PART VI: Sediments

Chapter 14

HETEROGENEITY OF PHOSPHORUS IN AQUATIC SEDIMENT

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ABSTRACT

Conventional thinking of phosphorus in aquatic sediments considers phosphorus, an internal loading nutrient most often responsible for harmful algae bloom formation in freshwater, as concentrating within the deepest part of a water body only to be released under summer, anoxic conditions. The author's field testing, laboratory results, and published literature findings by other authors document that phosphorus occurrence in and release from aquatic sediments can be spatially and temporally highly variable over a given water body. Areas of elevated phosphorus in sediment can be concentrated in shallow aerobic parts of a water body at the end of one year then released and taken up by algae or nuisance plants the following year, only to be deposited again at the end of the growing season at altogether separate and concentrated area(s) of the same water body, with the process repeating each year.

Field and laboratory analysis of surface water, sediment and algae collected from a lake between June 2010 and September 2012 documented the spatial and temporal heterogeneity of phosphorus in the lake, its release from sediment, and patterns of harmful algae blooms in the lake as a whole. By understanding the heterogeneity of phosphorus in aquatic sediment, areas of elevated phosphorus can be identified and efficiently removed in a controlled manner to reduce the magnitude of future harmful algae blooms or nuisance plant growth.

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1. INTRODUCTION

Phosphorus availability is regarded as the most important factor for determining the water quality of freshwater bodies (Søndergaard, Jensen and Jeppesen, 2003). For many years, it has been recognized that existing and historical external sources of phosphorus to water bodies often led to degradation of water quality, loss of aquatic habitat function, and impacts to human health and environmental receptors. In addition to health effects, all of these impacts can have a negative economic influence on real estate prices, fisheries, and ecotourism (Carpenter et al., 1998, and others). The growth potential of algae is also directly proportional to the available phosphorus concentration (Schindler, 1977; Carpenter et al., 1992; Stumm and Morgan, 1996; and others). Appropriately enough, much of the initial focus on reducing phosphorus-related impacts such as algae blooms, nuisance densities of plants, anoxic conditions and fish kills was directed at removing or controlling external sources of phosphorus loading (inflows) to water bodies. External control methods commonly included improvements to: storm water conveyance and treatment; land use practices; sanitary waste handling; and point source discharges. Once existing external sources of phosphorus were addressed, it was possible in some instances that internal sources may diminish over time due primarily to hydraulic flushing of a water body. Flushing of a water body is where the body of water volume is subject to loss over time through a stream or river (outflow); however, depending upon the characteristics of each water body, flushing may not occur or be minimal or restricted. In these high retention, low flushing rate situations, problems related to internal sources of phosphorus can persist for many years.

External loads to water bodies have been estimated by a combination of modeling and assigning loads to various watershed contributing land uses by identification of point sources, and to varying degrees, by using laboratory analysis of water quality within the receiving water body and its surface water inflows and outflows. When combined, this approach helped to identify existing areas of high nutrient external loading sources, and these external sources could then be targeted for improvement. Under this external input-output evaluation of phosphorus loading, the internal loading within the water body itself is often treated as a well-mixed receiving pool with a determined output flushing rate. If measured inflows in a particular contaminant like phosphorus exceeded the measured or estimated outflow volume, the difference was assigned as an internal

loading gain. High output concentrations relative to input would be assigned as a loss from a water body. With an initial focus on controlling external sources, there was little consideration given to defining the internal loading cycle itself. If completed at all, sediment sampling and laboratory analysis to evaluate internal loading was often limited to deeper parts of the receiving water body.

While researching the historical background regarding this deep water sediment sampling rationale, it seems that the origin of this approach was based on the assumption that the deepest portion would provide results representative of: 1) changes in nutrients/phosphorus over time as a whole within the receiving water body; 2) release of phosphorus under anoxic conditions; and, 3) to minimize the year to year variance posed by shallower water column sediment quality.

The input-output external loading assessment approach worked well enough for existing external loading but less so for: 1) historical external loading sources; 2) water bodies with minimal to no surface water inflows and outflows (high retention, low flushing); and, 3) for water bodies that already contained excess phosphorus.

Once excess phosphorus is present in a water body, it can be reused or recycled by aquatic biota (including harmful algae blooms and nuisance plant growth) for many years; this is the internal load. Recycling and reuse of phosphorus originates primarily from the microbial degradation and recycling of biogenic and particle-sorbed phosphorus when deposited onto aquatic sediment (Hallberg et al, 1973; Kamp-Nielsen, 1975; Gächter and Meyer, 1993; and others). As documented by this study and by others, phosphorus can also be released from sediment under either aerobic or anoxic conditions.

Now that the focus is turning towards addressing internal sources of phosphorus, it is important to recognize that phosphorus occurrence in water bodies can be both spatially and temporally variable, and not necessarily well mixed and uniformly distributed as often assumed under the earlier external loading assessment approach. When found, areas where phosphorus concentrates can be targeted to more efficiently remove excess phosphorus from a water body. There are also three primary, physical forms of available phosphorus in a water body: soluble reactive, colloidal or suspended, and fixed (either bound in sediment or within aquatic biota). Once the phosphorus is taken up by algae and plants, its distribution in the water body is directly related to where these algae and plants are located at the end of each growing season. When water temperatures in New England drop below about 12 degrees Celsius (about 50 degrees Fahrenheit) and sunlight radiance diminishes, the planktonic algae are less able to control their buoyancy, they drop out of the water column, and aquatic plants begin to die back. Some forms of harmful algae bloom species also form

the equivalent of seeds (akinetes and heterocysts) with sufficient carbohydrates and phosphorus to hatch when light radiance and water temperatures increase in the spring (Brunberg and Boström, 1992; Pettersson et al., 1993; Brunberg and Blomquist, 2003). Some algae species simply rest until water temperatures increase above 10 to 12 degrees Celsius in the spring.

Soluble reactive forms of phosphorus can be released from sediment when bottom waters of the hypolimnion become anoxic (Selig, 2003; Kleeberg and Kozerski, 1997; Gächter and Meyer, 1993; Cyr et al, 2009; and others). In New England, anoxic conditions can occur from late May through early September when water temperatures increase, the solubility of oxygen in water decreases, and aerobic bacterial degradation of biogenic detritus increases. Under common pH ranges in fresh water bodies, anoxic conditions favor the geochemical release of labile and redox sensitive forms of phosphorus from the sediment surface and into the overlying water column by diffusion of soluble reactive phosphorus (SRP).

As documented in this study, a large portion of the sediment-recycled internal phosphorus load also originates from aerobic portions of water bodies. Sediment phosphorus content and release in aerobic portions of the water body are not uniformly distributed, and release mechanisms are more difficult to characterize than the diffusive release of SRP under anoxic conditions.

Mechanisms of phosphorus release from sediment within aerobic portions of a water body include: diffusion of interstitial sediment pore water through the commonly oxic sediment-water interface; decomposition of biogenic seston; bioturbation; ebulation; physical forcing of sediment and pore water release by wave action and convection currents; boat motor turbulence; or sediment resuspension (Holdren and Armstrong, 1980; Søndergaard et al, 2001; Eckert et al, 2003; Cyr et al, 2009; and others). The hydrologic interaction of ground water with surface water and sediment pore water would also contribute (positively or negatively) to phosphorus flux at the sediment-water interface. Another important, but less frequently referenced source of phosphorus release is directly related to recruitment {return of living and newly formed algal cells (germlings) to the water column} (Brunberg and Blomquist, 2003; Karlsson Elfgren, 2003).

