates for SRP from the N_2/no alum treatment for the 4 sampling sites.

Site	Category	Days used in calculation	SRP release rate (mg P/m^2/d)
Site 1	Low release rate	Days 0 – 4	3.55
	Medium release rate	Days 2 – 20	12.09
	High release rate	Days 12 – 20	23.95
Site 2	Low release rate	Days 0 – 12	2.19
	Medium release rate	Days 1 – 12	3.06
	High release rate	Days 1 – 2	32.11
Site 3	Low release rate	Days 0 – 28	0.97
	Medium release rate	Days 0 – 8	10.10
	High release rate	Days 0 – 4	14.80
Site 4	Low release rate	Days 0 – 20	4.72
	Medium release rate	Days 1 – 20	4.86
	High release rate	Days 1 – 8	12.29

Total Phosphorus. TP release rates exhibited similar patterns to those of SRP, being very low in both alum treatments (with and without oxygen), low in the O_2/no alum treatment, and statistically greater in the N_2/alum treatment (Figs. 3.2.5 – 3.2.8). Within a site, release rates ranged from 1.1-fold (Site 4) to 16.1-fold (Site 2; Table 3.2.2). "Low" release rates ranged from about 1.6 to 14.8 mg P/m^2/d, whereas high release rates ranged from about 12 to 34 mg P/m^2/d. The high release rates were greater at Sites 1 and 2 than at Sites 3 and 4 (Table 3.2.2), similar to the pattern detected for SRP.

