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Introduction

Long Pond in Brewster and Harwich, MA covers 740 acres with a mean depth of 29 ft and a maximum depth of about 70 ft. Precipitation and groundwater are the dominant sources of water, with a smaller amount of runoff from the very sandy watershed. Long Pond is a popular swimming, boating and fishing destination. It has two major town beach/boat launch facilities, one each in Brewster and Harwich, plus another less developed beach and boat launch area in Harwich. Both towns have actively sought to protect the desirable qualities of the pond. Erratic summer algal blooms and small fishkills raised concern and prompted further study in the 1990s.

Investigations revealed a lack of oxygen with hydrogen sulfide production and release of phosphorus from bottom sediments in >30 ft of water. Diffusion and upward mixing of deeper waters during storms may both contribute to effective internal loading, which was estimated to supply 405 kg/yr (65%) to the upper waters out of a total load of between 606 and 651 kg/yr. The remaining load is attributed mainly to watershed sources (26%) and precipitation (8%). Available phosphorus within the sediment ranged from 0.6 to 4.6 g/m². A summer release of 0.6 g/m² with only 10% reaching the epilimnion could raise the phosphorus concentration by more than 0.02 mg/L and support algal blooms. It was therefore determined that internal loading had to be controlled and a phosphorus inactivation treatment was appropriate and sufficient to improve conditions and support the designated uses of Long Pond.

The treatment planning and protocol are detailed in the permit submissions and the original post-treatment report (AECOM 2009). Treatment occurred on 17 days between September 13 and October 10, 2007 over a targeted area of 370 acres (Figure 1). The final chemical amounts applied to Long Pond were 70,291 gallons of aluminum sulfate and 37,856 gallons of sodium aluminate, applied at a ratio of 1.86:1. Doses per treatment area followed the guidance of 10 g/m² for the East Basin, 15 g/m² for the West Basin, and 30 g/m² for the Central Basin. The ratio of aluminum sulfate to sodium aluminate kept the pH within the desired range to avoid toxicity, and no animal mortality was observed despite frequent monitoring by multiple interested parties.

The treatment of Long Pond was the first fall treatment in Massachusetts, performed at that time to meet permit restrictions. Monitoring was conducted immediately before, during, and for a year after treatment by personnel from AECOM. A project completion report covering 2007 and 2008 was prepared and finalized in February 2009. Personnel from the Town of Brewster assumed monitoring duties in spring of 2009, and have conducted monitoring between April and October every year since then. This report extends the longer term monitoring elements of the 2007-2008 effort to provide a more complete picture of conditions in Long Pond as a consequence of phosphorus inactivation. There are four central questions to be addressed:

1. Has water clarity improved to the extent expected and has improved clarity persisted?
2. Has there been a shift in the phytoplankton community to lower abundance and less dominance by cyanobacteria?
3. Has deep water oxygen improved as an anticipated function of less internal production of organic matter and subsequent sinking and decay of that matter?
4. Have phosphorus levels remained low relative to pre-treatment levels?
Figure 1. Treatment area within Long Pond (Figure 2-1 from AECOM 2009)
Water Clarity

Clarity did improve immediately upon treatment (Figure 2), but those improvements did not last more than a few months. While the subject of some speculation, the consensus opinion is that this relates to the treatment occurring in the fall. Internal loading for 2007 had already occurred, and while some phosphorus (P) was stripped from the water column, the reaction is not that efficient at the relatively low surface water P concentrations encountered. Higher P levels, as observed in the deepest water, were dramatically reduced, and P in the surficial layer of the sediment was inactivated, but adequate P remained in the overlying water to support algal growth for multiple months. The initial increase in clarity was probably a function of slightly reduced water P concentrations and coagulation and sinking of phytoplankton during treatment. It is also possible that there was a “rebound” effect, whereby organically bound P was released into the water column in response to lower water column P and higher decomposition levels for the phytoplankton precipitated by treatment, but the true mechanism is unknown. Clarity is not typically monitored in lakes in winter, so the low values observed over the winter of 2007-2008 may not be unusual. They are, however, lower than desired for summer and lower than expected after treatment.

