East Alaska Lake

Kewaunee County, Wisconsin

Alum Treatment Implementation Final Report

May 2015

Sponsored by:

Tri-Lakes Association

WDNR Lake Protection Grant Program

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Onterra, LLC
Lake Management Planning

INTRODUCTION

East Alaska Lake, Kewaunee County, is an approximate 52-acre deep headwater drainage lake with a maximum depth of 50 feet and a mean depth of 17 feet (Figure 1). Studies completed as part of a lake management planning project in 1999 indicated that the lake was eutrophic and suffering from nuisance algae blooms brought about by excessive levels of nutrients, primarily phosphorus. The 1999 studies suggested that East Alaska Lake's unexpectedly high phosphorus concentrations were not only brought on by external sources that were impacting the lake at the time, but also by the latent affects of historical sources, many of which were curbed years before. One intense impact was runoff from a sizeable farm's feedyard that drained directly to the lake for decades and was finally diverted to a concrete manure storage facility in 1995. An additional significant phosphorus source impacting the lake until approximately 1960 was wash water and whey discharge from an adjacent cheese factory that entered the lake only after flowing through an inline settling tank and gravel filter. And during the mid-1990's, county staff investigated many of the private onsite wastewater treatment systems (POWTS) on East Alaska Lake. Of particular interest were 16 homes along the southern basin of the lake, of which the majority were found to be failing. With the exception of two, all of these systems were replaced with a holding tank within five years.
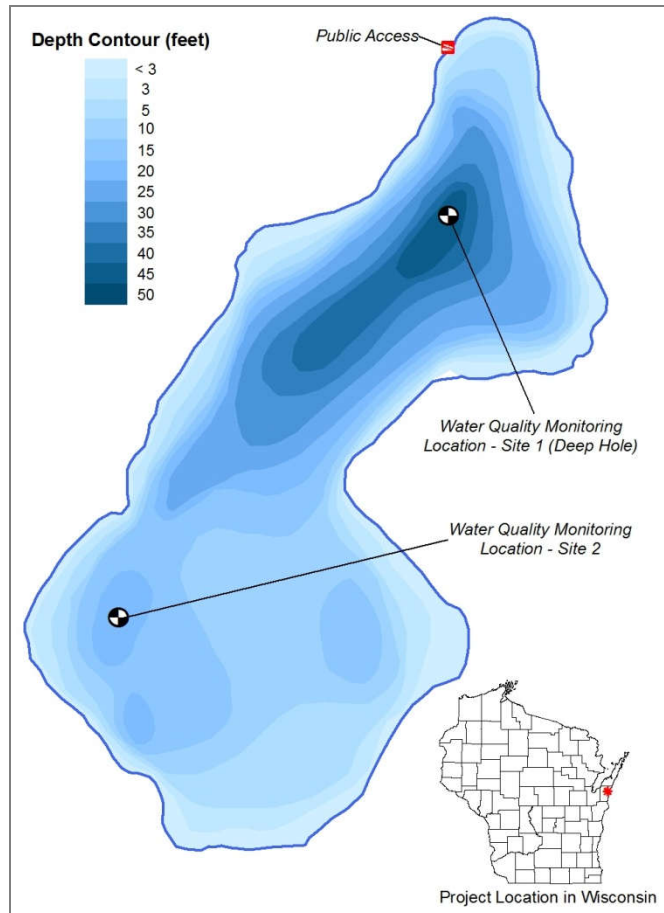

Figure 1. East Alaska Lake, Kewaunee County, Wisconsin.

The 1999 management plan contained four water quality-related recommendations; 1) divert two stormwater discharge pipes draining a section of county highway to an adjacent ditch and downstream wetland, 2) create a nutrient and pesticide management plan for a golf course partially draining to the lake, 3) create a sedimentation basin to intercept and treat water being discharged to the lake by an agricultural drain tile, and 4) investigate the significance of internal loading on the lake's phosphorus budget. Internal nutrient loading involves the release of phosphorus from lake bottom sediments into the overlying water column when anoxic (devoid of oxygen) conditions are present. The latter recommendation was prompted by the historical nutrient loading impacts to the lake, the lake's long retention time of just over a year, and high hypolimnetic phosphorus values exceeding 300 µg/l.

The first two recommendations were implemented immediately following the completion of the lake management plan, while the second two, being more complicated and costly, took a bit more time. In 2004, the Tri-Lakes Association received a second and a third grant from the State of Wisconsin to complete studies to quantify the phosphorus loading to the lake through its inlet from West Alaska

Lake, the agricultural drain tile described above, and internal nutrient loading (Onterra 2005). The project design was essentially an alum treatment feasibility study for East Alaska Lake. These studies indicated that while both the inlet and the drain tile each delivered approximately 57 lbs of phosphorus to the lake annually, the impact of the drain tile was more severe because basically no flushing of the lake was associated with the drain tile phosphorus input as it discharged only 6% of the flow delivered by the inlet. Mass-balance modeling of spring, summer, and fall in-lake phosphorus concentrations indicated that the lake could potentially be receiving over 280 lbs of phosphorus annually via internal loading. While this estimate was believed to be an exaggeration, it was still considered a strong indication that internal loading was a significant source of phosphorus fueling the lake's production.

East Alaska Lake is a dimictic lake, meaning that it completely mixes or turns over twice each year, once in spring and once in fall, when water temperatures are similar from the surface to the bottom. During the summer, the lake stratifies forming distinct layers of water based on temperature and density. The top-most, warmest, and least dense layer of water, called the epilimnion, floats above the bottom, coldest, and densest layer of water called the hypolimnion. The epilimnion and hypolimnion are separated by a thin layer of water called, the metalimnion, or thermocline, which is a transition zone where water temperature changes rapidly with depth. East Alaska Lake also stratifies during the winter beneath the ice; however, in contrast to the summer, the coldest water temperatures are found near the surface while the warmest water is found near the bottom.

Once ice forms on the lake, the water is 'sealed off' from atmospheric inputs of oxygen and water near the bottom of the lake starts to become depleted of oxygen through the decomposition of organic matter. While photosynthesis of algae and aquatic macrophytes under the ice provide oxygen to the upper layer of water in winter, due to the inability of the layers to mix, oxygen is not delivered to near-bottom waters. When anoxic conditions form near the lake bottom, iron which had been binding phosphorus within the sediment changes forms and releases the phosphorus into the hypolimnion. Phosphorus is released from bottom sediments and builds up within the hypolimnion over the course of the winter. In spring, the ice melts, surface water temperatures increase, and wind mixes the once distinct layers of water together. The phosphorus-rich water that had built up within the hypolimnion over the course of the winter is now mixed throughout the water column and made available to algae at the surface. This 'pulse' of phosphorus in spring was believed to elevate near-surface total phosphorus concentrations and fuel algae blooms over the course of the growing season.

Similarly, as surface water temperatures continue to warm, the lake again becomes stratified in the summer. Because of the difference in temperature and thus density between the epilimnion and hypolimnion, these two layers are unable to mix and the hypolimnion is again sealed off from atmospheric inputs of oxygen and oxygen is depleted through decomposition. Phosphorus is released from bottom sediments and builds up within the hypolimnion over the course of the summer. Most of the phosphorus likely remains within the hypolimnion during the summer and is not available to algae at the surface. However, in fall as surface waters begin to cool, the lake mixes again and the hypolimnetic phosphorus is mixed throughout the water column. This pulse of phosphorus in the fall may create elevated concentrations near the surface that persists over the course of the winter and into the following spring.

While the delivery of hypolimnetic phosphorus to surface waters likely only occurs in spring and fall in East Alaska Lake when water temperatures are cooler and most algae are not actively growing, it is

believed that these two delivery events maintain higher elevations of phosphorus within surface waters that can fuel algae blooms over the course of the growing season. Reducing hypolimnetic loading of phosphorus from bottom sediments, and therefore the amount of phosphorus being mixed into surface waters in fall and spring, would likely reduce the amount of phosphorus available to algae and improve the lake's water quality.

Although the 2004 studies confirmed internal loading to be significant in East Alaska Lake, the resulting report stopped short of recommending an alum treatment because of the unchecked drain tile load and continued uncertainties associated with impacts of lakeshore POWTS. Instead, it recommended additional septic system inspections and reiterated the need for a sedimentation basin for the treatment of the agricultural drain tile discharge.

The Tri-Lakes Association followed through on the recommendations stated in the report and in 2006, with assistance from Kewaunee County and the US Fish and Wildlife Service, completed construction of a 1-acre sedimentation basin on the lake's west shore to treat water entering the lake from the agricultural draintile. Furthermore, in 2007 the association prompted the county to inspect all POWTS around the lake, with the inspections resulting in 11 corrective actions.

While the 1999 East Alaska Lake Management Plan supported the investigation of utilizing an alum treatment to control internal sources of phosphorus within the lake, the plan did not include an action of implementing an alum treatment on the lake. Before an alum treatment could be completed, especially one that would be partially funded by the Wisconsin Department of Natural Resources (WDNR), the management action needed to be included within the lake management plan. In addition, the plan also needed to contain data supporting the implementation of an alum treatment and be accepted by the lake's stakeholder group. In 2011, a project funded through a WDNR Lake Management Planning Grant fulfilled this lake management planning requirement and included an addendum to the plan. This addendum included an updated water quality assessment, an introduction to the use of alum in lakes to reduce internal phosphorus loading, a description of the public's participation in approving the plan, and an implementation plan outlining the steps needed to construct a specific alum treatment plan for East Alaska Lake.

Using a combination of water quality data and phosphorus-release rates measured from sediment cores collected from eight locations around the lake in 2010, an alum treatment dosing and monitoring plan for East Alaska Lake was created in 2011, and a WDNR Lake Protection Grant was successfully secured to aid in funding the proposed alum treatment and associated monitoring. The alum treatment was completed utilizing two levels of aluminum dosing: in depths between 5 and 10 feet, a dose of 40 g/m^2 Al was applied, and in depths greater than 10 feet, 132 g/m^2 Al was applied. To complete the treatment, nearly 84,000 gallons of alum was applied over a two-day period in mid-October 2011. During the application, Onterra ecologists monitored the lake's pH at multiple locations around the lake to ensure that the treatment was not causing a decline in pH that would be ecologically harmful. Given East Alaska Lake's high alkalinity, or buffering capacity against changes in pH, the lake's pH was not anticipated to fluctuate greatly during the alum application and monitoring indicated that significant reductions in pH did not occur.

Post-treatment water quality data have been collected on East Alaska Lake annually since the 2011 alum treatment to assess its effectiveness and longevity. Sediment cores were also recollected at eight locations within the lake in 2014 to measure phosphorus release rates following the alum treatment.

This report discusses the post-treatment water quality data results that have been collected on East Alaska Lake through 2014. In addition, this report discusses assessments of the lake's aquatic plant community including native aquatic plants and the non-native plants Eurasian water milfoil and curly-leaf pondweed that were completed with surplus funding from the 2011 Lake Protection Grant.

ALUM TREATMENT RESULTS

Effect on Hypolimnetic Phosphorus Release

To determine if the alum treatment was effective at reducing the amount of phosphorus being released from lake bottom sediments in East Alaska Lake, total phosphorus concentrations measured at multiple water depths before and after the treatment were compared. These total phosphorus profiles were collected in early fall when the lake was still stratified and hypolimnetic phosphorus would be near its maximum concentration. Prior to the treatment in 2009 and 2011, hypolimnetic phosphorus concentrations ranged from approximately 200 µg/L to greater than 1,200 µg/L, indicating substantial phosphorus release from bottom sediments (Figure 2). Following the alum treatment, total phosphorus concentrations within the hypolimnion decreased significantly, declining to an average of 56 µg/L in 2012 and 2014 (Figure 2).