Figure 3.2.5. TP release rates for sediment cores from Site 1, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
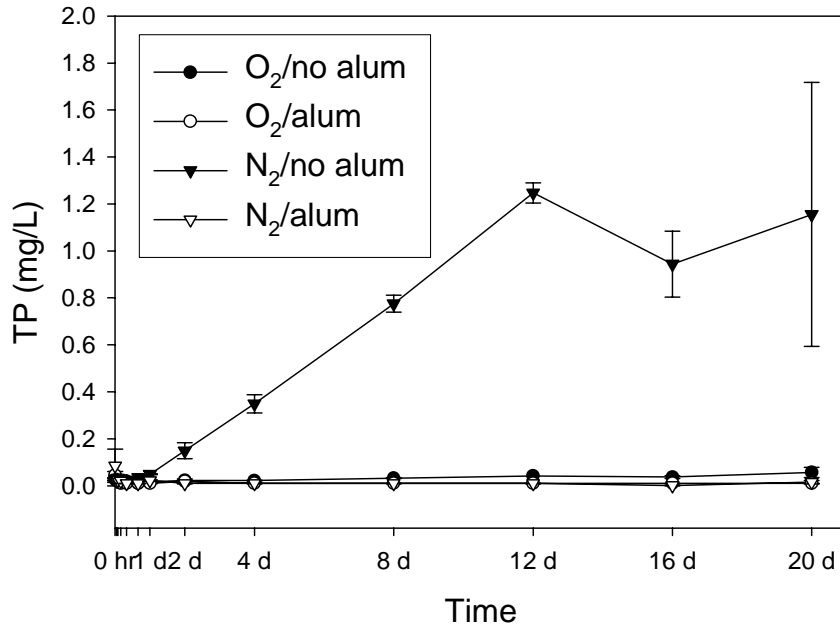
Figure 3.2.6. TP release rates for sediment cores from Site 2, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
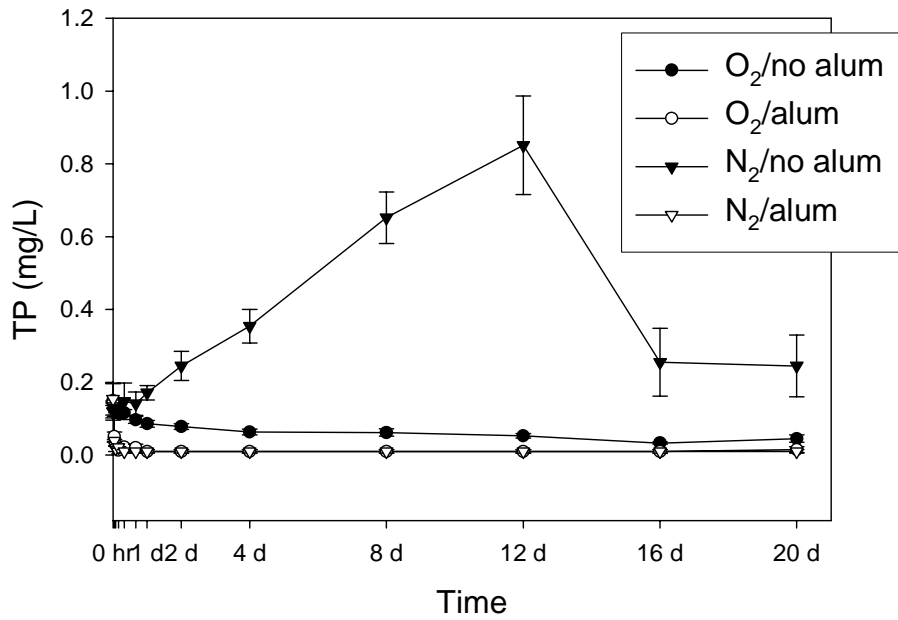
Figure 3.2.7. TP release rates for sediment cores from Site 3, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
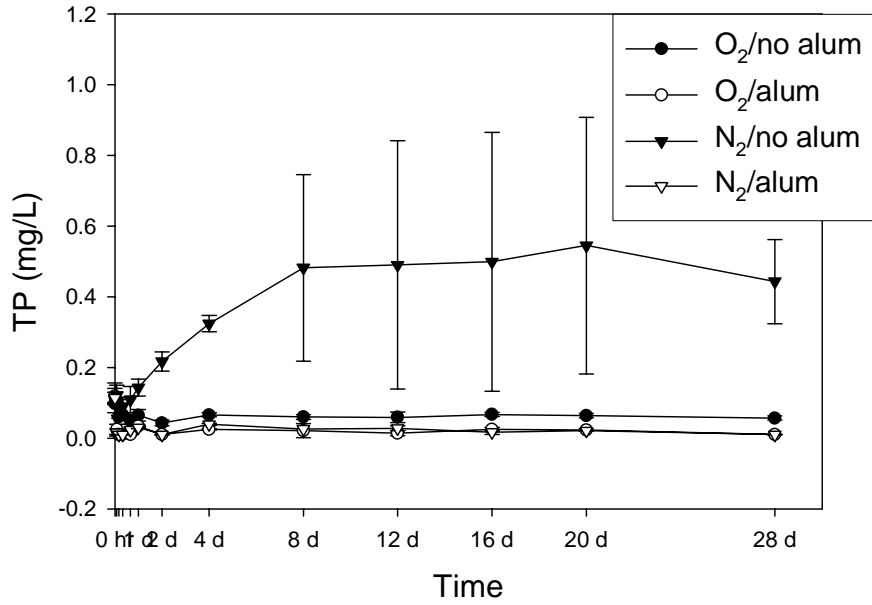
Figure 3.2.8. TP release rates for sediment cores from Site 4, exposed to four different treatments. Data are means (n = 3) ± 1 SD.
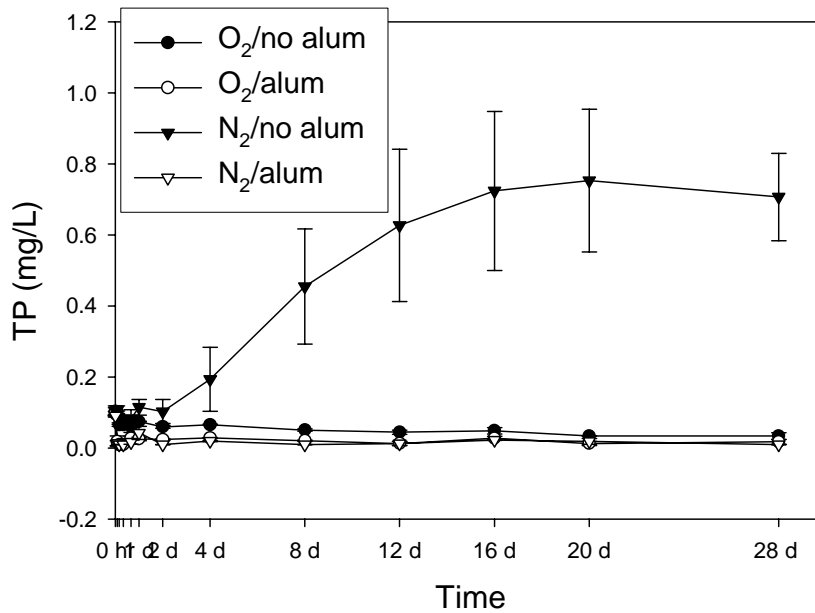
Table 3.2.2. Low, medium, and high release rates for TP from the N_2/no alum treatment for the 4 sampling sites.