Phosphorus is a particle-reactive element that rapidly binds or adsorbs to suspended and particulate matter, including to algae cells and plant surfaces. Once released to aerobic portions of the water column, SRP is commonly only soluble for a very brief time period, approximately 15 minutes. As such, once phosphorus is released into the water column it either remains in anoxic bottom waters, can be transported in aerobic waters as a particle or colloid, or bound to larger solid surfaces such as plants, debris and algae cells.

In any case, it is important to recognize that the majority of phosphorus returns to the sediment surface as organic phosphorus bound within biotic cells and seston, a very loose, predominantly organic material containing detritus from bacteria, plants and animals. Some of the settled seston algae matter remains viable to produce algae blooms when the sunlight increases and water warms in early to late spring. Other biologically-formed molecules containing phosphorus need to be broken down by bacterial action before the phosphorus can be recycled and made available for uptake by aquatic biota (Hallberg et al, 1973; Kamp-Nielsen, 1975; Gächter and Meyer, 1993; and others).

Treatment of harmful algae blooms or nuisance concentrations of plant life without actually removing the phosphorus, can lead to repeat or new occurrences of algae blooms and nuisance plant growth in the future. If excess phosphorus remains in a water body, algae and plants can continue to use any "recycled phosphorus" to proliferate at concentrations that may be harmful to humans and other environmental receptors/users.

Most of the phosphorus that leads to nuisance concentrations of algae and plants is then at some point organically-bound phosphorus. This is the phosphorus that is taken up and bound to other elements like carbon and nitrogen to help form algae and plant cell materials. When the algae and plant material die, or get eaten and excreted by aquatic fauna like zooplankton, shellfish and fish, the detrital matter falls to the bottom of the water body where ever the algae or plant material life cycle ended. These detrital or organic phosphorus accumulation areas can be in deep or shallow areas of the water body. For gas vacuolate algae, like some types of cyanobacteria, their seasonal life cycle essentially ends when the water temperature drops to below approximately 12 degrees Celsius, at which point they are no longer able to regulate their buoyancy and will sink to the bottom. Pelagic algae blooms are not always uniformly distributed within a water body, so depending upon water basin characteristics such as current, bathymetry, littoral characteristics, wind fetch, and water temperature dropping below the gas vacuolate critical temperature of 12 degrees Celsius, high volumes of algae bloom cells, detritus, and organic bound phosphorus can be concentrated in specific areas of a water body.

2. STUDY AREA, SAMPLING AND ANALYTICAL METHODS

From June 2010 until September 2012, the author has evaluated the spatial and temporal variability of phosphorus in the top five centimeters of sediment

within littoral and profundal portions of Lake Attitash in Amesbury, Massachusetts, USA. The Lake Attitash study location is depicted on Figure 1.

FIGURE 1 - General Study Area, Lake Attitash, Amesbury, MA

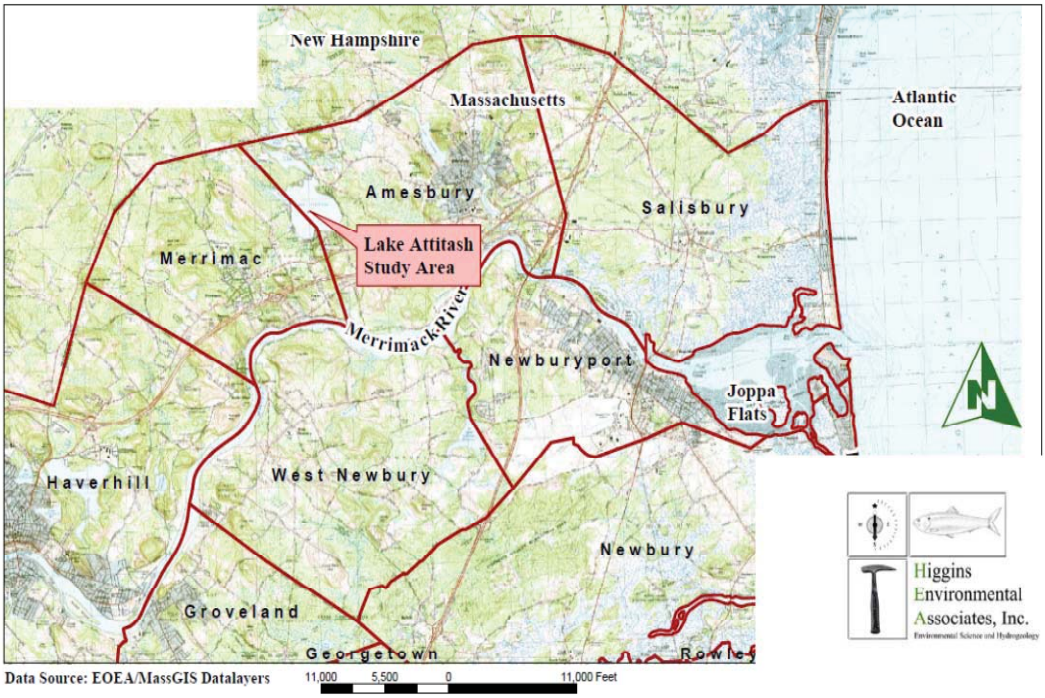


Figure 1. General Study Area, Lake Attitash, Amesbury, Massachusetts

Lake Attitash is an approximately 400 acre eutrophic water body in northeastern Massachusetts. The lake and its water quality have been extensively studied by the Massachusetts Department of Environmental Protection, the U.S. Environmental Protection Agency, the University of New Hampshire and others since the 1970s. Initial efforts to control external sources of phosphorus loading were formally implemented decades ago (connection of homes to public sewer in the 1980s), and efforts to assess and control other potential external sources have been ongoing since the 1980s. Yet, impacts from the internal recycling of phosphorus already in the lake remain in the form of recurring harmful algae blooms, water contact health-related restrictions, and nuisance densities of aquatic plant growth, and as such, the lake was well suited to evaluate the spatial and temporal heterogeneity of phosphorus in aquatic sediment.

The mean depth of the lake is between 2 to 3 meters with two deep basins approaching 6 to 10 meters in depth, respectively. As confirmed by the author and by hydroacoustic surveys of the U.S. EPA, littoral shallow water areas extend

up to approximately 100 feet from the shoreline around the majority of Lake Attitash with a larger, littoral area located within the northern portion of the lake. Profundal areas, deeper water areas where light penetration is minimal and seasonally anoxic conditions occur, as confirmed by SCUBA diving, U.S. EPA's hydroacoustic surveys, and long term field chemistry and Secchi disk readings since the 1970s, are located in areas of the lake where the depth of the water column exceeds 3 meters. Figure 2 depicts the relative extent of littoral and profundal areas by plant coverage. Based on the author's SCUBA diving surveys, mapped areas on Figure 2 with less than 40 percent plant coverage can be considered profundal.