During the spring of 2008 clarity improved, and by summer the clarity was as high as observed in over a decade. This high clarity was maintained through summer of 2008. As winter and spring algae, mainly diatoms and golden algae, used the available P and settled to the bottom, less P was available in the water column for phytoplankton to grow. This is a normal seasonal sequence, but the response in lakes with strong internal recycling is for P released from the sediment to provide a source of “new” P to support algal growth. Additionally, many cyanobacteria can absorb P while in the sediment as resting stages, then float to the surface with an adequate supply of P to form blooms. So the sediment is a source of P by multiple mechanisms, and the treatment with aluminum was intended to diminish this source. It appeared very successful in summer 2008, as evidenced by summer Secchi transparency comparison (Figure 3) with the long-term average prior to treatment.

The overall pattern of increased clarity has persisted through 2013 (Figures 2 and 3). The pretreatment spring-summer clarity range of 2-3 m has been increased to 4-5 m, with some spring values approaching or even exceeding 6 m (20 ft). Based on 17 years of post-treatment monitoring at Hamblin Pond in Marstons Mills, it was expected that clarity would increase into the range of 4-7 m, which has been the case beginning with the spring after treatment.

Yet there is a decline in water clarity in September of each year (Figures 2 and 3). This may be related to destratification (a normal seasonal process that occurs in September and October each year) and associated mixing (which will supply nutrients to upper waters from untreated areas or decay of material deposited since treatment). It may also relate to inputs from the watershed, most notably seasonal cottages and the cranberry bogs that drain to Long Pond and have maximum input in late summer. The long-term pattern has included a late summer decline in clarity, and the treatment did not change that pattern. Rather, the treatment appears to have shifted the progression to a higher range of clarity, such that conditions are acceptable at all times in the summer. The relatively low clarity levels in October of 2009 and 2010 raise some concern, and there was no clarity measure for 2011, but clarity in 2012 and 2013 was as high as has ever been observed. In terms of summer clarity, Long Pond has been substantially improved since treatment and appears fairly stable until autumn.
Figure 2. Water clarity in Long Pond
Figure 3. Summer water clarity in Long Pond.
Phytoplankton

Phytoplankton samples were not often quantitatively evaluated prior to treatment, but we know that cyanobacterial blooms were common and sometimes severe in summer in Long Pond from qualitative analyses. The quantitative samples from summer 1997 and September of 2007 just prior to treatment (Figure 4) indicate the presence and apparent dominance of cyanobacteria and the overall elevated abundance of phytoplankton. Blooms are typically associated with biomasses in excess of 3000 ug/L, although particle size also affects clarity (smaller particles impart more turbidity and therefore lower clarity per unit of biomass), so there is not an extremely strong proportional relationship between algal biomass and water clarity. Clear water is most often associated with biomass values <1000 ug/L, although again the particle size distribution has an effect.

The phytoplankton community features since treatment in September-October 2007 (Figure 4) include biomass levels mostly <1000 ug/L and rarely >2000 ug/L, with dominance by diatoms (Bacillariophyta) and golden algae (Chrysophyta), with some dinoflagellates (Pyrrophyta) and very few cyanobacteria (blue-green algae, or Cyanophyta). The genera of cyanobacteria that have historically caused blooms have included *Anabaena*, *Aphanizomenon*, *Microcystis*, and to a lesser extent *Planktolyngbya* (although only recently known by that name, and may be listed as *Lyngbya* or *Oscillatoria* in older lists). *Planktolyngbya* is present in a number of samples from 2008-2013 at moderate cell counts but low biomass; it is the most common blue-green algae in Long Pond after treatment, and is not a major threat to any uses of the pond. The other species have not occurred in samples after treatment until the end of summer in 2010, when both *Anabaena* and *Aphanizomenon* were found in September and October 2010 samples at low densities. While the presence of potential bloom forming cyanobacteria is never a good sign, quantities to date are low enough to represent no threat to lake ecology or human users. *Aphanizomenon* was again detected at low levels in late summer and early fall of 2011 and 2012, but no *Anabaena* was detected. No *Aphanizomenon* of *Anabaena* was encountered in 2013 samples. Blue-greens have not been eliminated from the pond, but have been greatly reduced in abundance and are not dominant among algae.