Site	Category	Days used in calculation	TP release rate (mg P/m^2/d)
Site 1	Low release rate	Days 0 – 20	14.82
	Medium release rate	Days 0 – 12	26.71
	High release rate	Days 4 – 12	33.76
Site 2	Low release rate	Days 0 – 20	1.64
	Medium release rate	Days 0 – 12	16.03
	High release rate	Days 4 – 12	26.43
Site 3	Low release rate	Days 0 – 28	4.16
	Medium release rate	Hr 4 – Day 16	6.92
	High release rate	Hr 4 – Day 8	12.99
Site 4	Low release rate	Days 0 – 16	10.16
	Medium release rate	--	--
	High release rate	Days 2 –16	11.67

Internal Load Calculations.   Internal phosphorus loads from the N_2/no alum treatment were estimated using Equation 1 and based on a number of assumptions: 1) release rates from sediments in the core tubes were representative of sediments and conditions in Spring Lake; 2) the measured P release rates applied whenever DO concentrations were < 1 ppm; and 3) the percent of the year that the Deep Hole station in Spring Lake had DO concentrations < 1 ppm, based on data from the *D.J. Angus*, was applicable to 2003 and

other sites in Spring Lake. The validity of these assumptions, and the inherent

uncertainty in these estimates, are examined in the Discussion.

Internal phosphorus loads varied approximately 3-fold from the mean low range

to the mean high range (Table 3.2.3). 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 phosphorus load to Spring Lake ranges from a low

of 0.6 tons/yr at Site 2 to a high of 12.4 tons/yr at Site 1 (Table 3.2.3).

Table 3.2.3. Internal total phosphorus load estimates (tons/yr). Assumptions are given in text.

Category	Internal TP Load (tons/yr)			
	Site 1	**Site 2**	**Site 3**	**Site 4**
Low	5.28	0.59	1.49	3.64
Medium	9.55	5.74	2.47	--
High	12.39	9.45	4.64	4.18

Internal vs. External Phosphorus Loads.   External total phosphorus load (i.e. coming

from the atmosphere or watershed) data for Spring Lake were available (Lauber 1999).

Lauber's calculations included loading estimates from tributaries, atmosphere,

stormwater, septic systems, waterfowl, and lawn fertilizer. She also indirectly estimated

internal phosphorus loading based on the rate of change in TP concentrations in Spring

Lake's hypolimnion (Lauber 1999; Table 3.2.4).

The external loading estimates by Lauber also include a range of values to reflect

the inherent uncertainty of these calculations. Error estimates from her water budgets

were used to generate seasonal low and high estimates (Lauber 1999). Internal load

(based on estimates from the current study) accounted for 56% (low), 66% (medium), or 62% (high) of the total phosphorus load to Spring Lake (Table 3.2.4). The indirect estimates of internal load (Lauber 1999), based on changes measured from whole-lake samples, were well within the range of the direct measurements made as part of this study (i.e. 57% of total load). This provides additional confirmation that these internal load calculations are realistic estimates.

Table 3.2.4. Comparison of internal (this study and Lauber 1999) vs external (Lauber 1999) total phosphorus loading (tons/yr) in Spring Lake.

Category	External load (Lauber 1999)	Internal load (Lauber 1999)	Mean internal load (all sites; this study)
Low	2.2	--	2.8 (56%)
Medium (this study) or Average (Lauber)	3.1	4.1	5.9 (66%)
High	4.7	--	7.7 (62%)

Sediment Fractionation Data. NaOH-extractable SRP represents Fe/Al-bound phosphorus, whereas HCl-extractable SRP corresponds to Ca/Mg-bound phosphorus. The results of the sequential extractions for phosphorus are displayed in Figs. 3.2.9 and 3.2.10, respectively. Phosphorus concentrations associated with iron/aluminum (NaOH extractable) ranged from 123 µg/g to 200 µg/g (Fig. 3.2.9). Sampling location had no statistically significant effect on the amounts of NaOH-extractable phosphorus ($p > 0.05$). In addition, no statistically significant differences between NaOH-extractable phosphorus and treatments (aerobic vs anaerobic, and alum vs control) were observed ($p > 0.05$).

With the exception of Station 3, the HCl-extractable phosphorus concentrations were higher than NaOH-extractable P concentrations, and ranged from 126 µg/g to 513 µg/g (Fig. 3.2.10). A statistically significant difference between sites was noted (p = 0.01) for the calcium/aluminum-bound fraction, with Stations 3 and 4 being significantly lower than Stations 1 and 2. As with the NaOH-extractable fraction, a statistically significant difference between HCl-extractable phosphorus was not observed with respect to treatment. The ratio of NaOH-extractable to HCl-extractable phosphorus for the Spring Lake sediments was not statistically significant different with respect to aerobic vs anaerobic conditions and alum treatment vs control treatments (Fig. 3.2.11).