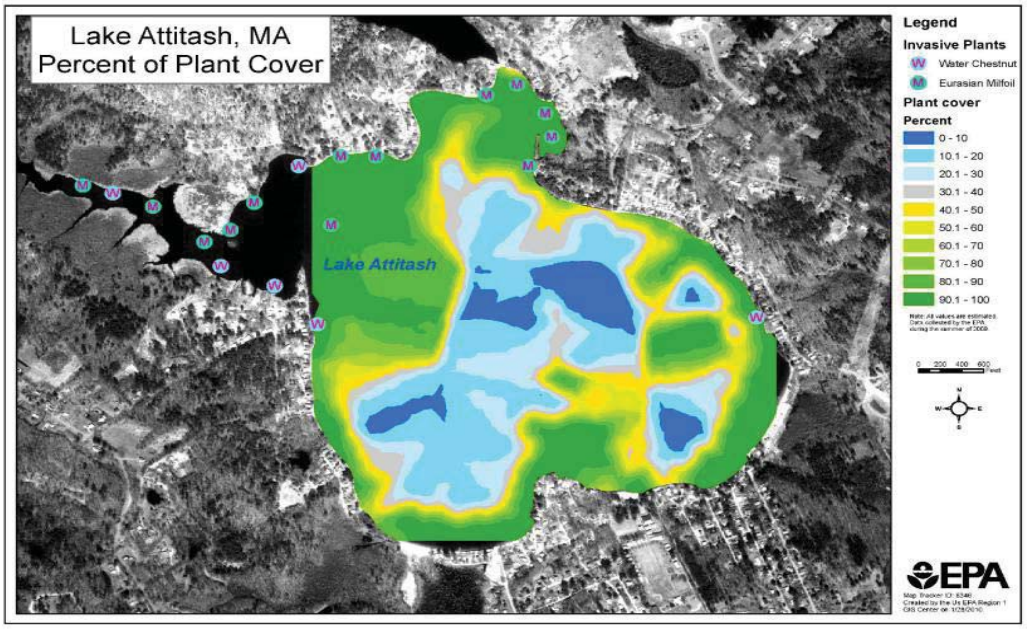


Figure 2. Percent Plant Coverage, Lake Attitash hydroacoustic survey, U.S. EPA, 2010.

In 2010-2011, the author initially completed a pilot study in Lake Attitash for an innovative phosphorus removal system, called the P-Pod™. As part of the pilot study, sediment samples were collected by SCUBA diving from the top five centimeters of sediment in this portion of the lake from June through December 2011. Water samples from the same portion of the lake were collected by either direct immersion of laboratory glassware, or through the use of a small peristaltic pump and a fixed-in-place, dedicated, polyethylene tubing.

In 2012, to expand upon information gained by the 2010-2011 pilot study, the author completed four (January, June, August and September) rounds of sediment

sampling (between 15 to 20 discrete samples per round) within littoral (less than 3 meters) and profundal (greater than 3 meters) areas of the lake. Sampling stations are depicted on Figure 3.

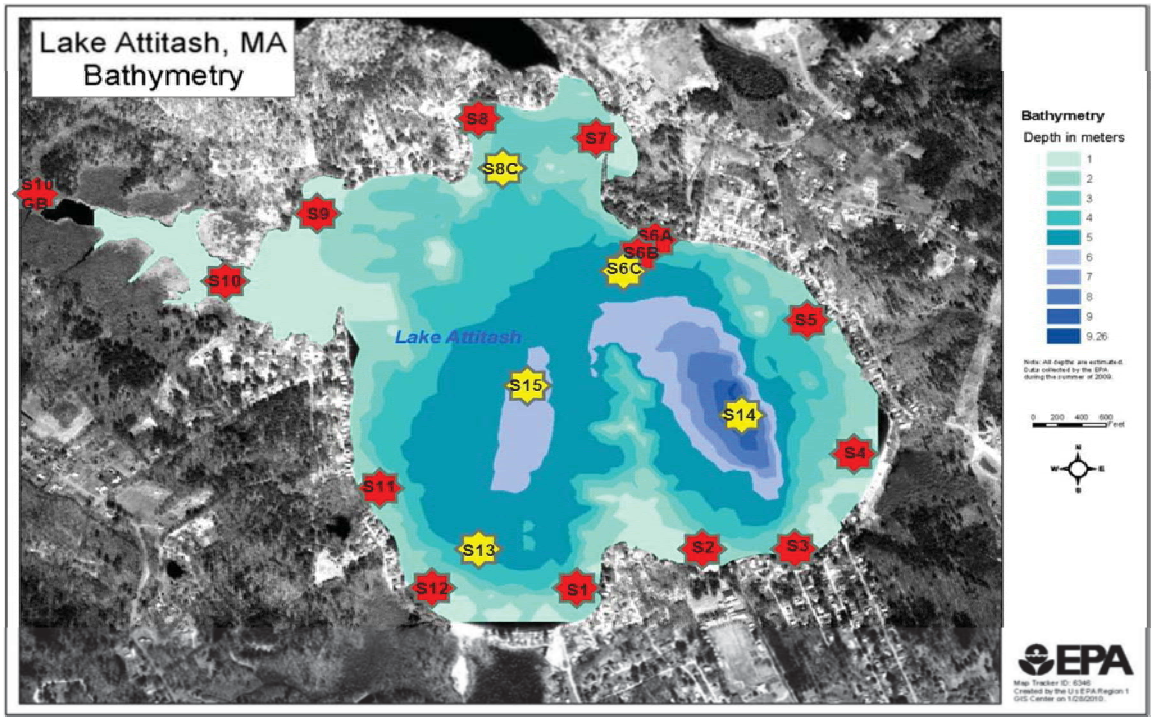


Figure 3. Sediment Sampling Locations, Lake Attitash (red symbols are littoral stations, yellow are profundal). Source of base map: U.S. EPA 2010 Assessment.

In 2012, sediment samples were collected through the use of a scoop and an impermeable bag attached to an extendable and graduated pole, as developed by the author for this sampling program. A string and weight system was used to open and close the bag at the desired sampling interval. Sediment samples were collected from approximately the top five centimeters of sediment at each location.

Each round of sediment sampling from Lake Attitash included one duplicate sample. The relative percent difference (RPD) between duplicate sample results for each sampling round was within acceptable limits (less than 25 percent). All samples were analyzed for total phosphorus content by U.S. Environmental Protection Agency (US EPA) Method 6010C (inductively coupled plasma- atomic emission spectrometry). Additionally, the June, August, and September 2012 sediment samples were also initially ashed by the ignition method described by Andersen (1976) at 550 degrees Celsius for one hour prior to laboratory extraction

and analysis. The acid digestion of the ashed samples used a combination of nitric and hydrochloric acid, and hydrogen peroxide. All results were reported on a dry weight basis.

During each sampling round from June to September 2012, water column measurements for pH, temperature, dissolved oxygen, conductivity, and oxidation reduction potential were collected at regular depth intervals at the deepest water column sampling station (S14) and at one or more littoral sediment sampling locations. Measurements were collected directly through the use of a Yellow Springs Institute (YSI) 650 MDS data logger and a 600XL multiparameter sonde on an eight meter cable. As such, the full depth of the water column at the deepest station (S14) of approximately 10 meters could not be assessed. The YSI was calibrated at the start and end of each field day using standard calibration solutions and a two point calibration curve for pH of between 7 and 10 pH units, the expected range for pH within the water column. Dissolved oxygen was calibrated at ambient, moist air conditions assumed to be representative of 100 percent dissolved oxygen in water.