The majority of algae present in the phytoplankton are excellent sources of food for zooplankton, but zooplankton are scarce in Long Pond in late spring through early fall when monitoring has been conducted. The presence of young-of-the-year alewife, while ecologically favorable for the marine food webs they will fuel upon departure from their nursery in Long Pond, does represent intense predation pressure that minimizes zooplankton abundance and body size. There is very little grazing pressure on algae in Long Pond, as zooplankton biomass is rarely >50 ug/L and by late summer is typically <10 ug/L. Values in excess of 100 ug/L of larger bodied forms are needed to generate enough grazing capacity to affect the phytoplankton community. Long Pond will have summer algae at the maximum level supported by the fertility of the pond, which translates into the level of available phosphorus. Lower observed algal abundance since treatment is related to reduced phosphorus availability, not any impact by zooplankton. The shift from cyanobacteria dominance to other algae is most likely a consequence of an increase in N:P ratio, with P reduced and N remaining roughly the same as prior to treatment.
Figure 4. Phytoplankton biomass in Long Pond over time.

(Values from two stations are averaged to generate bars for each date)
Oxygen

Dissolved oxygen is critical to the proper functioning of a lake ecosystem. It is natural for the bottom of deep lakes to lose oxygen, and even to become anoxic (devoid of oxygen), as they become more fertile over time and decay processes in deep water outstrip the ability of oxygen to diffuse downward through the water column from the atmosphere. Human activities that advance the fertilization process, known as cultural eutrophication, can accelerate this process, but the presence of low or no oxygen in deep waters can be natural. When oxygen is very low, chemical reactions that would not occur in the presence of oxygen can become important. Ammonium, which converts readily to nitrite and then nitrate in the presence of oxygen, builds up without oxygen and can cause toxicity. Sulfate metabolism, an anoxic, bacteria-mediated reaction, creates hydrogen sulfide, which most of us know as rotten egg smell. Iron, a natural phosphorus binder, reacts with hydrogen sulfide to form insoluble iron sulfides, thus removing an important natural mechanism for binding P. P that was bound to iron is released from the sediment under anoxia, and can move upward by diffusion or mixing events, reaching the upper water level where sunlight allows algae to grow when nutrients are available. Having oxygen throughout a waterbody is preferable for nearly all uses of the water, human and otherwise.

The aluminum treatment to bind P does not add oxygen and it does not provide mixing that would enhance downward movement of oxygen from the atmosphere. P inactivation is supposed to limit algal production, however, and this should limit the amount of organic matter raining down into the deep water and creating oxygen demand through decomposition. There will be oxygen demand (SOD) even without this extra organic matter, but it should be reduced over time. In this manner, P inactivation can indirectly lead to higher oxygen in deeper water. Usually this is manifest as a less sharp decline in oxygen below the thermal boundary between upper and lower water layers, called the thermocline or metalimnion. Hamblin Pond in Marstons Mills gained about 10 ft of water just below the thermocline with enough oxygen to support trout after P inactivation; prior to treatment there was no oxygen in the deeper water layer.