Sediment cores collected in 2014 from the same 8 areas collected in 2010 (Appendix A, Figure 1), and analyzed by Bill James at UW-Stout also revealed a marked decrease in phosphorus release rates from bottom sediments. His analysis revealed that phosphorus release rates from the sediment cores decreased by 88-100% following the alum treatment. A detailed report of his analysis can be found in Appendix A.
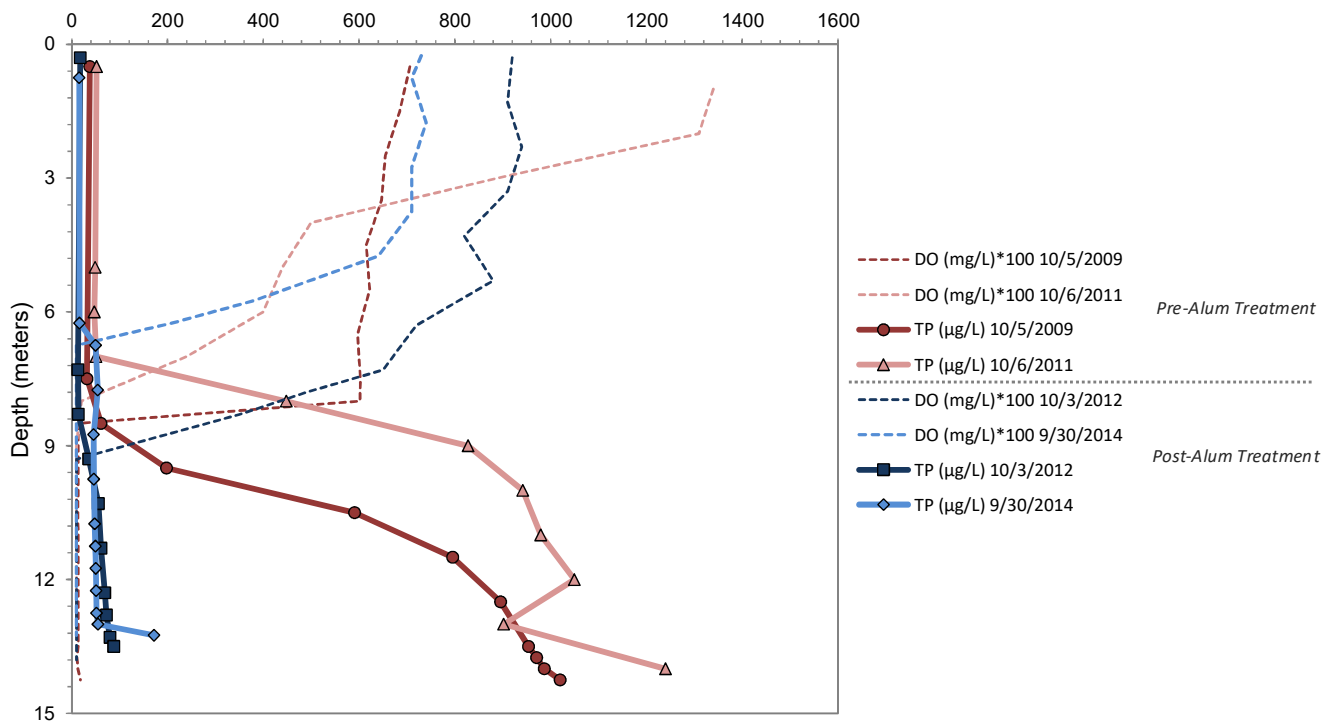

Figure 2. East Alaska Lake total phosphorus and dissolved oxygen profiles collected before (red) and after (blue) the 2011 alum treatment. Data collected from the Deep Hole sampling location.

Effect on Epilimnetic Phosphorus, Algae, and Water Clarity

As discussed in the Introduction, prior to the alum treatment in East Alaska Lake, near-surface total phosphorus concentrations would increase significantly in spring and fall as hypolimnetic phosphorus was delivered to surface waters during mixing events. It was theorized that these events elevated phosphorus concentrations within surface waters over the course of the growing season fueling nuisance levels of algae. Figure 3 displays near-surface total phosphorus concentrations in East Alaska Lake from 2001 through 2014. While historical data are available prior to 2001, the data are temporally sporadic and were left out of this figure. Prior to the alum treatment 2011, spring and fall near-surface total phosphorus values were highly elevated, exceeding 250 µg/L 2010 and 2011. The delivery of hypolimnetic phosphorus to surface waters resulted in an average pre-treatment near-surface growing season total phosphorus concentration of approximately 57 µg/L, falling into the *poor* category for deep headwater drainage lakes.

The elevated near-surface total phosphorus concentrations that plagued East Alaska Lake in the spring and fall prior to treatment, were no longer observed following the treatment (Figure 3). As a result of the alum, growing season near-surface total phosphorus concentrations were significantly reduced to an average of 15.9 µg/L, a reduction in total phosphorus concentration of approximately 72%. Post-treatment near-surface total phosphorus concentrations fall into the *excellent* category for deep headwater drainage lakes in Wisconsin. The post-treatment total phosphorus concentrations are lower than the predicted 29 µg/L based upon modeling of a 90% reduction in internal phosphorus loading.
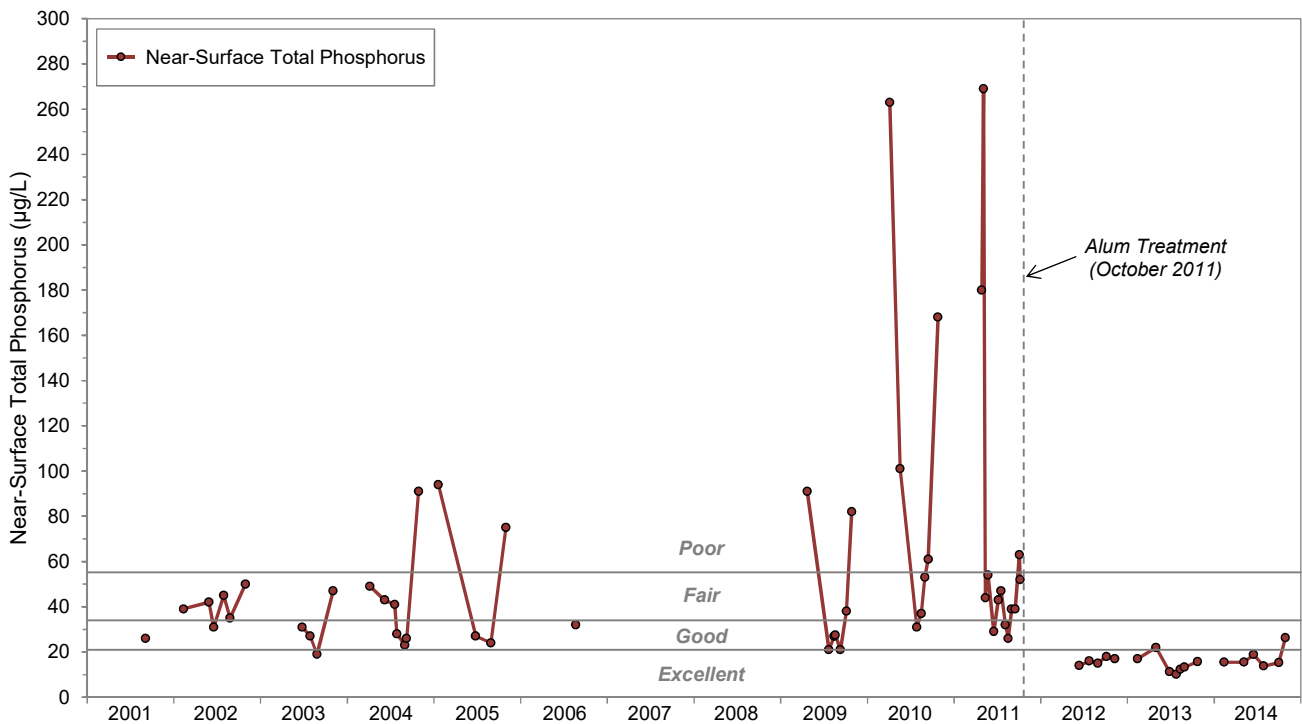

Figure 3. East Alaska Lake near-surface total phosphorus concentrations from 2001-2014. Data collected at the Deep Hole sampling location.

Chlorophyll-*a* concentrations, a measure of algal biomass, also declined following the alum treatment (Figure 4). Prior to the alum treatment, the average growing season chlorophyll-*a* concentration from

2001-2011 was 13.5 µg/L, falling into the *fair* category for deep headwater drainage lakes. However, often in spring and fall, chlorophyll-*a* concentrations often surpassed 20 µg/L, the threshold above which algae blooms become noticeable. Following the alum treatment, growing season chlorophyll-*a* concentrations declined by 39% to 8.2 µg/L, falling into the *good* category for deep headwater drainage lakes (Figure 4). While an algae bloom occurred in the spring of 2014 despite lower phosphorus concentrations, chlorophyll-*a* concentrations declined over the remaining course of the growing season. Post-treatment chlorophyll-*a* concentrations fell below the predicted value of 12 µg/L based upon modeling of a 90% reduction in internal phosphorus loading.

With a decrease in free-floating algal abundance, water clarity also increased following the alum treatment as indicated by Secchi disk transparency data (Figure 4). Prior to the alum treatment, average growing season Secchi disk transparency from 2001-2011 was 7.7 feet. Following the alum treatment, average growing season Secchi disk transparency from 2012-2014 increased to 8.2 feet.
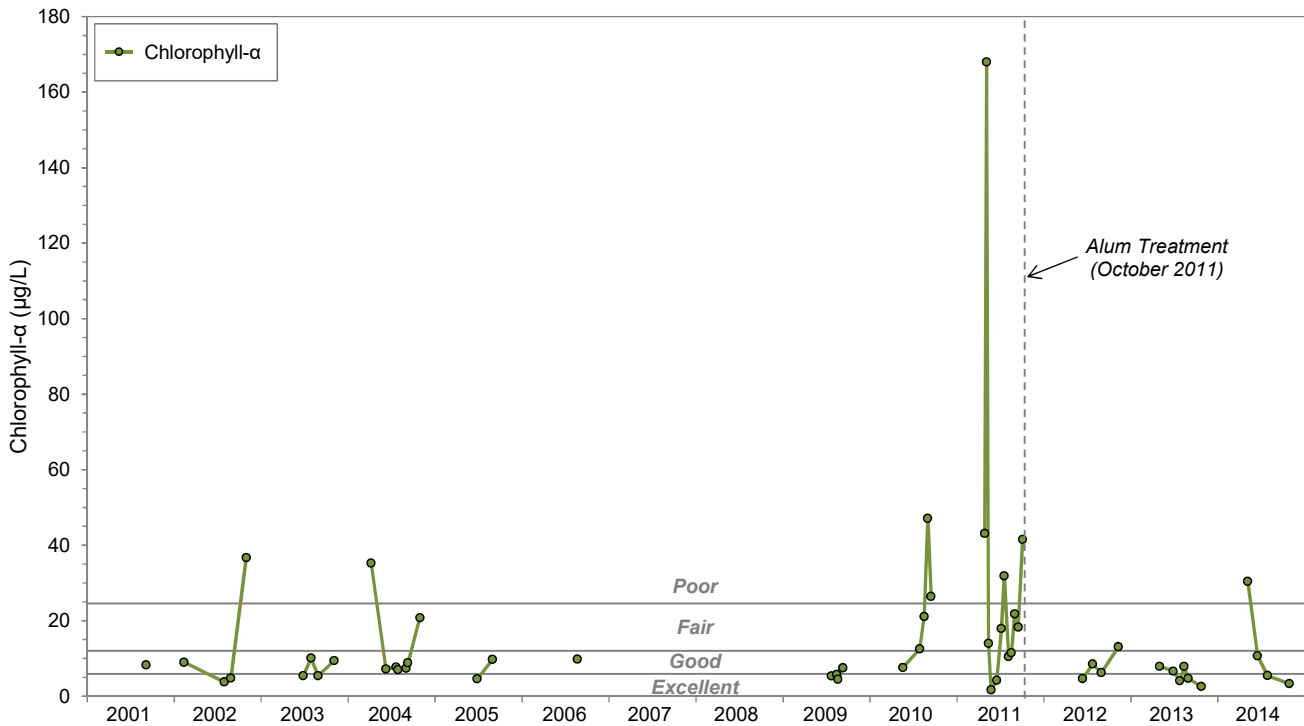

Figure 3. East Alaska Lake chlorophyll-α concentrations from 2001-2014. Data collected at the Deep Hole sampling location.
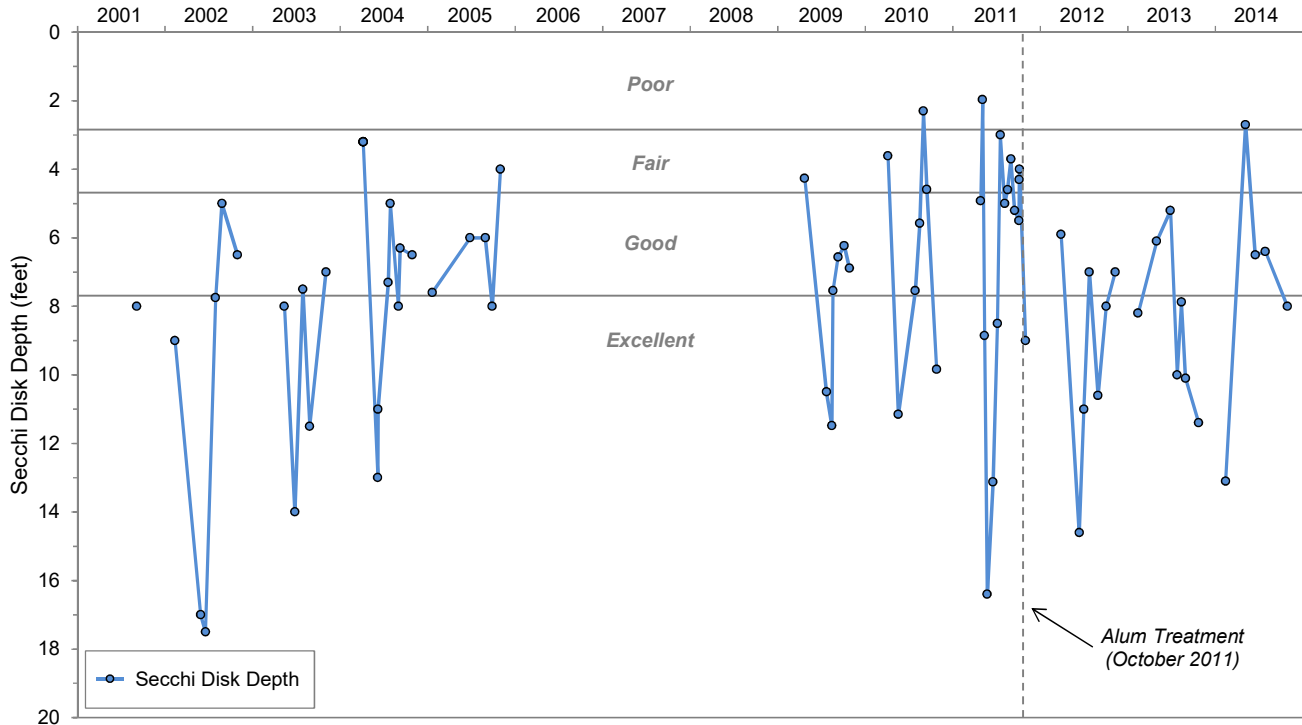
Figure 4. East Alaska Lake Secchi disk transparency from 2001-2014. Data collected at the Deep Hole sampling location.