Figure 3.2.9. Concentration of NaOH-extractable phosphorus (Fe/Al-bound) in Spring Lake Sediments. Data are means (n = 3) ± 1 SD. (Sites 1-4. O=oxygen. N=nitrogen, T=alum, C=control.)
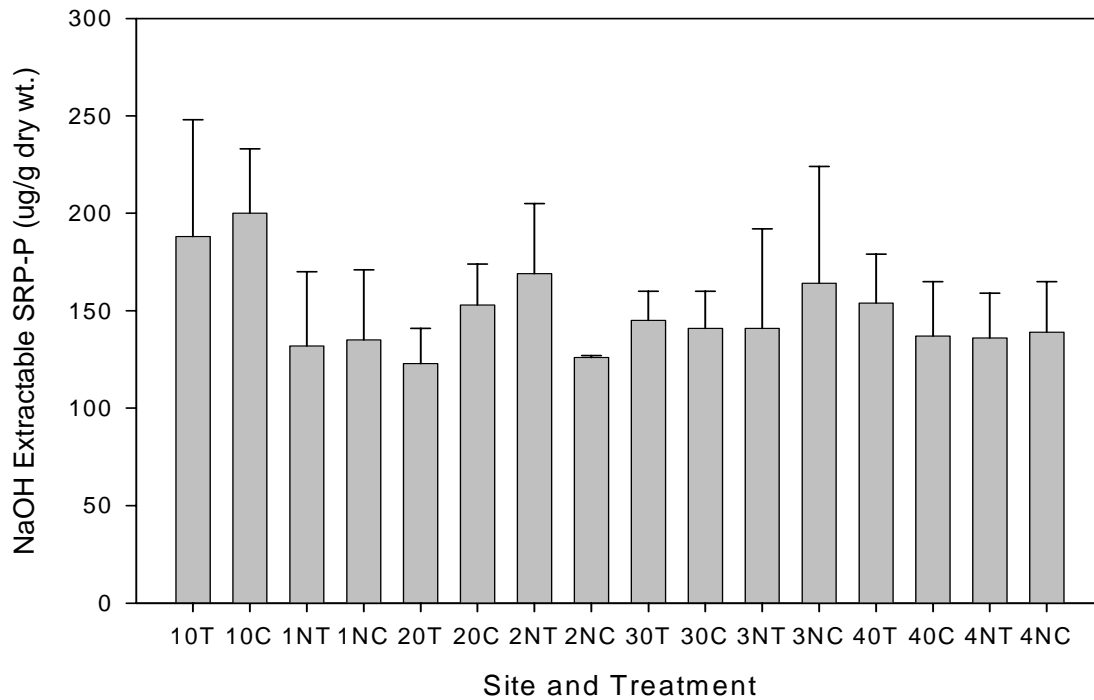
Figure 3.2.10. Concentration of HCl-extractable (Ca/Mg-bound phosphorus) in Spring Lake Sediments. Data are means (n = 3) ± 1 SD. (Sites 1-4. O=oxygen. N=nitrogen, T=alum, C=control.)
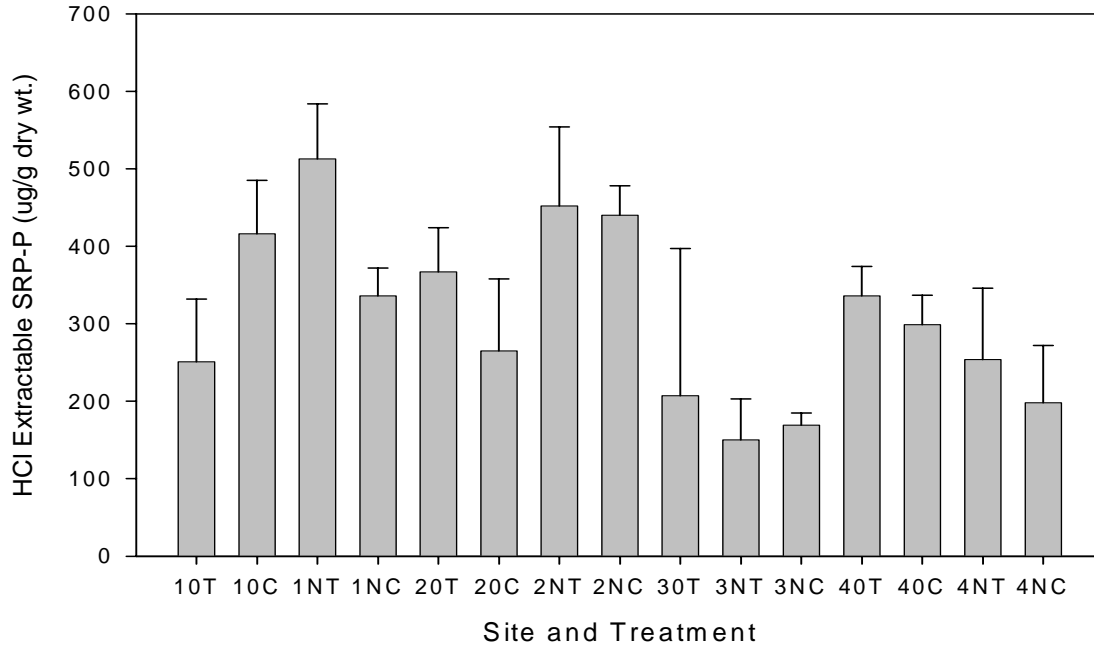
Figure 3.2.11. The NaOH-extractable/ HCl-extractable phosphorus ratio in Spring Lake Sediments. Data are means (n = 3) ± 1 SD. (Sites 1-4. O=oxygen. N=nitrogen, T=alum, C=control.)
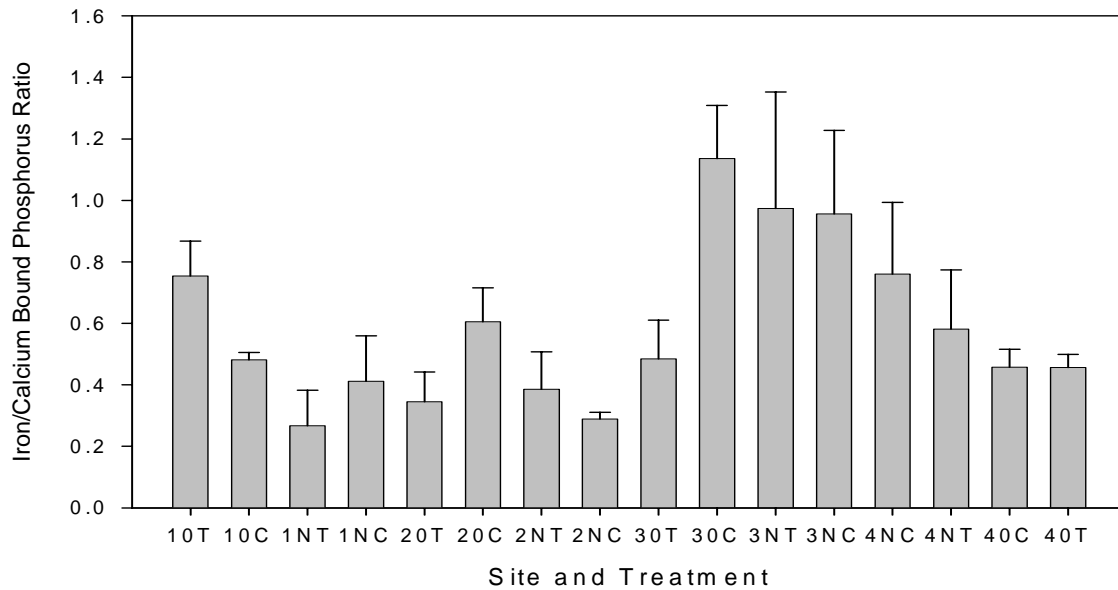
4.0 Discussion