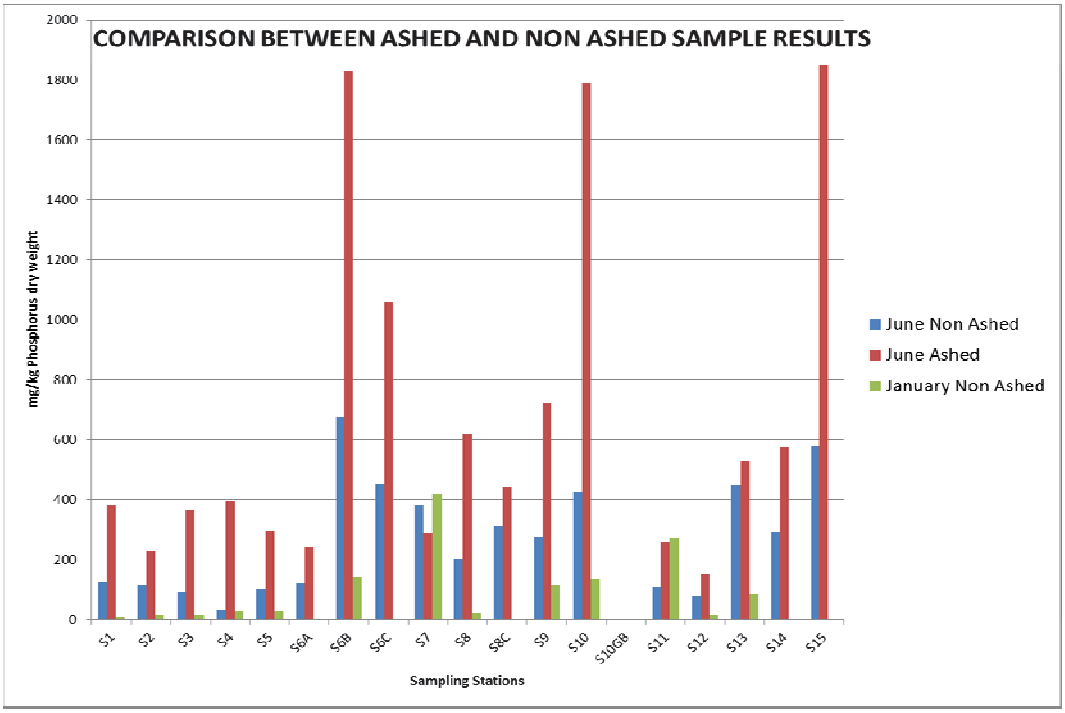
In September 2012, when present at sampling locations, samples of benthic algae (Nitella or filamentous algae, depending upon location) were collected using a small rake and submitted for the same analysis by ashing and acid extraction as the sediment samples. Benthic algae was not present at each sampling station and when present, degrees of coverage varied. Benthic algae were not visibly present at profundal sampling locations (water column depth of greater than 3 meters).

3. RESULTS

For Lake Attitash sediment samples, total phosphorus concentrations at all stations varied from 30 to 2,370 milligrams per kilogram (mg/kg) dry weight for ashed samples. Non-ashed samples typically had much lower total phosphorus results for the same sampling locations. Non-ashed total phosphorus concentrations ranged from 8.69 mg/kg to 667 mg/kg dry weight for all stations. A sediment sampling round collected in January 2012 was not ashed. In June 2012, each sediment sample was analyzed separately by both non-ashing and ashing the sample prior to acid digestion and extraction in accordance with U.S. EPA Method 6010C. Figure 4 depicts a comparison between ashed and non-ashed sediment samples from January 2012 to June 2012. As a trial run, ashing was also completed at a lower temperature (330 degrees Celsius) for one hour and compared to a duplicate run at 550 degrees Celsius for the same sample. Total phosphorus results for the lower temperature were less than that obtained at 550 degrees Celsius. This was an important evaluation as phosphorus can be lost to

sublimation at temperatures greater than approximately 525 degrees Celsius; depending primarily upon calcium content (Andersen, 1976).

Figure 4. Variance between Total Phosphorus for ashed and non ashed sediment samples.



All subsequent sampling rounds in August and September were also ashed at 550 degrees Celsius following the method by Andersen (1976) prior to analysis by U.S. EPA Method 6010C for total phosphorus. Laboratory results for each sampling round from June through September 2012 are summarized in Figure 5.

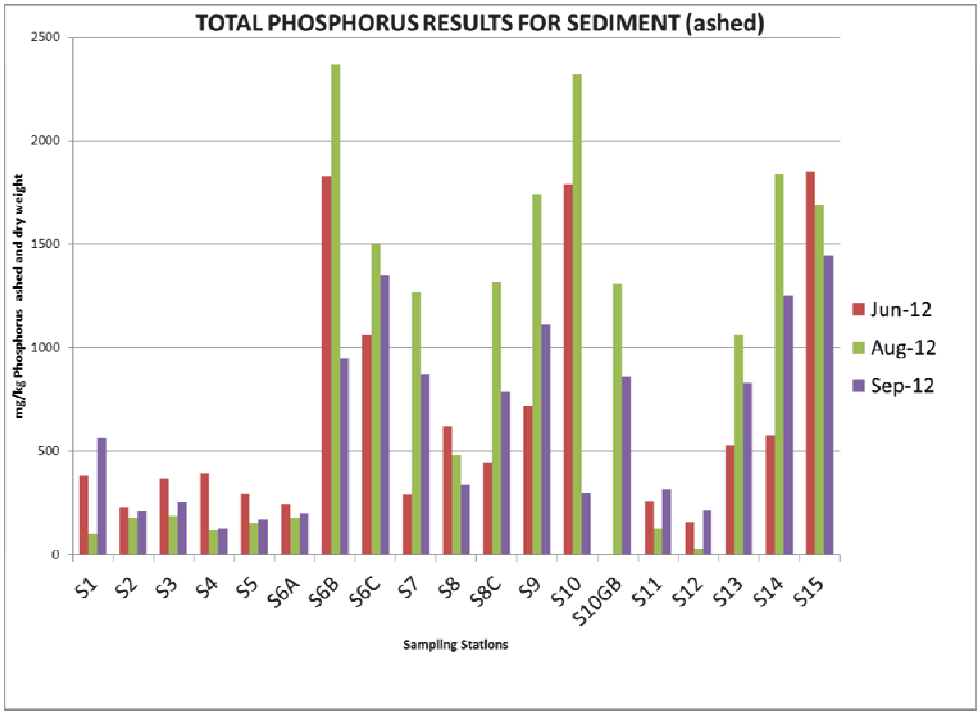


Figure 5. Summary of Total Phosphorus Results for Sediment June to September 2012, Lake Attitash. Results are ashed, extracted and reported as dry weight.

To summarize water column field geochemical parameters for the deep station (S14) from June through September 2012 (by minimum and maximum dissolved oxygen depths):

June 2012 Field Parameters Deep Station (S14)

D.O. (mg/l)	**Depth (ft)**	**ORP (mV)**	**pH (s.u.)**
2.65 (minimum)	14	-9.9	7.46
4.19 (maximum	4.5	5.6	8.14

August 2012 Field Parameters Deep Station (S14)

D.O. (mg/l)	Depth (ft)	ORP (mV)	pH (s.u.)
0.58 (minimum)	23.6	-204	7.55
8.96 (maximum	10.7	2.2	7.7

September 2012 Field Parameters Deep Station (S14)

D.O. (mg/l)	Depth (ft)	ORP (mV)	pH (s.u.)
1.24 (minimum)	20.5	-205.4	7.16
9.21 (maximum	5.2	44.4	7.68

During June, we were unable to identify an anoxic layer (dissolved oxygen less than 2 mg/l) in the water column for a maximum depth of monitoring of 19 feet on that day. Near anoxic conditions were noted in June at the 14 foot sampling interval, but dissolved oxygen content increased above and below 14 feet. However, during an initial monitoring event on May 20, 2012 we confirmed anoxic conditions at the deep station (S14) at a depth of 18.1 feet with a corresponding oxidation reduction potential of -116 millivolts and a pH of 8.83 units. In August and September 2012, anoxic conditions (<2 mg/l DO) in the water column were noted at depths greater than 11 and 20 feet, respectively.

So based on field data collected by this study, as summarized in the preceding tables and text, from May to September 2012 the lake was anoxic at depths greater than 18 feet (6 meters). Monitoring at littoral stations (< 3 meters) during all sampling rounds and within one foot of the sediment surface noted dissolved oxygen concentrations at or near saturation, oxidation reduction potentials between 5 to 182 millivolts, and a range of pH between 7.66 to 8.25 units. Historically, the author has obtained elevated pH readings throughout the water column (surface to 19 feet) of up to 10.35 units, with dissolved oxygen concentrations in excess of 100 percent saturation (October 2009 sampling at deep station S14). During the author's 2011 pilot test for the P-Pod^{TM}, used in this case to capture phosphorus released from sediment, pH in this littoral area ranged between 4.97 to 10.84 units from June to December 2011.