Water quality data were also collected from a location within East Alaska Lake's southern basin (Site 2) from 2010-2014. Comparing these data with data collected from the northern basin (Site 1-Deep Hole) shows that near-surface total phosphorus concentrations, chlorophyll-*a* concentrations, and Secchi disk transparency are not statistically different between the two locations (Figure 5).
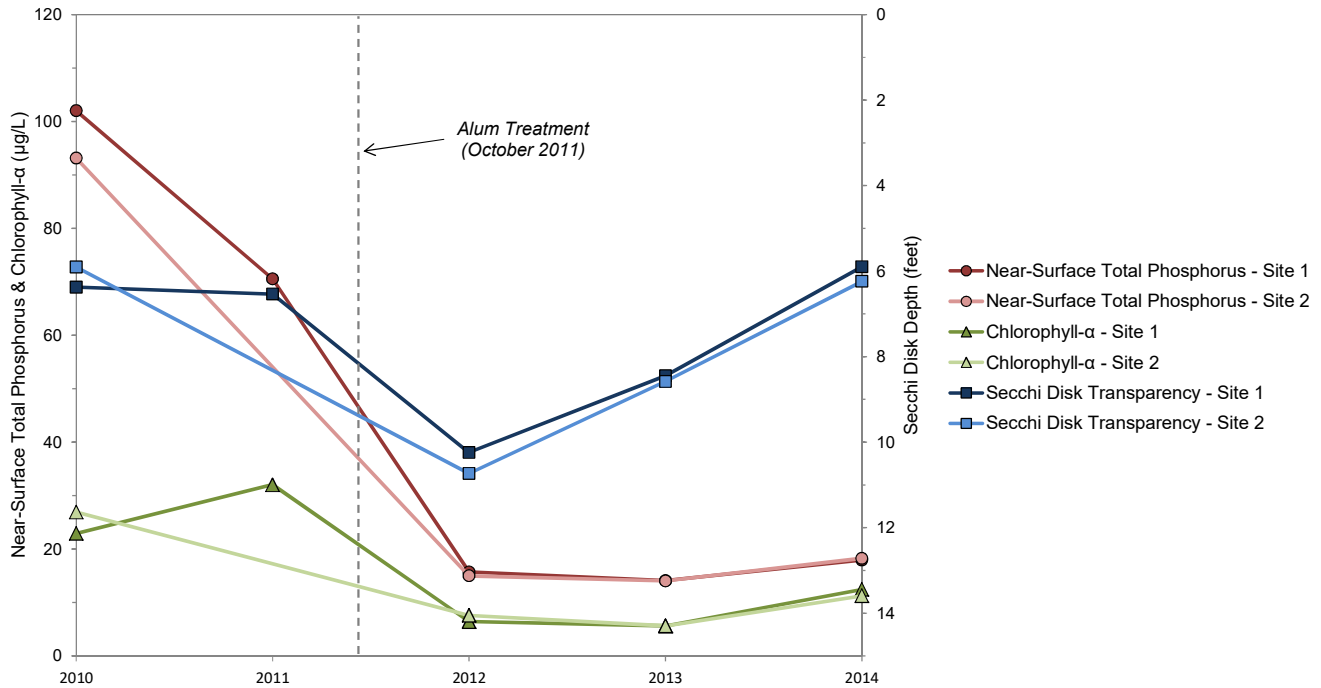
Figure 5. **East Alaska Lake average growing season near-surface total phosphorus, chlorophyll-α, and Secchi disk transparency from north basin (Site 1) and south basin (Site 2) from 2010-2014.**

AQUATIC PLANT COMMUNITY RESULTS

Eurasian water milfoil (*Myriophyllum spicatum*; EWM) was first discovered in East Alaska Lake in 1993 (Photo 1). Onterra ecologists mapped EWM in East Alaska Lake in 2011 and revealed that the lake contained approximately 0.5 acres of colonized EWM, comprised of *dominant* and *surface matted* EWM (Figure 6). The 0.5 acres was comprised of two main colonies: one near the lake's public access point and the other along the lake's western shore. A repeat of this mapping survey in 2014 revealed that the EWM population has since expanded significantly, with EWM colonial acreage increasing to approximately 9.0 acres (Figure

Photo 1. Eurasian water milfoil on East Alaska Lake. Taken in June 2014.

6). In 2014, the majority of East Alaska Lake's littoral zone, aside from the southeast portion of the lake, contained large contiguous colonies of EWM.

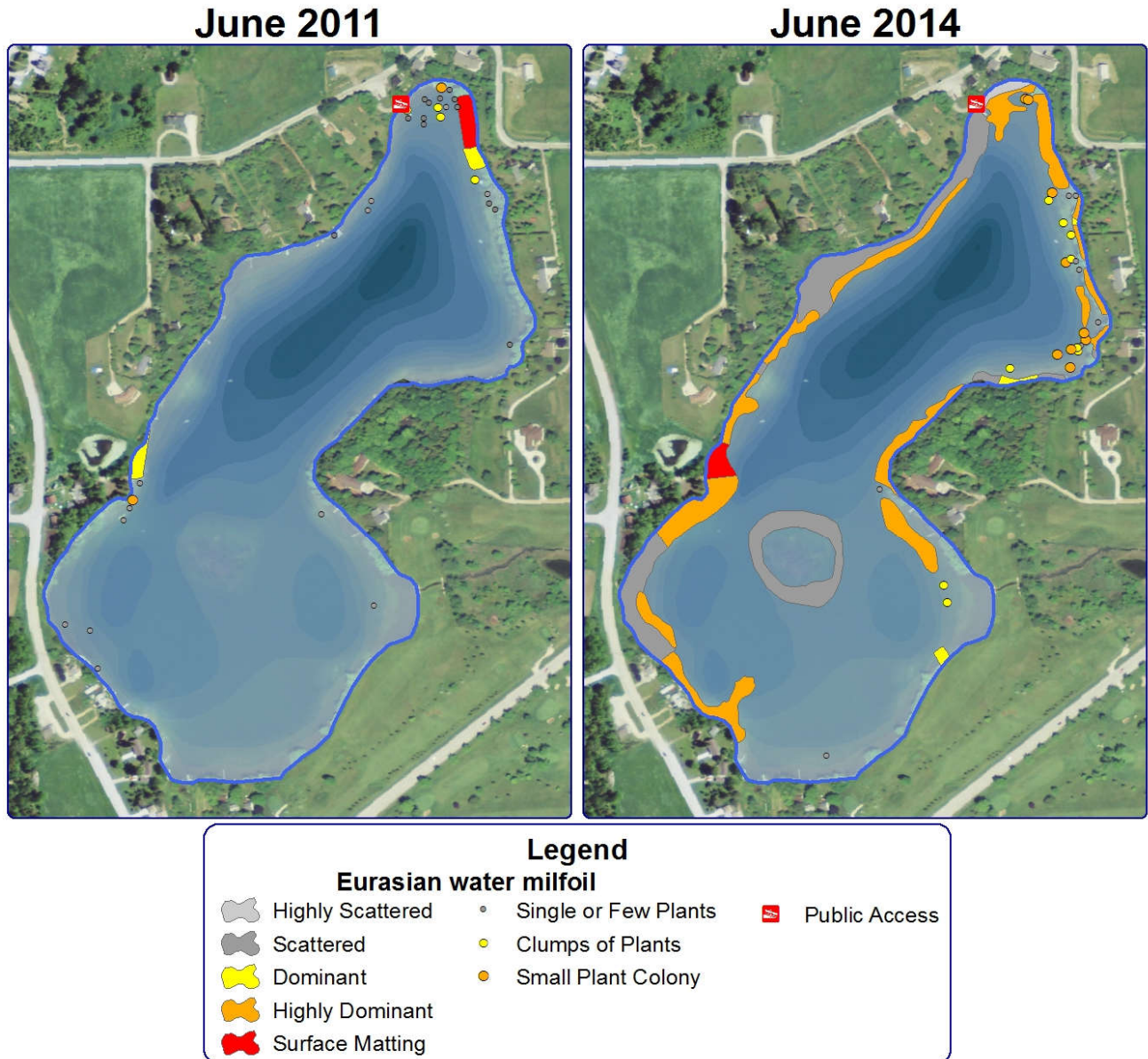Onterra LLC
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Figure 6. East Alaska Lake Eurasian water milfoil locations from June 2011 and June 2014.

This increase in the EWM population within East Alaska Lake was also documented by whole-lake aquatic plant point-intercept surveys completed by the WDNR in 2009 and 2014 (Figure 7). In 2009, 0 (0%) of the 108 point-intercept sampling locations that fell within East Alaska Lake's littoral zone contained EWM. In 2014, 56 (63%) of the 106 point-intercept sampling locations that fell within the littoral zone contained EWM. Between this five-year period, the EWM population went from being undetectable during the point-intercept survey to the most dominant plant within East Alaska Lake.

A few native aquatic plants exhibited statistically valid reductions in their littoral occurrence between the 2009 and 2014 point-intercept surveys (Figure 7). Coontail, hardstem bulrush, and flat-stem pondweed exhibited statistically valid reductions in their littoral occurrence (Chi-square α = 0.05). Coontail, which had been the most frequently encountered species in 2009 with a littoral frequency of

occurrence of 45%, had declined to an occurrence of 6% in 2014, representing a decline in occurrence of 88%.

This large reduction in the occurrence of coontail has been observed on other lakes which have seen reductions in phosphorus concentrations. Unlike rooted aquatic plants which obtain nutrients from bottom sediments, coontail does not produce true roots and obtains all of its nutrients directly from the water. Consequently, coontail is most abundant in lakes with higher nutrient concentrations, like East Alaska Lake prior to the alum treatment. Following the alum treatment, there were no longer sufficient phosphorus concentrations within the water to maintain the level of coontail biomass observed in 2009.

While hard-stem bulrush and flat-stem pondweed were not recorded on the rake during the 2014 point-intercept survey, they were still observed to be present in the lake. The occurrences of muskgrasses, white water lily, sago pondweed, northern watermilfoil, white-stem pondweed, cattails, and pickerelweed were not statistically different between the two surveys.
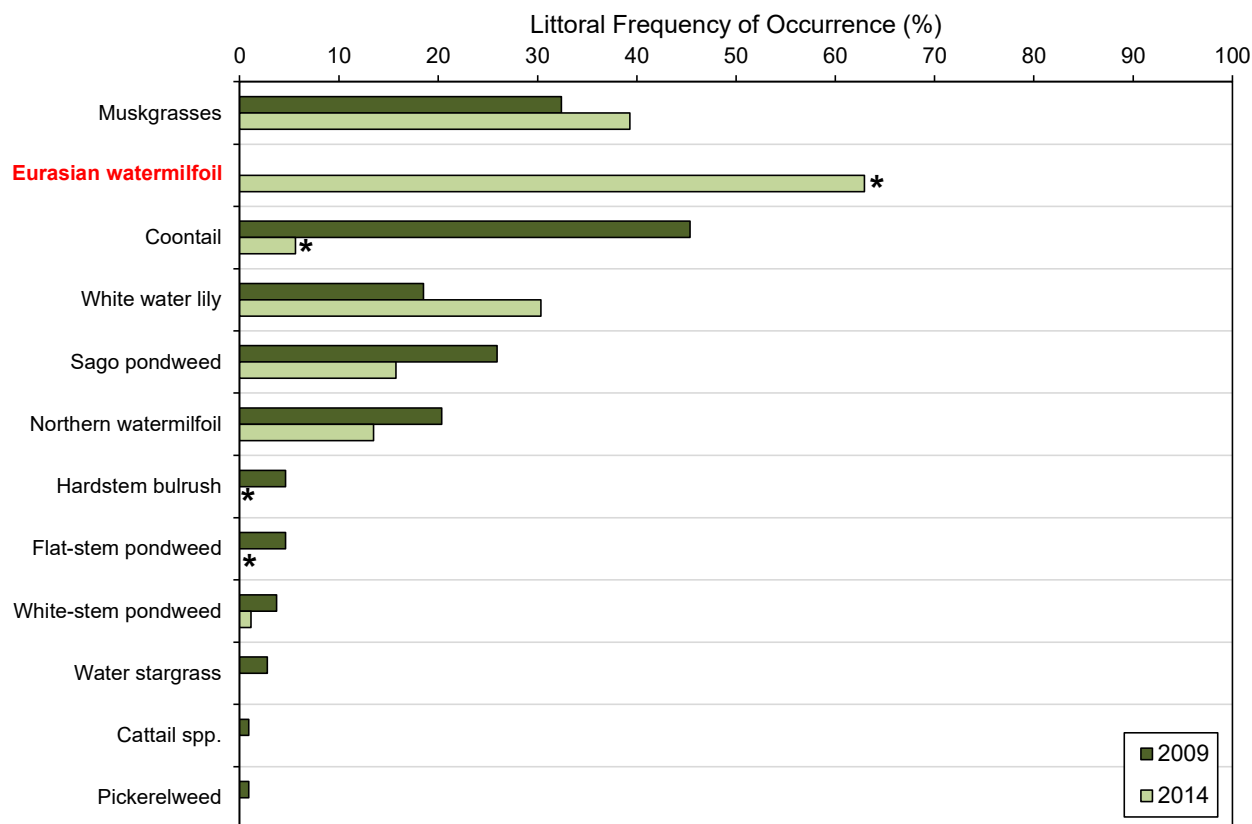

Figure 7. East Alaska Lake littoral frequency of occurrence of aquatic plant species from 2009 and 2014. Created using data from WDNR 2009 and 2014 whole-lake point-intercept surveys.