Internal loading can be a significant source of nutrients in shallow, eutrophic lakes, and result in serious impairment to water quality (Welch and Cooke 1995, Steinman et al. 1999, Søndergaard et al. 2001). 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 tax dollars and created 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 data from this study clearly indicate that internal phosphorus loading is a significant source of P in Spring Lake, potentially accounting for somewhere between 56 to 66% of the total P load to the system. Given that the data in this study may play a role in deciding whether or not alum is applied to Spring Lake, it is critical that the assumptions built into these calculations are evaluated.

First, are the external load estimates (Lauber 1999) accurate? It is likely that these loads are underestimates because tributaries were not sampled during all the storm events, when much of the phosphorus attached to particles enters the lake. However, this is offset by the fact that tributaries accounted for a relatively low percent of external load in the summer when algal blooms are most severe. As a consequence, we conclude that these external load data are reasonable estimates.

Second, are the release rates from sediments in the core tubes representative of sediments and conditions throughout Spring Lake? Given the very small sediment area

covered by our cores relative to the entire lake, it is highly likely that not all sediment types were addressed in this study. We attempted to cover as much of the geographic range in Spring Lake as possible, but if we missed a large area that has high (or low) release rates, our data may be biased. In addition, it is likely that the laboratory set-up represented an optimal situation for release of phosphorus (constant anaerobic conditions), which would result in an overestimate of internal loading. It is encouraging that Lauber's estimates of release rates, generated independently and by an entirely different approach, were similar to ours, and suggests our internal loading estimates are good first-order approximations.

Third, how appropriate is the < 1 ppm threshold for P release? Under aerobic conditions, the basic premise is that oxidized iron will remain bound to phosphorus 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 phosphorus release rates (Boström et al. 1982, Søndergaard et al. 1992, and Petterson 1998). We used a 1 ppm threshold for DO; although there is no one universal threshold, reducing conditions are incipient at this point, and it was a value that we could measure accurately. Finally, were the extrapolations of anoxia to other years and other sites in Spring Lake appropriate? It is likely that the DO values at "Deep Hole" were lower, on average, than 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 likelihood that anoxic conditions occurred, at least occasionally, between October and April (thereby releasing P), when we assumed only oxic conditions. Even taking these factors into account, it is clear that internal loading is a significant contributor of total phosphorus to Spring Lake.