The P-Pod^{TM} is a new and innovative device and process (patent pending) developed by the author to remove excess nutrients/contaminants from water bodies. Using the present study findings on phosphorus heterogeneity in sediment as a potential P-Pod^{TM} application example, the author has documented that there are relatively mobile and fixed pools (concentrated areas) of phosphorus in aquatic sediment. The primary purpose of the P-Pods would then be to remove selected areas of concentrated phosphorus from sediment before the phosphorus (or phosphorus containing biotic cells) could be released back into the water column and used by future harmful algae blooms or nuisance/invasive plant species.

The year 2012 was an unusually warm period with record breaking and consistently elevated air temperatures from March through July. Lake Attitash did not completely freeze over during the winter of 2011-2012. Water temperatures during 2012 ranged from 14.75 degrees Celsius (18.1 feet at the deep station S14) in May to 28.5 degrees Celsius (83 degrees Fahrenheit) in August (at 1.3 feet from the deep station). Field chemistry and water temperatures were not recorded during the January 2012 sampling round. From June through September 2012, the littoral stations (even those with full southerly exposure) were up to 5 degrees Celsius cooler than the shallow water at the deep station (S14). This temperature difference may be related to ground water baseflow contribution into the lake and amelioration of water temperatures within thinner water column littoral areas of the lake.

Of the approximately fifteen sampling stations sampled in June, August and September 2012, three sampling locations routinely contained the highest concentrations of total phosphorus in sediment: samples S6B, S10 and S15. The first two sampling locations are located within littoral areas of the lake at water column depths of 3 meters or less. These areas have been documented as consistently being within aerobic portions of the lake's water column. The last sampling location, S15, is located within a profundal area of the lake at a depth of approximately 5 meters within one of the two deepest basins. This deeper area is commonly subject to anoxic (<2 mg/l dissolved oxygen) conditions for part of each summer (May through early September). Total phosphorus results for ashed sediment samples from June to September 2012 are depicted on Figure 5. Samples collected at depths of 3 meters or less (littoral areas) include samples: S1, S2, S3, S4, S5, S6A, S6B, S7, S8, S9, S10, S10GB, S11, and S12. Profundal sediment samples collected at depths greater than 3 meters include: S6C, S8C, S13, S14 and S15.

Total phosphorus results varied significantly throughout lake sediment stations, and between littoral and profundal areas. From June to September, total phosphorus results by station showed a general decrease (release of phosphorus)

in littoral stations. Total phosphorus in sediment at littoral stations S1 and S7 increased slightly (gained phosphorus) from June to September. In contrast to littoral sampling areas, with the slight exception at station S15, profundal and anoxic, deep sampling stations generally increased (gained) in total phosphorus content from June to September.

For the three stations with the highest concentrations of total phosphorus in June (Stations S6B, S10 and S15), by September two of these continued to have high concentrations of total phosphorus in sediment (S6B and S15), but the total phosphorus concentration at S10 had a significant decrease (release) of total phosphorus. Figure 6 depicts the concentration of total phosphorus released (+) or gained (-) at each station from June to September 2012.

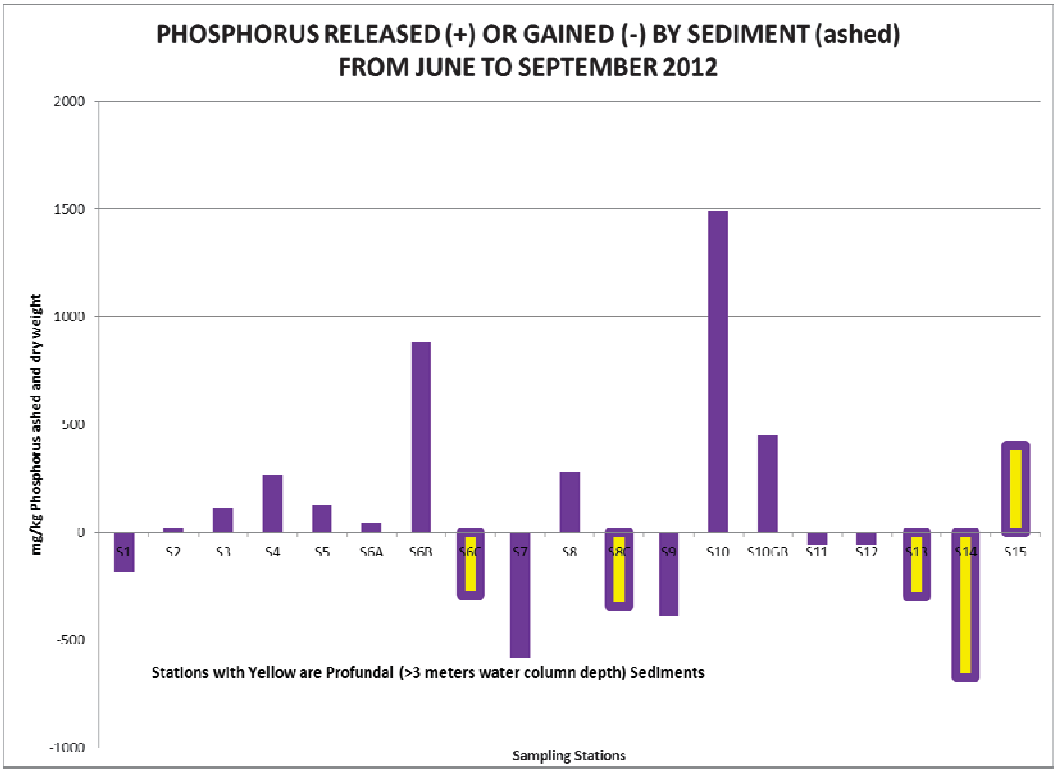


Figure 6. Total Phosphorus Released (+) or Gained (-) at each sample station. Stations with yellow inserts are profundal, all others are littoral.

Littoral sampling stations included sediment types ranging from a coarse to fine sand and fine gravel to a thin layer of very fine silt and detritus. Higher concentrations of total phosphorus were noted within areas of very fine sediment or detritus. Based on SCUBA diving visual observations, areas of very fine sediment in littoral and profundal areas were easily disturbed and almost smoke-

like. A wave of the hand would cause the upper layer of sediment to be resuspended. In littoral areas, the very fine silt layer was typically only a few centimeters thick. The thickness of very fine silt in profundal areas increased with water column depth (greater than three feet near stations S14 and S15).

By September 2012, benthic coverage of submerged algae and macrophytes at some stations became readily apparent. Coverage by benthic algae approached 100 percent at Stations S1, S6B, S7, S8, S9, S10, S10GB, and S12. Other stations contained pockets of near complete benthic algae coverage or less with approximately 40 percent coverage overall within 10 feet of the sampling stations. Laboratory results for samples of benthic algae collected in September 2012 are summarized on Figure 7. Results for total phosphorus in all algae samples were elevated and in part likely included particulate total phosphorus settling or attaching to benthic algae. During sampling, care was taken to keep fine sediments on algae intact.