Ongoing WDNR aquatic plant studies on Wisconsin lakes indicate that EWM populations have the capacity to naturally fluctuate in size between years, believed to be driven by variations in climatic and other environmental conditions from year to year. In East Alaska Lake, there are a few theories as to why the EWM population was found to have increased over a relatively short amount of time. One theory is that the EWM population was able to expand due to the increased water clarity in the lake following the alum treatment. However, average growing season water clarity following the alum

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treatment was only found to have increased by 0.5 feet, which is not believed to be significant enough to cause the rapid expansion of EWM.

The second theory, which is believed to be more likely, is that the reduced water clarity conditions present in 2010 and 2011 prior to the alum treatment were less favorable for native aquatic plants and provided EWM with a competitive advantage. Some of the native aquatic plants in East Alaska Lake, like muskgrasses and northern water milfoil, require higher water clarity to persist. The summers of 2010 and 2011 had some of the lowest historical water clarity measurements, and these conditions may have suppressed the growth of native aquatic plants and allowed the more shade-tolerant EWM to take advantage and expand.

A third possibility is that hybrid water milfoil (HWM), a genetic cross between EWM and the indigenous northern water milfoil, was introduced to East Alaska Lake. Certain strains of HWM have been shown to grow more rapidly and more prolifically than pure-strain EWM. Hybrid water milfoil became the most dominant plant within the littoral zone of English Lake (Manitowoc County) within just a few years following its introduction. While a milfoil specimen from East Alaska Lake was genetically tested and confirmed as pure-strain EWM in 2013, it is possible that the lake contains both pure-strain EWM and HWM. It is recommended that multiple specimens from multiple locations around the lake be genetically tested for hybridity in 2015.

As mentioned earlier, EWM populations have the capacity to fluctuate naturally from year to year. Continued monitoring is recommended to further understand the dynamics of East Alaska Lake's population by conducting another whole-lake point-intercept survey in 2017 along with full mapping of the population based upon density, as was completed in 2014. Not only will this allow for a documentation of the EWM population, but it will also allow for a determination of how the native aquatic plant community is fairing. Following the 2017 surveys, a planning meeting with the Tri-Lakes Association should be conducted to discuss continued monitoring and possibly control strategies for EWM.

Curly-leaf pondweed (*Potamogeton crispus*; CLP), another non-native invasive plant, was first documented in East Alaska Lake in 1993. Onterra ecologists mapped CLP locations in East Alaska Lake in June 2011 and June 2014 (Figure 8). In 2011, an approximate 0.4-acre colony of *scattered* CLP was located near the public access location, while a number of single plants and clumps of plants were located in littoral areas around the lake. However, in June 2014, only two single CLP plants were located in East Alaska Lake within the southern basin. It is not known why the CLP population appears to have declined, but most of the areas that contained CLP in 2011 are now occupied by EWM. It is possible that the EWM population took over areas and suppressed the growth of CLP throughout most of the areas in the lake. Periodic early-season meander-based surveys are recommended to continue monitoring of East Alaska Lake's CLP population.
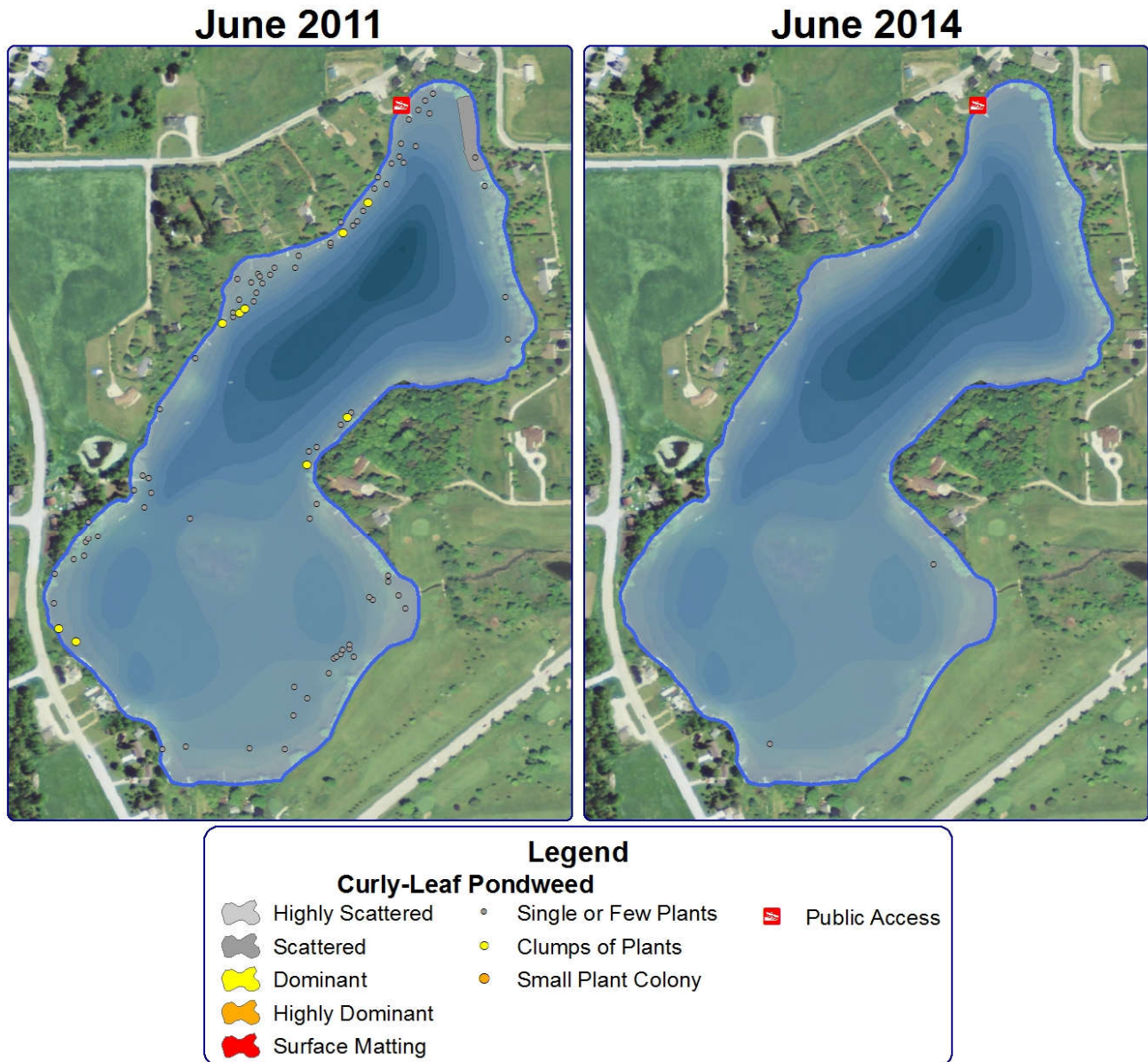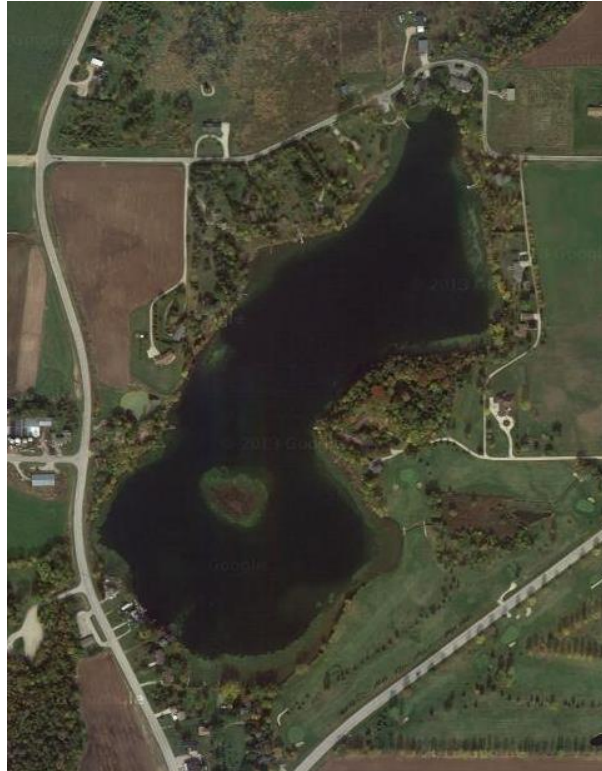
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Figure 8. East Alaska Lake curly-leaf pondweed locations from June 2011 and June 2014.

ACKNOWLEDGMENTS

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Post-Alum Treatment Assessment of Diffusive Phosphorus Flux and Sediment Characteristics in East Alaska Lake, Wisconsin

Google Maps

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1 April, 2015

EXECUTIVE SUMMARY

Sediment cores were collected from spatially-distributed stations in East Alaska Lake in 2014, three years after a 130 g/m^2 Al treatment, to evaluate internal phosphorus (P) loading reduction and P binding effectiveness. Rates of P release from anaerobic sediment, measured in laboratory incubation systems, declined by 88% to nearly 100% in 2014, relative to pretreatment rates that ranged between ~ 1 and 12 mg/m^2 d. For instance, the P release rate declined in the deep basin sediments of East Alaska Lake from 11.5 mg/m^2 d in 2011 to only 0.68 mg/m^2 d in 2014 in conjunction with Al treatment. Post-treatment P release rates were also very low at all other stations, ranging between undetected to 0.024 mg/m^2 d. The Al floc was clearly visible as a milky white precipitate in sediment sections and was visually located in the upper 4-cm layer in the sediment core collected from the deep basin of the lake (station 1). Moisture content and porosity (i.e., percent of the sediment volume occupied by interstitial space) at station 1 were very high, while sediment wet and dry bulk density were low, suggesting that the Al floc layer had mostly settled on top of the original sediment interface with minor to negligible sinking into the sediment. Concentrations of loosely-bound P at station 1 were nearly an order of magnitude lower in the Al floc layer versus concentrations at deeper depths below this layer. In contrast, aluminum-bound P concentrations were very high in the Al floc layer, reflecting sequestered P by $Al(OH)_3$. Total Al concentrations exhibited a similar peak in the upper 4-cm sediment layer at station 1 and the Al:P binding ratio was relatively low at 18:1, suggesting efficient P binding. The proportions and sources of this sequestered P are not precisely known. Some of it may have originated from the water column during the Al floc settling phase in 2011 versus sequestration of redox-sensitive P (i.e., redox-P; the sum of the loosely-bound and iron-bound P fractions) in the original sediment surface layer. The post-treatment Al concentration in the upper 5-cm layer ranged between 33 and 61 g/m^2, much lower than the intended 130 g/m^2 Al dose. Reasons for this discrepancy are not precisely known. Perhaps gravity coring inadvertently disturbed and dispersed the very fluid Al floc during sampling. Nevertheless, the settled Al floc has been very effective in controlling internal P loading

in East Alaska Lake. Modest loosely-bound P concentration gradients immediately below the Al floc layer may lead to slow upward P diffusion toward the sediment-water interface over time (i.e., years). Even though $Al(OH)_3$ will lose P binding efficiency over time due to polymerization, the Al floc still appears to be effective at sequestering this P.

OBJECTIVES

East Alaska Lake, WI, received an aluminum sulfate (Al) treatment (130 g Al/m^2; Hoyman 2013) during the fall of 2011 to reduce summer internal P loading from anaerobic sediment. The objectives of these investigations are to evaluate post-treatment changes in rates of phosphorus (P) flux from sediments and sediment chemical characteristics (i.e., biologically-labile P species) in 2014. The results will be important in evaluating the effectiveness of Al in controlling internal P loading in the lake.