The P release rates from Spring Lake were greater than typically measured for eutrophic lakes (2 to 5 mg/m^2/d; Welch and Cooke 1995), and even approached some of the highest recorded release rates (30 to 60 mg/m^2/d; Nurnberg 1988). P release data from a number of shallow, eutrophic lakes were compiled in order to put the Spring Lake data into a broader context (Table 4.1). It is evident that internal loading rates in Spring Lake are reflective of rates measured in other problematic lakes around the world. If we apply the high release rates estimates for Spring Lake, then internal loading rates in Spring Lake approach some of the highest measured rates.

Table 4.1. Sediment flux rates of total phosphorus from lakes around the world.

Lake	Mean Depth (m)	P release rate (mg/m^2/d)
Arreso (DK)	2.9	40
Neagh (UK)	8.9	4.4
Alderfen Broad (UK)	0.6	3.5
Klamath (OR, USA)	2.4	6.0
Long (WA, USA)	2.0	2.6
Spring Lake (MI, USA)	6.0	1.6-33.8

Management strategies to control internal loading usually include sediment removal and chemical applications, such as aluminum, iron, or calcium salts (Cooke et

al. 1993). The main concerns associated with sediment removal (i.e. dredging) include:

1) liberation of nutrients and toxic materials associated with sediment resuspension, dredge agitation, and wind action; 2) finding appropriate disposal sites for dredged material; and 3) cost (Cooke et al. 1993). The main concerns associated with alum application include: 1) potential toxicity, especially under acidified conditions; 2) increased clarity of the water column, with a subsequent increase in submerged macrophyte growth; and 3) long-term effectiveness of treatment.

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, both SRP and TP release rates were virtually negligible when alum was applied. An in-lake alum treatment works primarily by generating an $Al(OH)_3$ blanket that covers the sediments, which sorbs and precipitates the phosphorus that otherwise would diffuse out of the sediments and into the water column (Cooke et al. 1993). The treatment also removes particulate organic and inorganic phosphorus-matter from the water column. It is critical that the integrity of the aluminum hydroxide be maintained for the treatment to remain effective.

Cost comparisons between sediment removal and chemical applications should be done with extreme caution due to the assumptions involved (cf. Peterson 1982). Prior analyses have shown that "end-of-treatment" costs (i.e. what it actually costs to complete a project) are approximately 30 times greater for dredging ($17,894/ha in 1991 dollars) compared to chemical application ($564/ha; Cooke et al. 1993). However, this difference goes down in size when the treatment costs are amortized over the effective life expectancy of a project; the amortized cost of a dredging project was $229/ha (1991

dollars) compared to the amortized cost of a nutrient inactivation project ($26.56/ha; Cooke et al. 1993).

In general, P release rates were higher at Sites 1 and 2 than at Sites 3 and 4. The Fe-bound phosphorus sediment fractions were similar among all sites, although the Ca-bound P sediment fraction was higher at Sites 1 and 2, but this should not account for higher P release rates. 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). These studies used 5 cm sample of the sediment core while this investigation utilized a 10 cm aliquot. It is possible that the inclusion of sediments from the deeper section introduced sufficient additional phosphorus to mask chemical changes from the alum treatment or the differences in redox conditions.

In summary, the findings from the current study: 1) confirm internal loading as an important source of phosphorus to the lake; and 2) show that alum application can be an effective method to control this internal load, at least based on these laboratory experiments. While an alum treatment is likely to have short-term benefits, an important management question remains: how long would an alum treatment 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 usually varies between 3 to 15 years, and is dependent on many factors, including:

(1) the morphometry of the lake, which influences the likelihood that the alum will be resuspended by wind-wave action, and no longer covers the sediments uniformly (Welch and Cooke 1995)

(2) the amount of alum added to the sediment, to ensure there is sufficient aluminum to bind to the P, but not add more than necessary because of financial or environmental concerns (Rydin and Welch 1998, Lewandowski et al. 2003)

(3) activity from bottom-swelling animals (i.e. bioturbation) in the sediments 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

(4) 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 Schrieve 1994)

(5) Water column pH, as circumneutral waters (pH 6-8) are optimal for creating an alum floc (Rydin and Welch 1998, Lewandowski et al. 2003)

(6) Rate of sedimentation in the water column because new organic matter that settles on top of the alum can reduce its ability to bind P (Lewandowski et al. 2003)

(7) 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 Deneke 1995, Søndergaard et al. 1999)

5.0. Conclusions and Recommendations

Based on the data generated in this study, we conclude the following:

- The internal load of phosphorus coming from the sediments in Spring Lake is approximately twice the external load of phosphorus entering Spring Lake.