To assess any oxygen effect from P inactivation of Long Pond, one compares oxygen profiles from summer among years, pre- and post-treatment. Looking at profiles from July and August of 1997 and 2000 (pre-treatment) vs. profiles from 2008 through 2013 (post-treatment), we see relatively little difference in the oxygen distribution over depth (Figure 5). Anoxia occurs below about 10 to 12 m in July and August each year. There was more oxygen between 10 and 12 m of water depth in July 2008, the year after treatment, but in July 2010 the anoxic level went back to 10 m. If this was an effect of treatment, it was short lived. It may take a number of years for SOD to subside to the point where oxygen will be significantly increased, but there is no evidence that the treatment has improved deep water oxygen at this time.

An alternative method for assessing any impact of treatment on oxygen involves comparison of the rate of oxygen loss in late spring, when the lake stratifies and the bottom water layer becomes isolated. Pre-treatment oxygen demand was calculated several ways, the simplest of which involves calculating the loss of oxygen between late spring dates when stratification is forming. For the pre-treatment period of 1997-2000, the range of oxygen demand was 1182 to 2647 mg/m²/day. For the post-treatment period of 2008-2013, that range was 818-2537 mg/m²/day, suggesting a possible slight decrease in oxygen demand. The pattern over time (Figure 6) among stations suggests a decrease at the deeper LP-1 and no appreciable change at the shallower LP-2. P inactivation has not increased summer deep water oxygen levels to a substantial degree.
Figure 5. Temperature-Dissolved Oxygen profiles
The direct target of the aluminum application is phosphorus. The one-way hydrolysis reaction that aluminum undergoes will capture some phosphorus from the water column, but is particularly intended to bind surficial sediment reserves of P that are loosely bound or tied to iron in Long Pond. The result should be less P in the bottom water and less P movement into the upper waters during stratification. By eliminating this source of P, algal production is limited and the buildup of algae in surface waters is reduced. In addition to the limit to overall productivity, reduced P shifts the N:P ratio in favor of algae other than cyanobacteria. So P inactivation should result in less algae overall and a lesser percent of algal biomass as cyanobacteria. Clearer water will result, although shifts in particle sizes may skew the change in a non-linear manner. These changes have been observed in Long Pond and discussed previously in this review.

It is no surprise that the total P concentrations in 2008 were lower than prior to treatment (Figure 7). Surface concentrations are not especially high at any time, and at the scale of the figure it is hard to discern any major change, but the reduction in deep water P, some portion of which makes it to the upper waters, is quite evident. Total P values from sampling in 1997 and 2000 are provided for comparison, and are similar to the observed total P level in September 2007, just before treatment. Bottom total P levels in excess of about 0.1 mg/L represent a potential problem, and one can see the build up to excessive levels over the summer in the pre-treatment values. In 2008, the year after treatment, total P in bottom waters was universally low, with only one out of 22 values >0.05 mg/L, an acceptable deep water P concentration in most cases.
Figure 7. Total phosphorus concentrations in Long Pond.
Figure 8. Dissolved phosphorus concentrations in Long Pond.
However, this pattern does not hold up in 2009 and beyond, with a return to elevated total P levels in bottom water in July and August. The reason for this shift is not clear, and there is variability among years, but total phosphorus can include considerable particulates that are not readily available to algae. Such particulates may represent settled solids or resuspended solids. Knowledge of the portion of total phosphorus that is dissolved is therefore important.

The P released by sediment should be in dissolved form, and while some conversions will occur in the deep zone, there should be a buildup of dissolved P in that zone if significant sediment P release is occurring. We have almost no dissolved P data from before the treatment in 2007. Based on the data from 2008-2013 (Figure 8), there is virtually no buildup of deep water dissolved P in 2008, a very slight buildup in 2009, and a more significant buildup in July of 2010. The 2010 data suggest a major flux of P from the sediment in July, with values declining again in August. Data for dissolved phosphorus in 2011 were again high in deep water of LP-1 in late summer, but not at LP-2. Values from 2012 and 2013 suggest an intermediate increase in dissolved P at LP-1 but lower values at LP-2. While lower values are desirable, dissolved P is not high most of the time in the deep water of Long Pond.