APPROACH

Laboratory-derived rates of P release from sediment under anaerobic conditions

An intact sediment core was collected from 8 stations in late September, 2014, corresponding to locations sampled in 2010, before the Al treatment (Figure 1 and Table 1). Sediment collected from station 7 was, unfortunately, lost during sectioning and is not included in the results. The cores were drained of overlying water and the upper 10 cm of sediment transferred intact to a smaller acrylic core liner (6.5-cm dia and 20-cm ht) using a core remover tool. Surface water collected from the lake was filtered through a glass fiber filter (2.0 μ nominal pore size, Gelman A-E), with 300 mL then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. Sediment incubation systems consisted of the upper 10-cm of sediment and filtered overlying water contained in acrylic core liners that were sealed with rubber stoppers. They were placed in a darkened environmental chamber and incubated at a constant temperature (20 ºC). The oxidation-reduction environment in the overlying water was

controlled by gently bubbling nitrogen (anaerobic conditions) through an air stone placed just above the sediment surface in each system. Bubbling action insured complete mixing of the water column but did not disrupt the sediment.

Water samples for soluble reactive P were collected from the center of each system using an acid-washed syringe and filtered through a 0.45 μm membrane syringe filter (Nalge). The water volume removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured for determination of dilution effects. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA 2005). Rates of P release from the sediment (mg/m^2 d) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m^2) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

Sediment chemistry

Sediment cores were collected at 7 spatially-distributed stations for analysis of sediment chemistry in the upper 5 cm sediment layer (Figure 1). An additional core was collected from the deepest region of the lake (station 1) for examination of vertical variations in sediment chemistry. This core was sectioned at 1-cm intervals over the upper 5-cm layer and 2-cm intervals below that depth. Section sections were analyzed for sediment moisture content, density, organic matter content, loosely-bound P, iron-bound P, aluminum-bound P, and total Al (Table 2).

Subsamples were dried at 105 °C to a constant weight and burned at 550 ºC for determination of moisture content, sediment density, and organic matter content (Avnimelech et al. 2001, Håkanson and Jansson 2002). Phosphorus fractionation was conducted on fresh wet sediment sections according to Hieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of ammonium-chloride-extractable P (1 M NH_4Cl; loosely-bound P), bicarbonate-dithionite-extractable

P (0.11 M BD; iron-bound P), and sodium hydroxide-extractable P (0.1 N NaOH; aluminum-bound P). Additional sediment was dried to a constant weight at 105 °C in a forced-air oven and ground with a mortar and pestle for determination total Al. Total Al was analyzed using inductively-coupled plasma atomic emission spectroscopy (EPA method 200.7 rev 4.4) after microwave-assisted digestion.

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface as a result of chemical and bacterial reduction reactions under anaerobic conditions that lead to desorption of P from sediment and diffusion into the overlying water column (Mortimer 1971, Boström 1984, Nürnberg 1988; Table 3). The sum of the loosely-bound and iron-bound P fraction is redox-sensitive P (i.e., the P fraction that is active in P release under anaerobic and reducing conditions). Aluminum-bound P reflects P that has been adsorbed to the Al floc (Rydin and Welch 1999).

RESULTS AND INTERPRETATION

Diffusive phosphorus flux

P mass and concentration increases were either low or negligible in the overlying water column of sediment systems maintained under anaerobic conditions (Figure 2). The station 1 sediment system, which was collected from the deepest region of the lake, exhibited approximately linear P increases in the overlying water column during the first 7 days of incubation. SRP concentrations approached 0.10 mg/L during this period, then leveled off and remained constant after day 8 of incubation. P mass and concentration increases were lower in the overlying water column of station 2, 3, 4, and 8 sediment systems compared to station 1. These stations were also located in the deep main basin of the lake. Linear concentration increases occurred over the first 3 to 5 days then leveled off and remained constant. SRP concentrations in the overlying water column at the end of the incubation period were relatively low at 0.05 mg/L, 0.025 mg/L, 0.023 mg/L, and 0.018 mg/L for station 2, 3, 4, and 8 sediment systems, respectively. In contrast, SRP

accumulation was not detected in station 5 and 6 sediment systems, located at shallower depths in the lake.

Overall, rates of P release under anaerobic conditions were low post-alum treatment compared to pre-treatment rates (Table 4). Station 1 exhibited the highest post-alum treatment P release rate at ~ 0.7 mg/m^2 d. Rates at other stations were less than 0.25 mg/m^2 d to undetectable. By comparison, anaerobic P release rates exceeded 11 mg/m^2 d at station 1 in 2010, before alum treatment (Figure 3). They were also relatively high at the other stations prior to alum treatment, ranging between 0.7 mg/m^2 d and 3.9 mg/m^2 d. Three years post-treatment, anaerobic P release rates have declined by 88% to nearly 100% (Figure 3).

Sediment vertical and spatial characteristics

The Al floc was clearly visible as a milky white precipitate during laboratory sediment sectioning (Figure 4). In addition, cores consisted of very flocculent material with white precipitated Al floc in the upper ~ 4 cm overlying more homogeneous sediments (Figure 5). Vertical patterns in sediment characteristics at station 1 indicated that moisture content and porosity (i.e., percent of the sediment volume occupied by interstitial space) were very high in the apparent Al layer at > 98% (Figure 6). Moisture content declined sharply below this depth to ~ 93% (range = 90.2% to 94.7%; Table 5). Wet bulk density approached 1.00 g/cm^3 in the Al layer and increased to 1.034 g/cm^3 below the 4-cm depth (Figure 6). These patterns suggested that the Al floc has probably not settled much below the original sediment interface three years after application due to density differences between the Al floc and the pre-treatment sediment.

Loosely-bound and iron-bound P concentrations were lowest in the upper 4-cm layer and increased below that depth (Figure 7). The mean loosely-bound P concentration was only 0.03 mg/g in the Al layer compared to a mean 0.17 mg/L below the 4-cm depth (Table 5). In contrast, vertical differences in the iron-bound P concentration were minor (Figure 7). While the mean iron-bound P concentration in the Al layer was relatively low

at 0.08 mg/g, the mean concentration below 4 cm was only slightly higher at 0.10 mg/g (Table 5).

Both total Al and aluminum-bound P concentrations exhibited a peak at the 3-cm depth and concentrations were greatest between 0 and 4 cm (Figure 8). Below 4 cm, total Al and aluminum-bound P concentrations declined substantially and were relatively constant at 7.4 mg/g and 0.13 mg/g, respectively. In addition, the mean aluminum-bound P concentration was an order of magnitude higher over the upper 4-cm sediment layer versus the 4-8 cm depth (Table 5). Clearly, elevated total Al and aluminum-bound P concentrations in the upper 4-cm layer represented P sequestered by the Al floc. An unknown portion of this sequestered P could have originated from the water column during initial aluminum sulfate application, reaction to $Al(OH)_3$, and deposition through the hypolimnion in 2011, while another portion was likely derived from the redox-sensitive P pool in the sediment after floc deposition onto the sediment surface. However, these proportions cannot be quantified because the location of the original sediment interface prior to Al application is not precisely known.

Since an Al dosage of 130 g/m^2 was estimated as the concentration required to bind redox-P in the upper 10-cm layer of East Alaska Lake sediment, the implied assumption was that the Al floc would settle through the upper sediment layers and sequester redox-P. However, an unknown is Al floc density in relation to sediment density. In order to meet the treatment objectives for East Alaska Lake, the newly deposited Al floc layer needed to be denser than the upper sediment layer and sink through that layer relatively quickly (i.e., within 3 months or less). Vertical patterns of very high moisture content and low wet bulk density for station 1 sediment, coupled with high concentrations of Al and aluminum-bound P in the upper 4-cm sediment layer, suggested the possibility that the Al floc mostly formed a new layer on top of the original sediment interface and has not sunk appreciably since initial application in 2011. In addition, the organic content was much higher in the upper 4 cm compared to deeper layers (Figure 6 and Table 5). This vertical pattern may be attributable to breakdown and mineralization over time as new sediment accretes. Or, it could also represent organic matter that was sequestered by alum during

initial settling to the sediment surface. If the latter case, results would suggest that a significant portion of the aluminum-bound P might have originated via sequestration of water column P.

Recent research has suggested that $Al(OH)_3$ binding efficiency for P decreases significantly (i.e., > 75% decrease) if it has not been exposed to and reacted with sediment redox-P within 90 days, due to changes in crystalline structure and polymerization in the absence of adsorbed P (de Vicente et al. 2008). Furthermore, as binding sites on the $Al(OH)_3$ floc become saturated with redox-P, additional P diffusing into the alum layer from deeper sediments over time can become re-adsorbed to $Fe\sim(OOH)$ (i.e., redox-P; Lewandowski et al. 2003), eventually diffuse out of the sediment under anaerobic and reducing conditions, and again become an important internal P loading source years after alum treatment. For East Alaska Lake sediments, there is a potential loosely-bound P concentration gradient between the 5- and 7-cm depths (Figure 7) that could drive upward P diffusion into the Al floc layer over time. While the Al floc can continue to adsorb P (Lewandowski et al. 2003), P binding efficiency could decline. However, loosely-bound and iron-bound P concentrations are very modest in East Alaska Lake sediment, compared to other eutrophic systems (i.e.> 1 mg/g to > 8 mg/g), suggesting that the Al floc will continue to be effective in sequestering P diffusing from deeper layers. Indeed, rates of P release under anaerobic conditions continue to be negligible 3 years after initial alum application.

Surprisingly, total Al concentrations in the upper 5-cm sediment layer at station 1 accounted for only 25% of the intended 130 g/m^2 application in 2011 (Table 6). Instead, total Al in the upper $\sim$ 20-cm layer approximated 130 g/m^2. Reasons for this discrepancy are not known, but additional replicate sediment cores should be examined to confirm results reported here. Some of the $Al(OH)_3$ could have migrated downward below the 5-cm sediment depth. Gravity core sampling may have also disturbed and dispersed the almost completely fluid sediment surface containing the Al floc. The Al:P binding ratio (i.e., parts Al required to bind 1 part P) was relatively low in the upper 5 cm at 18:1, suggesting efficient P binding in the Al floc layer (Table 6).

Pre- and post-treatment variations in sediment physical-textural and chemical characteristics over the upper 5-cm sediment layer are, perhaps, misleading because some of the sediment below the Al floc was inevitably included in the section. However, the 5-cm section protocol was used for comparison with pre-treatment analyses of the 5 cm. Moisture content and porosity tended to be higher, while wet and dry bulk densities were lower, in post-treatment, 2014, sediments (Figure 9). A similar pattern was observed for organic matter content. As with vertical trends for station 1 sediment, these results suggested that sediments were very flocculent post-treatment; a pattern most likely related to Al floc density characteristics.

With the exception of station 6, loosely-bound P concentrations in the upper 5-cm sediment layer were usually much lower post-treatment (Figure 10). Post-treatment reductions in iron-bound P were much less pronounced. However, loosely-bound P accounted for most of the redox-P prior to Al treatment. Redox-P concentrations were also lower in the upper 5-cm layer for station 1, 4, 5, and 8 sediments, reflecting declines primarily in the loosely-bound P fraction (Figure 10). Pre- versus post-treatment changes in the redox-P concentration were either minor or insignificant for station 2, 3, and 6 sediment. However, this pattern may be attributable to the sectioning process and inclusion of sediment below the Al floc rather than poor sequestration by $Al(OH)_3$ because rates of P release were either minor or not detectable for these same sediments (Figure 3). Aluminum-bound P concentrations were generally higher in the upper 5-cm layer of sediment collected 3 years after application, reflecting sequestered P by the Al floc. An exception was station 6.

Total Al concentrations in the upper 5-cm sediment layer varied between 8 and 56 mg/g (Figure 11 and Table 7). The areal Al concentration (g/m^2) was greatest at stations 1, 2, 3, 5, and 8, ranging between 41 and 61 g/m^2 (Figure 11 and Table 7). Similar to the vertical Al profile at station 1, these ranges represented only 25 to 47% of the intended 130 g/m^2; but some of the Al floc may have been located below 5 cm and, therefore, not accounted for in the estimate. In general, the nearly uniform range of areal Al concentrations was also surprising given that sediment focusing processes have been

shown to result in transport of the Al floc to deepest regions in other Al-treated lakes (Huser et al. 2011, Huser 2012).

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Table 1.Sediment sampling locations and numbers of sediment cores collected for determination of rates of phosphorus (P) flux under anaerobic conditions and P fractions (see Table 2).

Station	P Flux	P fractions	
		upper 5 cm	Vertical profile
1	1	1	1
2	1	1	
3	1	1	
4	1	1	
5	1	1	
6	1	1	
8	1	1	

Table 2. Sediment physical-textural characteristics, phosphorus species, and metals variable list.	
Category	**Variable**
Physical-textural	Moisture content
	Wet and dry sediment bulk density
	Organic matter content
Phosphorus species	Loosely-bound P
	Iron-bound P
	Aluminum-bound P
Metals	Aluminumium

Table 3. Sediment sequential phosphorus (P) fractionation scheme, extractants used, and definitions of recycling potential.