- Phosphorus release from the sediments is greatest under anaerobic conditions.

- Phosphorus release rates, at least for the medium and high range calculations, were greater at Sites 1 and 2 than Sites 3 and 4, suggesting internal loading may be more problematic at the southern ends of Spring Lake.

- Alum treatment was very effective at reducing phosphorus flux from the sediments in Spring Lake.

We recommend the following:

- Continue laboratory studies, as practicable, to reduce the uncertainty regarding the long-term effectiveness of alum treatment. Prior studies have shown that alum treatments are not a permanent solution, so it is important to estimate the shortest and longest periods of time than an alum treatment would be effective.

- A pilot study, involving an alum application in a localized area of Spring Lake, to provide information on alum movement and effectiveness, under natural conditions.

- A vital prerequisite for restoring lake water quality is the removal of the underlying reasons for the impairment. Thus, regardless of the long-term effectiveness of an alum treatment, it is critical that external load reduction complement the chemical additions (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 and incentivized wherever possible.

6.0. References

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7.0 Appendix

A. Field data - Site 1.

Spring Lake Site 1   **Date:** 6/10/03

Depth	Temp	% DO	DO	Cond	TDS	Turb	pH	ORP	Chl a
m	C	% sat	mg/L	μS/cm	g/L	NTUs		mV	μg/L
1	17.76	126.5	11.31	601.9	0.3859	8.2	8.61	338	23.9
2	17.76	102.8	9.77	604.2	0.3865	8.2	8.69	328	28.3
3	17.76	101.7	9.68	604.3	0.3865	7.9	8.68	325	26.7
4	17.76	102.1	9.73	601.8	0.3854	7.6	8.64	323	23.3
5	17.56	92.8	8.92	608.8	0.3898	7.3	8.54	324	16.9
6	17.12	85.0	8.19	596.9	0.3839	6.8	8.43	325	14.2
7	16.78	75.7	7.28	590.1	0.3776	7.0	8.32	327	7.5
8	16.58	62.7	6.04	590.2	0.3777	8.0	8.17	330	6.2

Depth	Light	%
m	Umol/m2/s	of surf.
Surface	436	
0.1	207	47.477
0.5	90	20.642
1.0	42	9.633
1.5	21.3	4.885
2.0	10.6	2.431
2.5	5.9	1.353
3.0	3.1	0.711
3.5	1.7	0.390
4	1.0	0.229
5	0.34	0.078
6	0.12	0.028
7	0.06	0.014

27 ft

Secchi: 1.25 m   **Bottom:** 8.23 m

Conditions:

		Field Crew:
Time	9:45am - 11:20am	Al Steinman, Rick Rediske
Air temp	~20 C	Lori Nemeth, Eric Nemeth
Wind	slight breeze from SE	Bob Pennell - Deckhand
Sky	cloudy, some rain	Tony Fiore - Captain
Water	relatively calm	Pam Tyning (Progressive)

Extinction
Coefficient
1.439

Other Notes:

N 43deg 04.94'
W 86deg 12.25'

Site 2.

Date: 6/11/03

Depth	Temp	% DO	DO	Cond	TDS	Turb	pH	ORP	Chl a		Depth	Light	%
m	C	% sat	mg/L	µS/cm	g/L	NTUs		mV	µg/L		m	Umol/m2/s	of surf.
1	17.75	98.5	9.34	566.0	0.3618	9.5	8.63	318	21.7		**Surface**	1304	
2	17.75	94.1	8.97	566.0	0.3624	9.6	8.76	309	24.6		**0.1**	689	52.837
3	17.75	91.6	8.73	566.4	0.3626	9.1	8.77	306	28.2		**0.5**	240	18.405
4	17.73	89.9	8.56	566.2	0.3625	8.9	8.76	305	29.7		**1.0**	123	9.433
5	17.74	88.5	8.42	566.7	0.3624	9.0	8.75	305	28.1		**1.5**	55.4	4.248
6	17.73	88.4	8.41	565.8	0.3622	8.7	8.72	306	21.8		**2.0**	39.29	3.013
7	17.11	65.1	6.21	576.7	0.3689	7.8	8.40	311	11.9		**2.5**	18.54	1.422
8	16.70	50.0	4.74	575.7	0.3685	7.9	8.16	317	7.8		**3.0**	12.3	0.943
9	15.29	6.7	0.62	581.2	0.3721	7.8	7.93	323	3.3		**3.5**	4.058	0.311
											4	1.721	0.132
											5	0.4988	0.038
											6	0.1611	0.012
											7	0.05314	0.004
											8	0.012	0.0009

33 ft

Secchi: 1.0 m   **Bottom:**   10.06 m

Conditions: Field Crew:

Time	3:30pm - 5:30pm	Rick Rediske	
Air temp	75 F	Lori Nemeth	
Wind	calm	Eric Nemeth	
Sky	partly cloudy	Bob Pennell - Deckhand	
Water	calm	Tony Fiore - Captain	

Extinction
Coefficient
1.525

Other Notes:
N 43deg 05.34'
W 86deg 11.15'

Site 3.