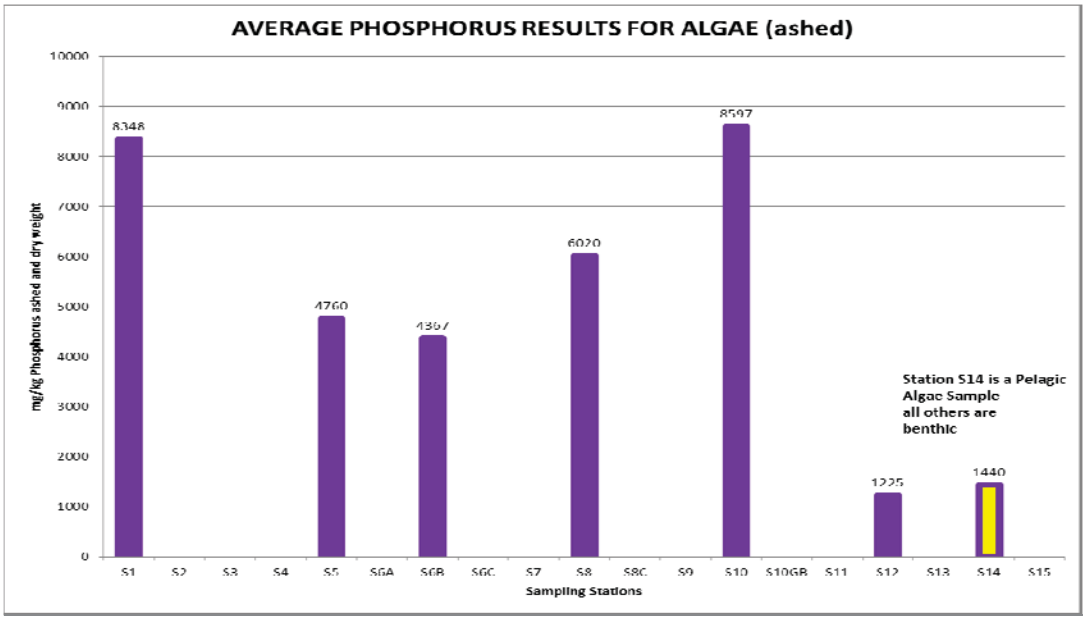


Figure 7. Total Phosphorus Results for Algae. Algae samples were ashed, extracted and reported as dry weight. The yellow insert designates a pelagic (suspended) algae sample collected from the deep station. All others are littoral, benthic algae samples.

By comparing total phosphorus in sediment results to total phosphorus in algae at the same locations where sufficient benthic algae was present for sampling, it is apparent that some portions of the lake have relatively stationary (or fixed) pools of phosphorus that may be exchanged primarily between sediment and overlying benthic algae and plants (Stations S6B and S10), whereas

other areas such as at stations S1, S5 and S8 have gained phosphorus (mobile phosphorus pools) during the 2012 monitoring event.

From June through September 2012, a dense layer of suspended (pelagic) algae (cyanobacteria species) was present at approximately 5 to 6 meters within the deepest portion of Lake Attitash at Station S14. The deep algae layer was apparent by echo sounding from the sampling boat, and also confirmed by discrete water column sampling by the author and by the University of New Hampshire during class field trips (personal communication with Lake Attitash Association representatives). Based on the author's assessments, the deep suspended algae layer was not present within the second deep basin at Station S15. Laboratory results of the suspended algae collected at Station S14 (deepest area of the lake) by the author in September 2012 are summarized on Figure 7. Total phosphorus content of the suspended algae was similar to the level of total phosphorus in sediment at this same location.

From 2009 to present, the Massachusetts Department of Public Health (MassDPH), and to varying degrees others including the U.S. EPA and University of New Hampshire (UNH), have sampled primarily water within Lake Attitash to evaluate the nature and occurrence of nutrients, the phytoplankton cyanobacteria, and in part to test for the presence of the cyanobacteria-related toxin microcystin. During weekly monitoring events from June through September 2012, MassDPH frequently detected algae cell counts greater their 70,000 cells per milliliter (cells/ml) guideline and/or confirmed the presence of algae scums in excess of their guidelines for water contact. In 2009, a maximum algal cell count of 350,000 cells/ml was detected by MassDPH in Lake Attitash. The 2009 harmful algae bloom persisted for eight weeks and a fish kill was confirmed by MassDPH during the bloom event and reported to the Center for Disease Control. Fish kills were observed by the author in 2009 through 2012, and have been reported by lake front property owners in the past. In 2010, UNH completed an algae survey of the lake and confirmed that algae cell counts (density) varied throughout the lake surface (top 3 feet). The spatial distribution of cyanobacteria detected in lake water and documented in the 2010 survey report is depicted on Figure 8. Algae cell counts in lake water reported earlier by UNH in October 2009 were 200 times greater in concentrated (algae bloom) areas near the shoreline than in the deepest portion of Lake Attitash (S14).

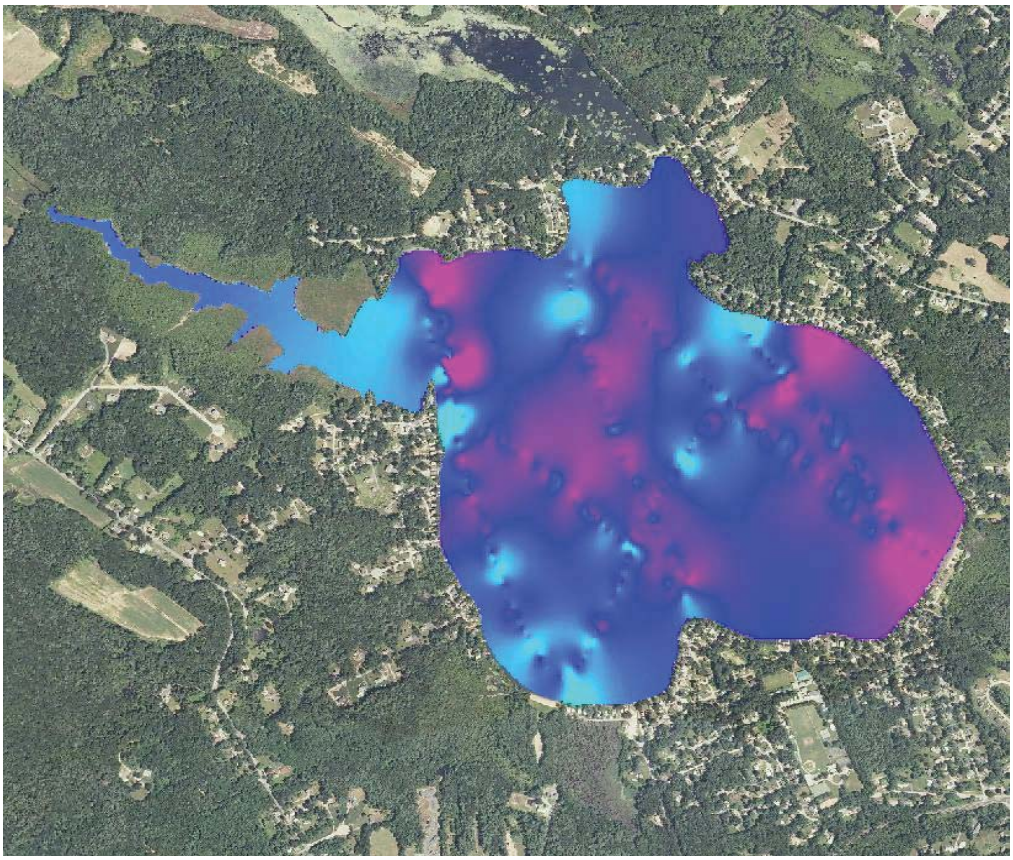


Figure 8. Spatial Distribution of Cyanobacteria in lake water, 2010. Source: University of New Hampshire, Citizens Cyanobacteria Monitoring Program Report for Lake Attitash, Amesbury, Massachusetts. 2010. Areas in "red" color are concentrated algae cell areas.