Variable	Extractant	Recycling Potential
Loosely-bound P	1 M Ammonium Chloride	Biologically labile; Soluble P in interstitial water and adsorbed to $CaCO_3$; Recycled via direct diffusion, eH and pH reactions, and equilibrium processes
Iron-bound P	0.11 M Sodium Bicarbonate-dithionate	Biologically labile; P adsorbed to iron oxyhydroxides (Fe(OOH); Recycled via eH and pH reactions and equilibrium processes
Aluminum-bound P	0.1 N Sodium Hydroxide	Biologically refractory; Al-P minerals with a low solubility product. Also extracts P sequestered by the Al floc.

Table 4. Rates of phosphorus (P) release under anaerobic conditions and the P concentration in the overlying water column near the end of the incubation period for intact sediment cores collected at various stations in East Alaska Lake.

	Anaerobic P release		
Station	2010	2014	Change
	(mg/m^2 d)		(%)
1	11.5	0.68	94.1
2	2.1	0.24	88.6
3	2.5	0.17	93.2
4	1.3	0.16	87.7
5	0.7	N.D.	99.9
6	1.3	N.D.	99.9
8	3.9	< 0.10	97.9

Table 5. Mean sediment physical-textural and phosphorus fraction characteristics in the 0 - 4 cm and 4 - 8 cm layers in the sediment core collected at station 1, East Alaska Lake.

	Moisture content	Bulk density		Organic content	Loosely-bound P	Iron-bound P	Redox P	Aluminum-bound P
		Wet	Dry					
	(%)	(g/cm^3)	(g/cm^3)	(%)	(mg/g)	(mg/g)	(mg/g)	(mg/g)
0 - 4 cm	98.3	1.006	0.018	41.4	0.029	0.083	0.112	2.301
4-8 cm	92.5	1.034	0.078	28.3	0.171	0.098	0.269	0.218

Table 6. Variations in total aluminum, aluminum-bound P, and the aluminum:aluminum-bound P binding ratio (Al:P) in the sediment core collected at station 1 in 2014. The integrated Al:P binding ratio represents the mean above the section bottom depth. For instance, the depth-integrated Al:P ratio of 18:1 represents the ratio between 0 and 5 cm.

Section	Aluminum		Aluminum-bound P		Al:P binding ratio	
(cm)	(mg/g)	(g/m^2)	(mg/g)	(g/m^2)	(by depth)	(integrated depth)
0-1	21.4	2.97	1.27	0.176	17	17
1-2	33.5	7.55	1.96	0.443	17	17
2-3	67.2	17.68	3.87	1.027	17	17
3-4	31.6	26.26	2.11	1.599	15	16
4-5	11.7	32.67	0.49	1.866	24	18
5-7	6.4	40.36	0.19	2.096	34	19
7-9	5.6	48.98	0.17	2.356	33	21
9-11	6.4	62.02	0.13	2.611	51	24
11-13	7	75.08	0.12	2.829	60	27
13-15	6.4	92.58	0.10	3.111	62	30
15-17	6.4	111.56	0.10	3.392	67	33
17-19	6.4	133.55	0.09	3.688	74	36

Table 7. Variations in total aluminum, aluminum-bound P, and the aluminum:aluminum-bound P binding ratio (Al:P) in the upper 5-cm layer of sediment cores collected at various stations in East Alaska Lake, 2014.

Station	Aluminum		Aluminum-bound P		Al:P binding ratio
	(mg/g)	(g/m^2)	(mg/g)	(g/m^2)	
1	55.7	53	1.943	1.859	29
2	22.3	41	0.547	1.004	41
3	42.1	45	0.850	0.900	50
4	17.4	33	0.268	0.513	65
5	31.7	61	0.508	0.979	62
6	7.9	33	0.103	0.430	77
8	19.3	51	0.498	1.321	39
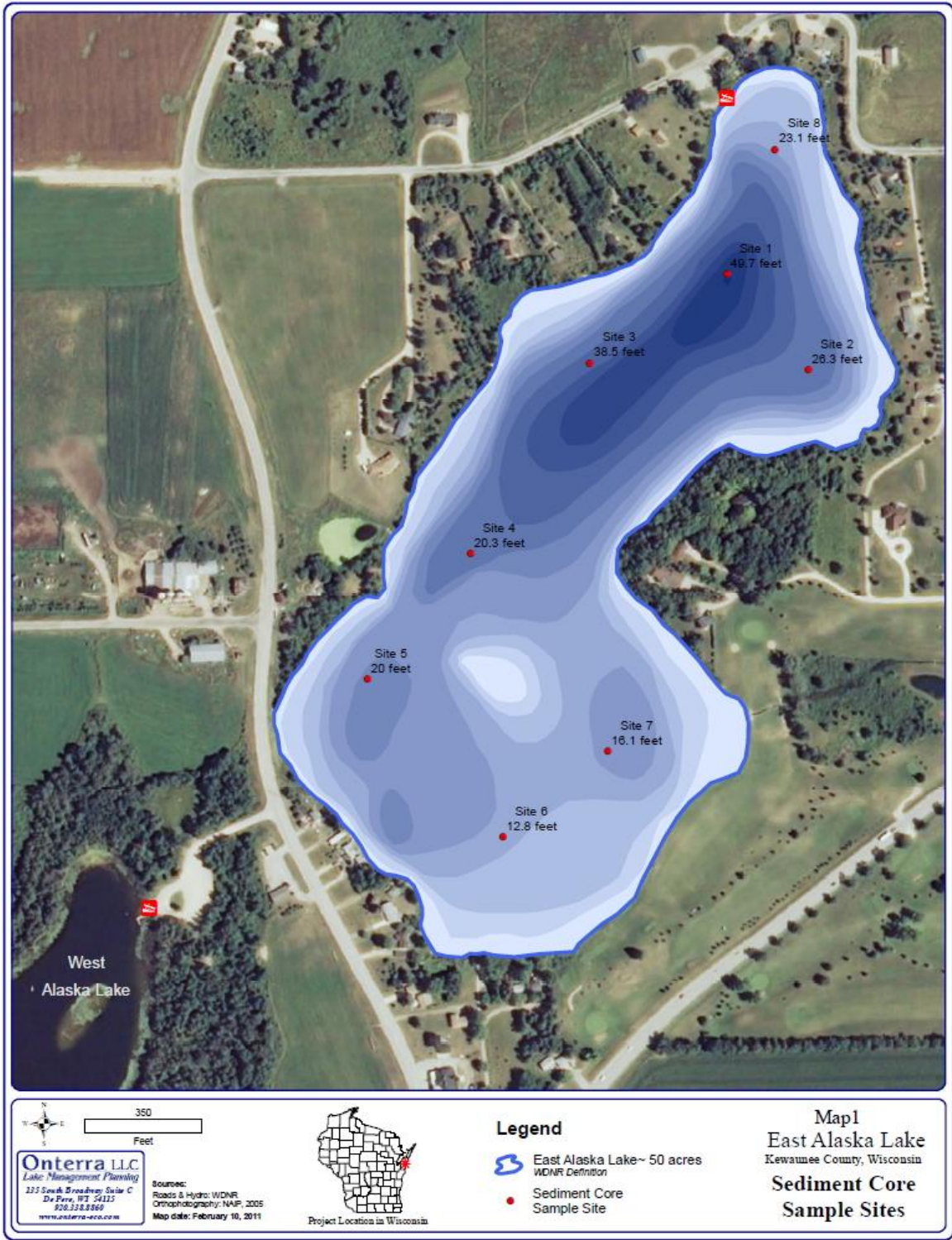
Figure 1. Station locations in East Alaska Lake.