Spring Lake Site 3   **Date:** 7/16/03

Depth m	Temp C	% DO % sat	DO mg/L	Cond µS/cm	TDS g/L	Turb NTUs	pH	ORP mV	Chl a µg/L
1	24.40	73.5	6.12	564.8	0.3616	18.5	8.53	306	5.3
2	24.14	70.9	5.92	566.9	0.3631	18.2	8.54	305	6.5
3	24.11	70.2	5.87	568.1	0.3634	17.2	8.51	307	6.5
4	24.04	68.0	5.68	569.2	0.3640	17.1	8.46	310	7.3
5	23.79	62.8	5.24	573.5	0.3671	17.3	8.35	314	7.5
6	22.73	17.0	1.47	600.5	0.3840	16.5	8.04	323	3.8

Depth m	Light Umol/m2/s	% of surf.
Surface	2417	
0.1	1859	76.914
0.5	739.2	30.583
1.0	235.5	9.743
1.5	91.83	3.799
2.0	44.12	1.825
2.5	22.81	0.944
3.0	10.79	0.446
3.5	5.345	0.221
4	2.505	0.104
5	0.588	0.024
6	0.1406	0.006

                                                    22 ft
Secchi: 1.0 m   **Bottom:**   6.71 m

Conditions: Field Crew: Extinction
    Time   10:45am - 12:15pm   Rick Rediske   Coefficient
    Air temp   _____   Lori Nemeth   1.721
    Wind   slight breeze   Eric Nemeth
    Sky   100% clear and sunny   Bob Pennell - Deckhand
    Water   calm   Tony Fiore - Captain

Other Notes:
    N 43deg 06.22'
    W 86deg 11.11'

Site 4.

Spring Lake Site 4 **Date:** 7/16/03

Depth	Temp	% DO	DO	Cond	TDS	Turb	pH	ORP	Chl a
m	C	% sat	mg/L	µS/cm	g/L	NTUs		mV	µg/L
1	24.76	65.2	5.41	552.3	0.3533	20.4	8.36	326	3.6
2	24.71	61.2	5.07	556.1	0.3561	20.0	8.39	325	7.8
3	24.24	55.3	4.53	573.6	0.3679	17.1	8.32	327	5.2
4	23.56	50.0	4.22	595.7	0.3812	10.8	8.27	330	4.9

Depth	Light	%
m	Umol/m2/s	of surf.
Surface	2253	
0.1	1174	52.108
0.5	308.1	13.675
1.0	93.43	4.147
1.5	32.69	1.451
2.0	12.88	0.572
2.5	5.618	0.249
3.0	2.918	0.130
3.5	1.344	0.060
4	0.6206	0.028

16 ft

Secchi: 0.75 m   **Bottom:** 4.88 m

Extinction
Coefficient

2.247

Conditions: Field Crew:

Time   9:00am - 10:30am   Rick Rediske

Air temp   25 C   Lori Nemeth

Wind   calm   Eric Nemeth

Sky   100% clear and sunny   Bob Pennell - Deckhand

Water   calm   Tony Fiore - Captain

Other Notes:

N 43deg 07.04'

W 86deg 09.98'

B. Phosphorus Release Data

Mean ($n = 3$) release rates of SRP and TP (mg P/m^2/d) from moderate release treatments. Data with different letters within a site are significantly different from one another.

Treatment	Site 1	Site 2	Site 3	Site 4
SRP				
O_2/no alum	$0.659^{A,B}$	0.0702^{B}	-0.827^{B}	-0.133^{B}
O_2/alum	0^{B}	-0.2661^{B}	-1.502^{B}	0.025^{B}
N_2/no alum	12.096^{A}	3.2376^{A}	10.084^{A}	4.852^{A}
N_2/alum	0^{B}	-0.4539^{B}	-1.905^{B}	0^{B}
TP				
O_2/no alum	0.3948^{X}	-1.988^{X}	0.161^{X}	-1.038^{X}
O_2/alum	-0.8481^{X}	-3.056^{X}	0.336^{X}	-1.652^{X}
N_2/no alum	26.7105^{W}	16.008^{W}	9.042^{X}	13.553^{W}
N_2/alum	-1.6375^{X}	-3.290^{X}	0.146^{X}	-1.477^{X}