Through all of this, water clarity has remained improved over pre-treatment levels, so any released P is apparently not being transferred to the overlying water during the period of stratification. As water clarity remains high during the summer, there is no immediate cause for alarm. However, continued assessment is warranted to evaluate any possible threat from release of P from the sediment to Long Pond.

**Conclusions and Recommendations**

The fall 2007 inactivation of phosphorus by aluminum in Long Pond has roughly doubled water clarity in the summer through 2013, although the annual pattern of a decrease in early fall is still evident and may be related to nutrient inputs at that time. There has been a concurrent shift in the phytoplankton community to less algae overall and far less cyanobacteria, although several problem species from the pre-treatment period have been observed in late summer of 2010-2012 at low levels. This bears continued tracking, although those problem cyanobacteria were not observed in 2013. The observed changes in water clarity and phytoplankton are desirable and consistent with expectations from other P inactivation treatments, but the duration of benefits is uncertain.

The addition of aluminum does not directly enhance oxygen, but by lowering phytoplankton production the oxygen demand can be lowered and oxygen levels have increased after some P inactivation projects. Examination of summer oxygen profiles and calculation of late spring oxygen demand do not indicate any major changes in the oxygen regime of Long Pond following P inactivation in fall of 2007; there is a slight decrease in oxygen demand at LP-1 but not at LP-2, and the deepest areas still become anoxic each summer.

P inactivation with aluminum strips some P from the water column and binds much of the P in surficial sediments. Reduced release of P from sediments during summer stratification under anoxic conditions will substantially lower the deep water P concentration, which will in turn reduce the amount of P that can reach the upper water layer by diffusion or mixing. Where P is the limiting nutrient, lowered P will result in less phytoplankton and a shift in the N:P ratio that moves the composition of the phytoplankton away from cyanobacteria. For Long Pond, deep water P was dramatically reduced in 2008, the year after treatment, but the summer buildup of total P has increased since that time. There is less increase in dissolved P, which is the form that should be dominant if sediment release is the source. Only the July values in 2010 and one July value in 2011
are high enough to be of concern; more recent values are acceptable and indicate relatively little
generation of available P in deep water in Long Pond.

The overall pattern of total P buildup in the bottom of Long Pond could indicate insufficient
inactivation, but may just represent an accumulation of particles that have either settled as the upper
waters warm or have become resuspended by internal currents. Water clarity has not been affected,
surface P levels are not excessive, and the distribution of P since 2009 does not appear to represent
a major threat.

It is very important to obtain the highest quality results possible from monitoring. Careful attention to
sample labeling and data recording is essential, both in the field and lab. Detection limits have
improved with the use of the SMAST lab, and field procedures are appropriate, but a few values
collected since the treatment do appear strange in vertical series; those values may be accurate, in
which case there are some field anomalies that bear scrutiny. Oxygen meters should be checked
and carefully calibrated to obtain accurate results. Observers should strive to narrow the range
between Secchi disk disappearance and re-appearance, which is sometimes rather wide. Data
management and maintenance of the data base are important as well; missing values should be
minimized. Ongoing evaluation of Long Pond is dependent on data quality as well as quantity and
timing of sampling.

Monitoring should continue in the months of June through September. If monitoring in April, May and
October is feasible, it should also continue, but it is important that the months of June through
September not be skipped, and it is desirable to space the monitoring roughly evenly over this time
period. Secchi transparency measurements can be made more frequently and over the complete
period of April through October, but the current pattern of data acquisition is adequate to assess
conditions. Although there are differences between LP-1 and LP-2, it may be sufficient to sample
LP-1 for water quality features measured in the lab, thereby saving some expense. Data should be
reviewed annually.

It may also be appropriate to sample the surficial sediments at LP-1 and LP-2 and test for iron-
bound P, the form that is released under anoxic conditions. Comparison with values from the pre-
treatment period would allow an evaluation of whether available sediment P levels have remained
reduced since treatment, or are high enough to potentially be responsible for the observed increase
in deep water P during stratification.