Anaerobic P Release Rate
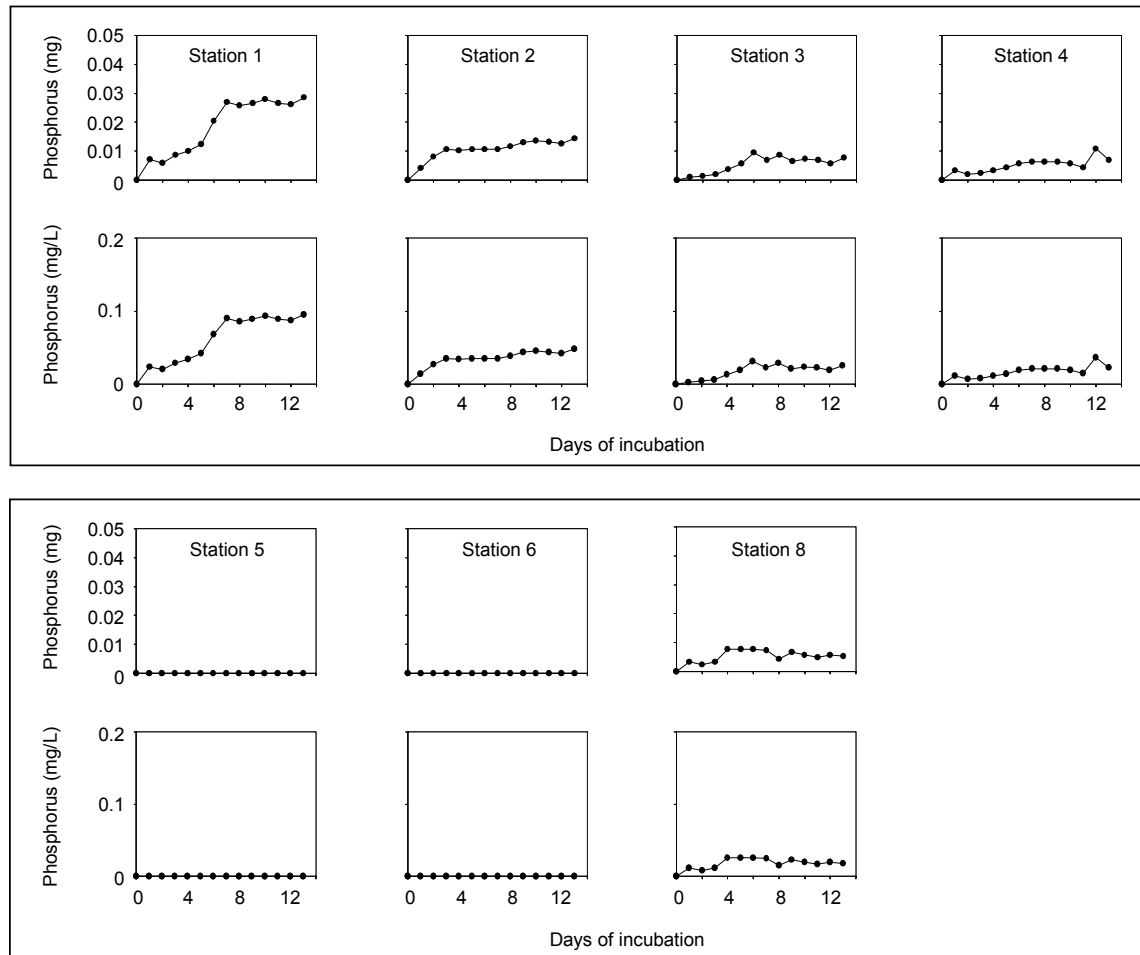
Figure 2. Changes in soluble reactive phosphorus mass (upper panels) and concentration (lower panels) in the overlying water column under anaerobic conditions versus time for sediment cores collected in East Alaska Lake.
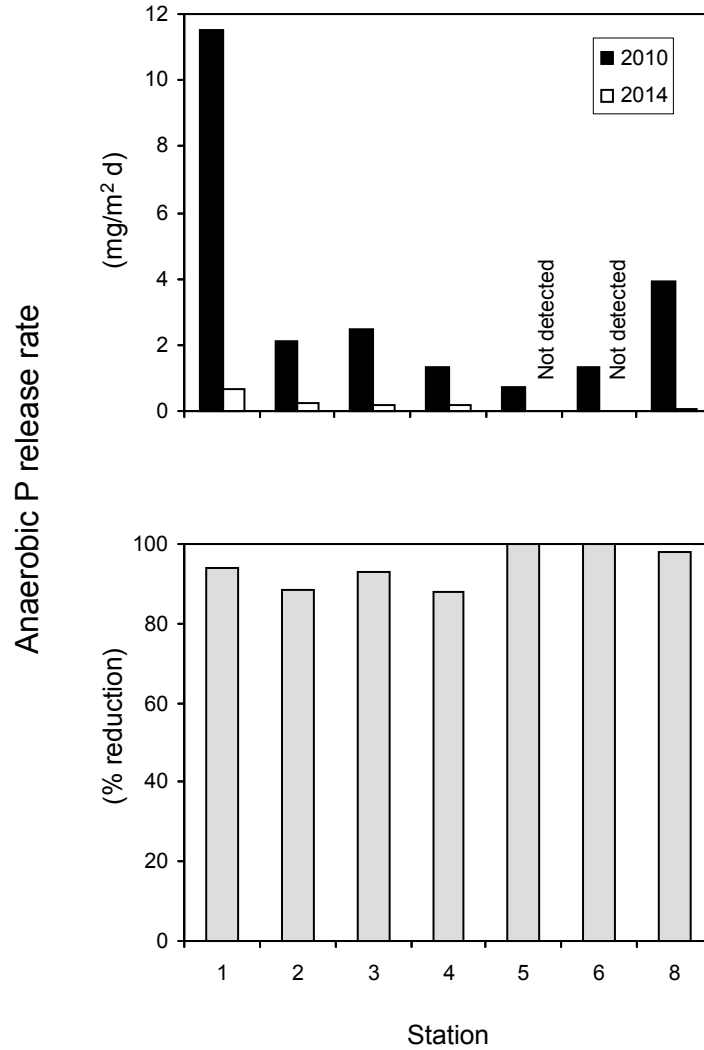
Figure 3. Rates of phosphorus (P) release from sediment under anaerobic conditions in 2010 (i.e., before aluminum sulfate treatment) and 2014 (i.e., 3 years after treatment; upper panel) and post-treatment percent reduction in the anaerobic P release rate (lower panel) for various sediment sampling stations in East Alaska Lake.
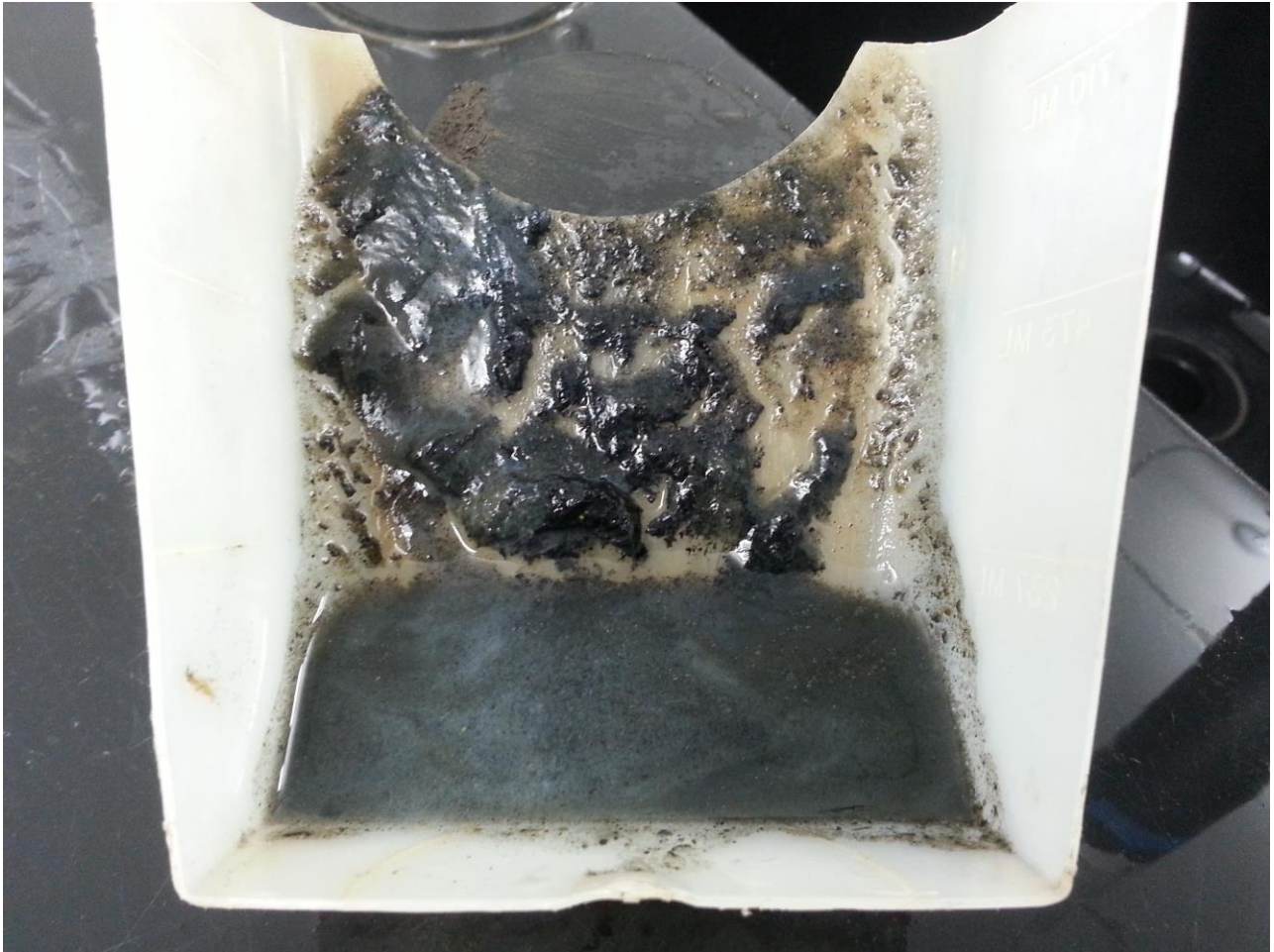
Figure 4. Sediment section showing evidence of a milky white alum precipitate.
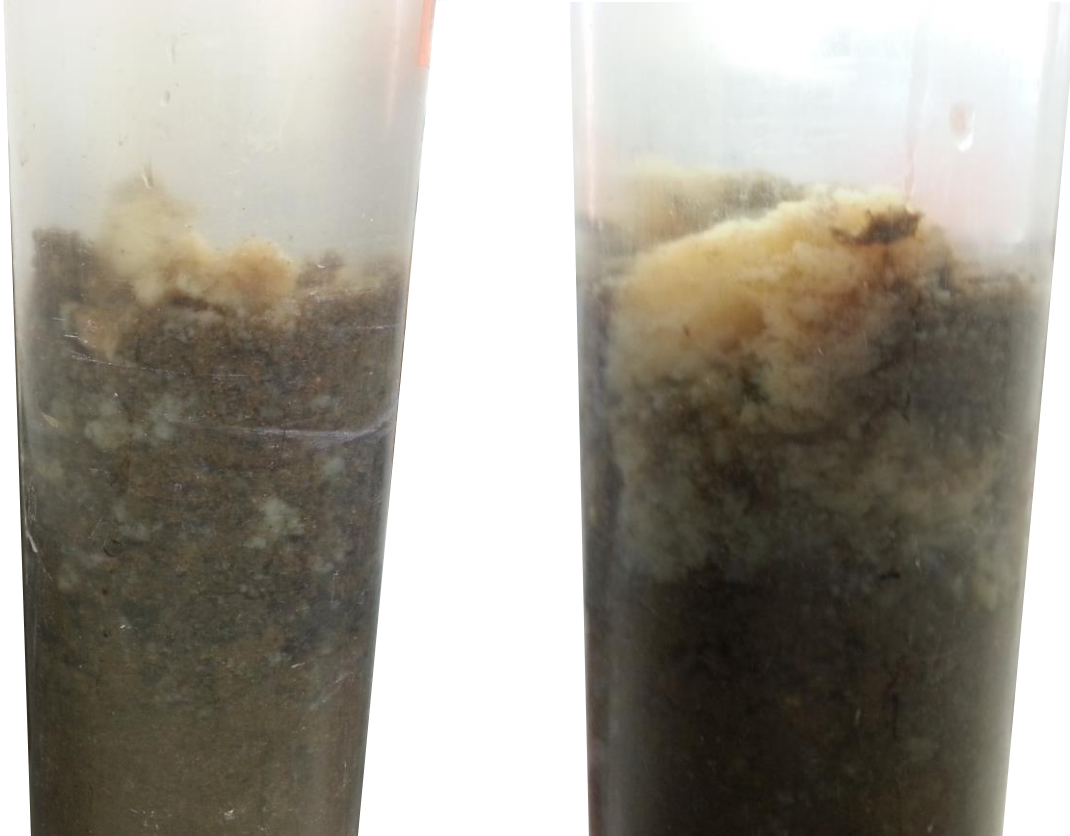
Figure 5. Alum floc layer visible in intact sediment cores collected in East Alaska Lake.
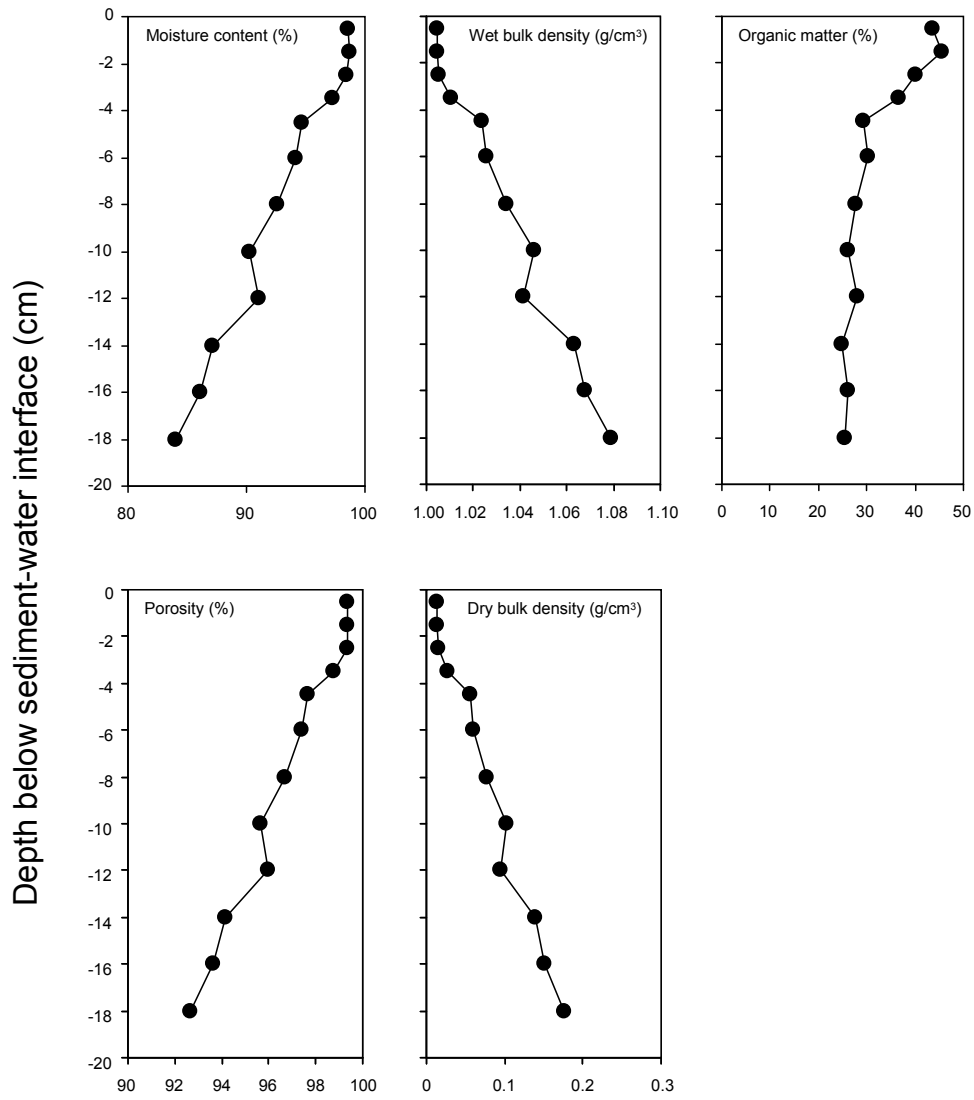
Figure 6. Vertical variations in sediment moisture content, porosity, wet and dry bulk density, and organic matter content in the sediment core collected at station 1.
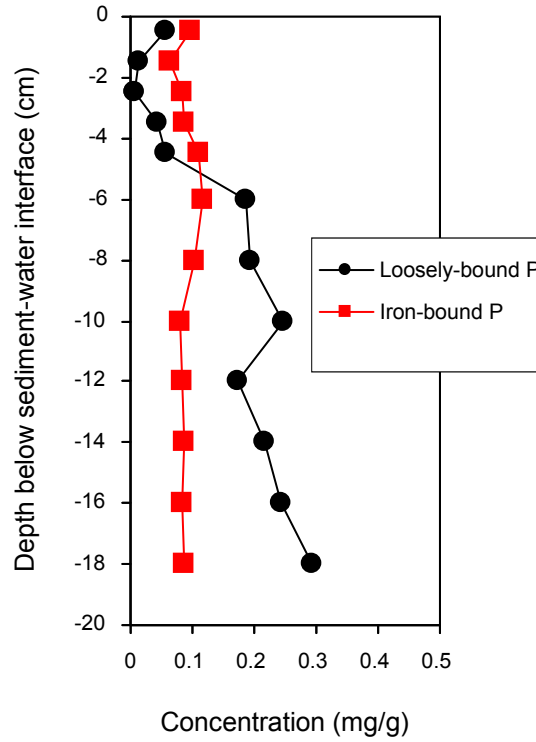
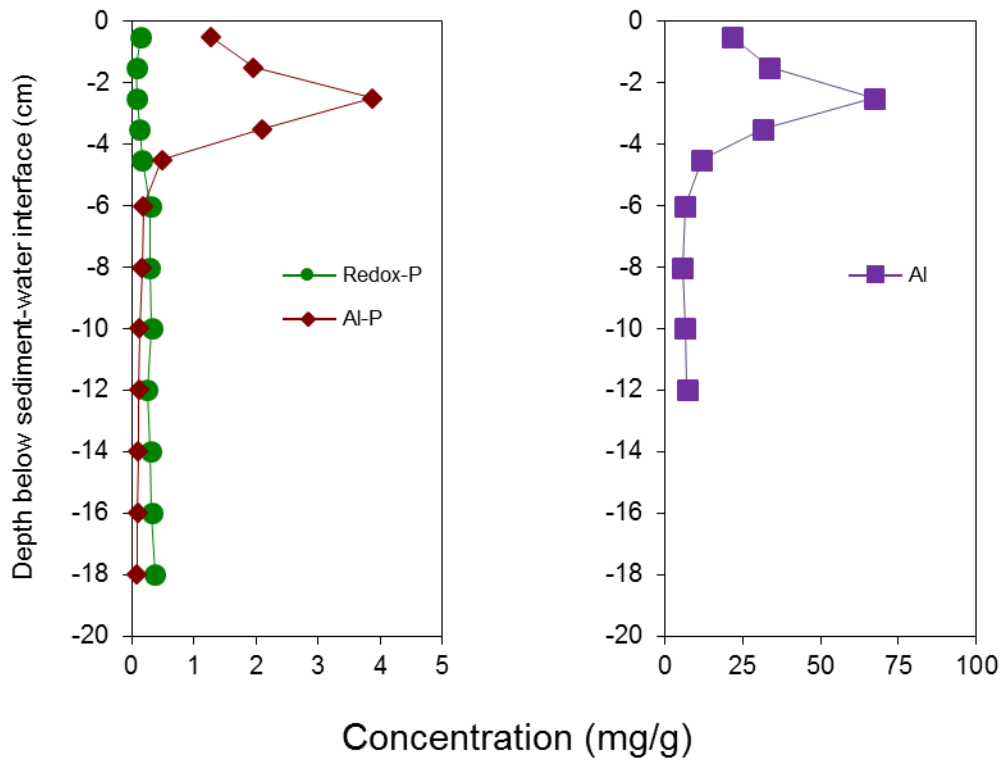*Figure 7. Vertical variations in loosely-bound and iron-bound phosphorus (P) fractions in the sediment core collected at station 1.*