4. DISCUSSION AND CONCLUSIONS

Study results of aquatic sediment and algae monitoring from 2010 through 2012 in Lake Attitash have documented that phosphorus in aquatic sediment and harmful algae blooms in lake water are spatially and temporally variable throughout the lake. The majority of total phosphorus in sediment released from June through September 2012 occurred within aerobic, littoral areas whereas deeper, seasonally anoxic areas were typically net gainers for total phosphorus. While these results contradict the general convention that phosphorus release is greatest under anoxic conditions, it is important to note that anoxic conditions were present in deeper portions of the lake prior to the June 2012 sampling round and to some undetermined extent in this study, some more labile, redox-sensitive

portions of the total phosphorus content in sediment within the deeper basins may have already been released under anoxic conditions present before sampling of sediment in June 2012. 2012 was an unseasonably warm year and anoxic conditions within deeper basins occurred earlier than in most prior monitored years since the 1970s.

We interpret the variance in total phosphorus results between ashed and non-ashed analytical methods for the same sediment sample set as attributable to some combination of high moisture content, low percent solids, and an organic fraction of total phosphorus that without ashing may not be readily amenable to acid digestion by common laboratory methods. As phosphorus is the primary limiting nutrient in fresh water systems, once present, it would be readily taken up by the biotic community and bound, often strongly, within living and dead cells, akinetes and heterocysts, and to some extent used again by the same biotic communities when growth conditions (temperature and light radiance) are favorable.

Although classifying the actual modes of phosphorus release from sediment in aerobic, littoral or anoxic, profundal areas of the lake was not the objective of this study, it is important to note that in addition to well documented and conventionally prescribed diffusive release of redox sensitive forms of phosphorus under anoxic conditions, other mechanisms of phosphorus release contribute to internal loading including: resuspension of sediments; release of phosphorus from sediment pore water; temperature sensitive release mechanisms associated with increased biological activity; and direct transport of phosphorus from sediment to the water column by algae cells. Cyanobacteria, other forms of benthic and suspended algae, and macrophytes have evolved over millions of years, competing with each other in varied environments to acquire the nutrients they need to proliferate. In freshwater, the limiting nutrient is usually phosphorus. As the concentration of phosphorus increases, so do the algae and plant communities that are best able to thrive in a particular environment. This creates a dynamic environment where the spatial and temporal concentrations of phosphorus, algae, and plant communities tend to vary within each water body. Some water bodies may have very limited littoral zones, or have dominance by one or several algae or plant species that may lead to more uniform distributions of phosphorus in water or sediment.

The findings of this study have documented the importance of taking into account the spatial and temporal heterogeneity of phosphorus content in aquatic sediment. By understanding the spatial and temporal changes for phosphorus in a water body, areas of excess phosphorus can be efficiently captured and removed. As the overall volume of internal loading phosphorus is reduced, the occurrence and density of harmful algae blooms and nuisance plants would diminish.

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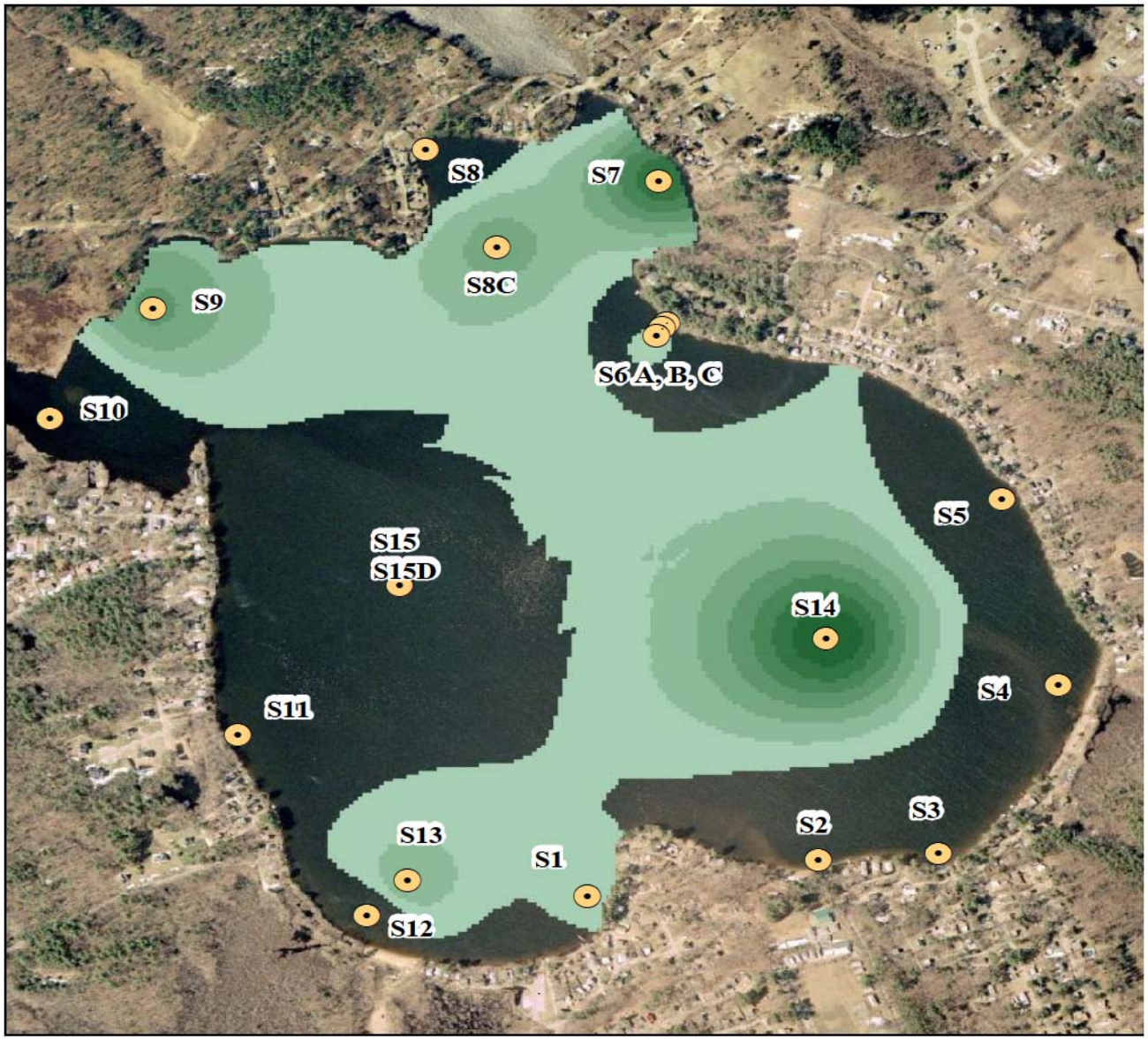
Areas of Total Phosphorus Gain (June to September)



Legend

June to September Gain (mg/kg)

- 0 - 75
- 75 - 150
- 150 - 225
- 225 - 300
- 300 - 375
- 375 - 450
- 450 - 525
- 525 - 600
- 600 - 675