Figure 8. Vertical variations in redox-P (i.e., the sum of the loosely-bound and iron-bound phosphorus fraction; redox-P is subject to Eh and pH reactions and typically correlated with anaerobic P release rates), aluminum-bound P (i.e., Al-P; P sequestered by the alum floc), and total aluminum (Al) in the sediment core collected at station 1.
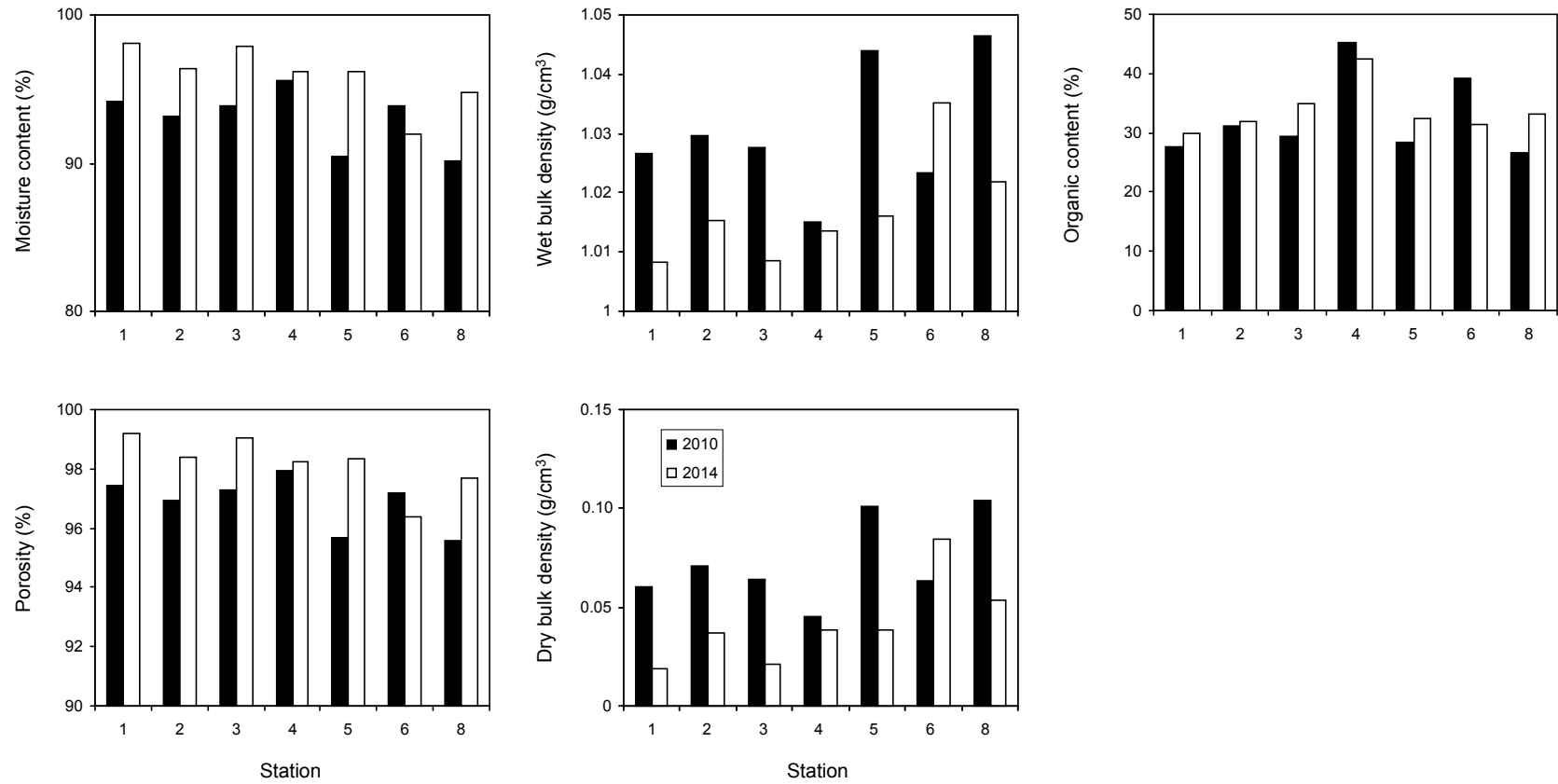
Figure 9. Variations in sediment textural-physical characteristics in 2010 (i.e., before aluminum sulfate treatment) and 2014 (i.e., 3 years after treatment) for the upper 5-cm section collected from various sediment sampling stations in East Alaska Lake.
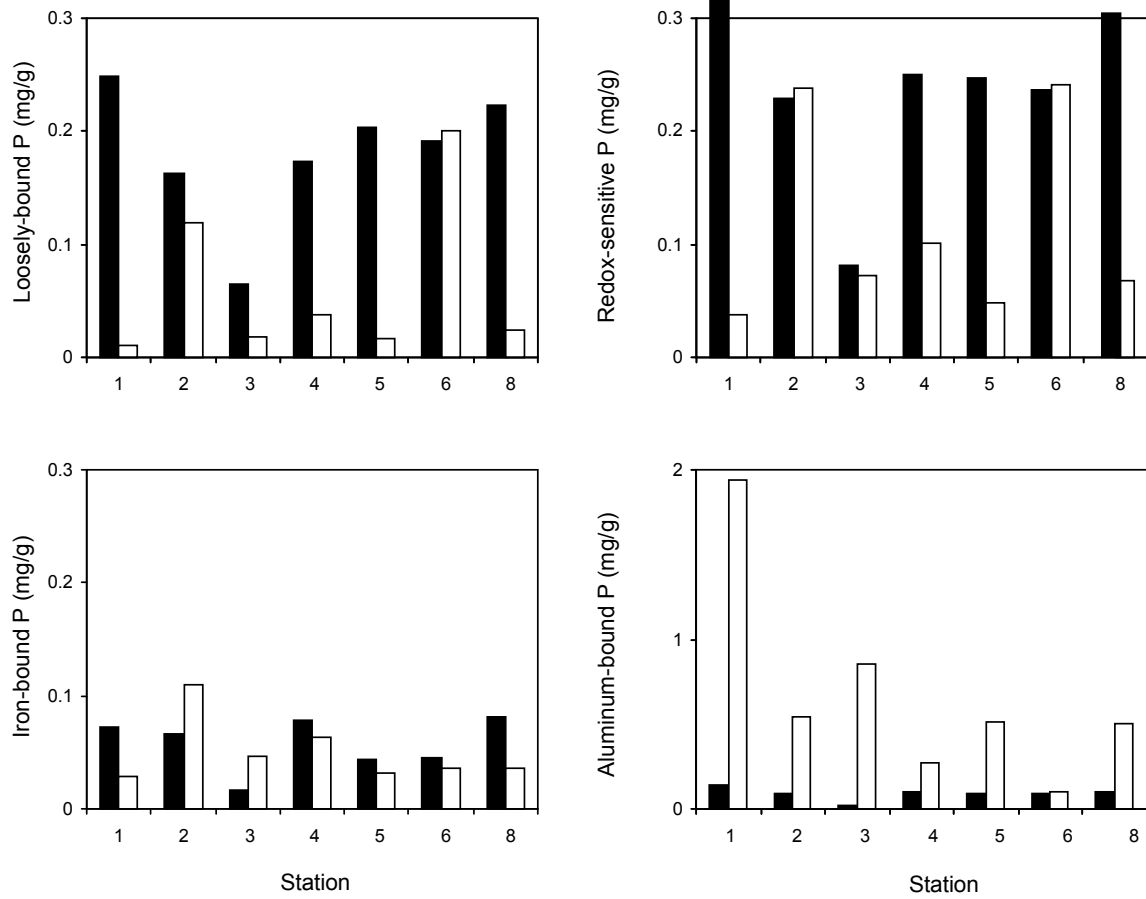
Figure 10. Variations in sediment phosphorus (P) fractions in 2010 (i.e., before aluminum sulfate treatment) and 2014 (i.e., 3 years after treatment) for the upper 5-cm section collected from various sediment sampling stations in East Alaska Lake. Redox-sensitive P = the sum of the loosely-bound and iron-bound P fractions.
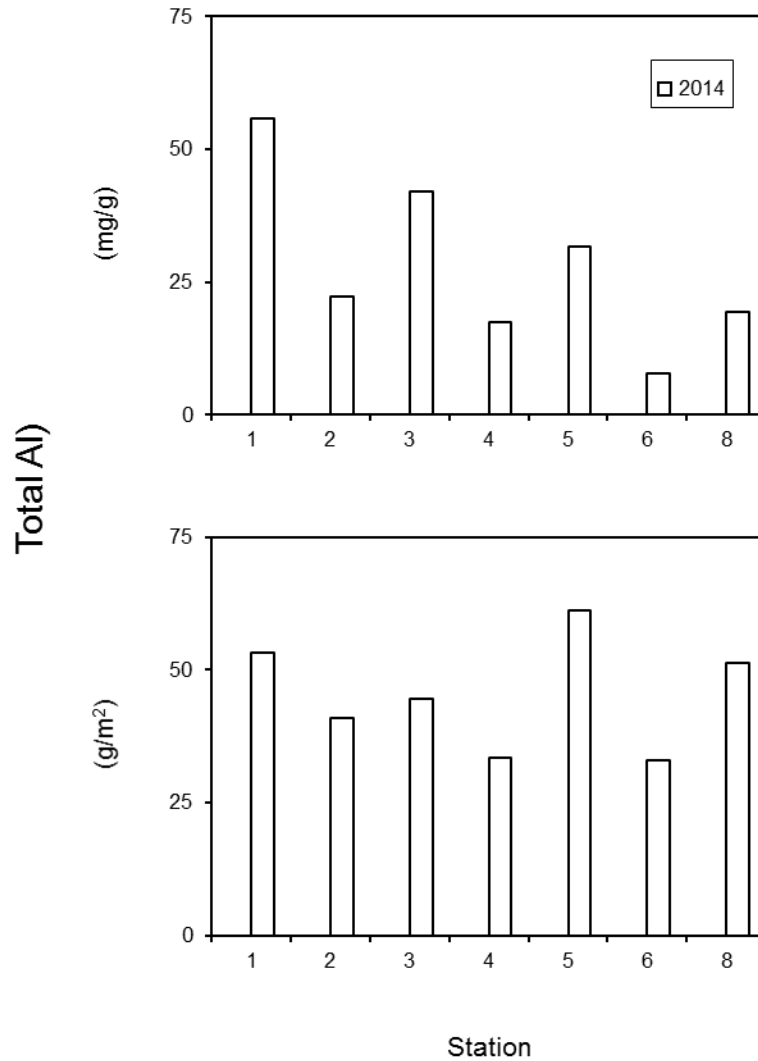
Figure 11. Variations in sediment total aluminum (Al) concentration in 2014 (i.e., 3 years after treatment) for the upper 5-cm section collected from various sediment sampling stations in East Alaska Lake. Al concentrations were not measured in 2010. However, a baseline of 7.4 mg Al/g, estimated from the vertical sediment profile determined from the station 1 sediment core, can be used as an approximate pre-treatment Al concentration.