N

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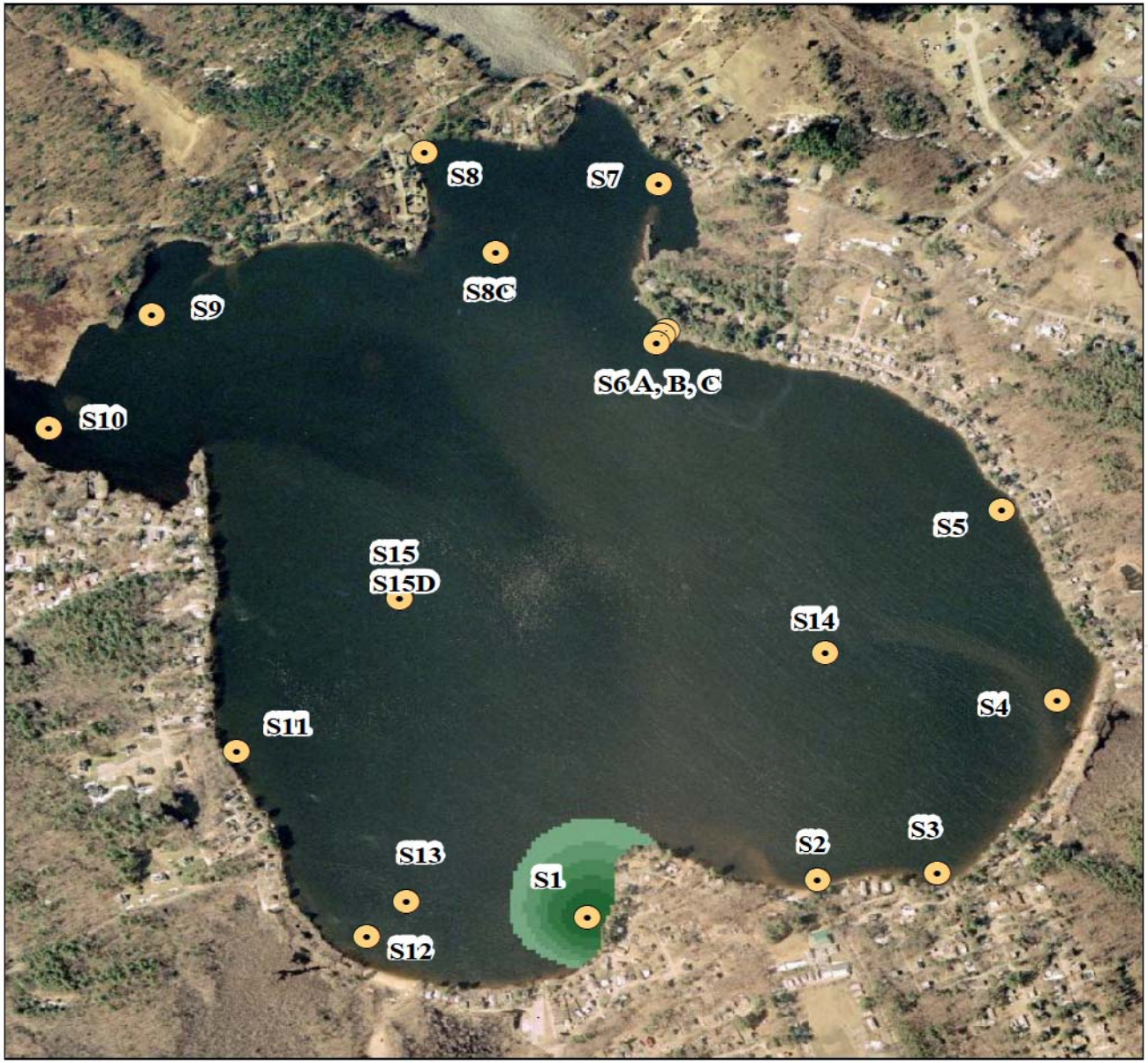
Areas of Total Phosphorus Gain (August to September)



Legend

August to September Gain mg/kg

- 0 - 51
- 51 - 103
- 103 - 154
- 154 - 206
- 206 - 257
- 257 - 308
- 308 - 360
- 360 - 411
- 411 - 462

N

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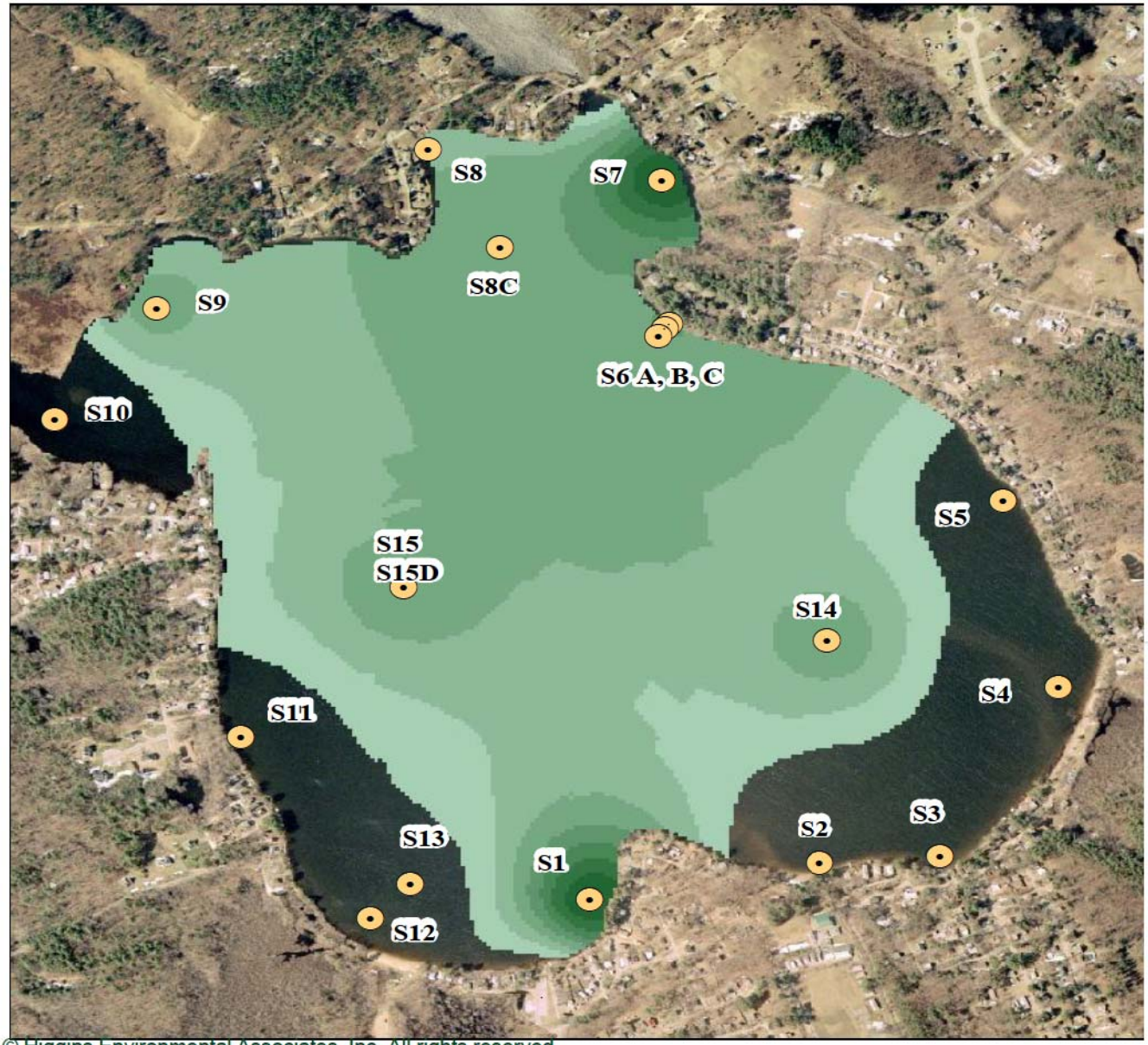
Areas of Total Phosphorus Gain (September to November)



Legend

September to November Gain (mg/kg)

- 0 - 139
- 139 - 279
- 279 - 419
- 419 - 558
- 558 - 697
- 697 - 836
- 836 - 976
- 976 - 1,115
- 1,115 - 1,254

N

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