

Preliminary interpretation of alum treatment performance in Cedar Lake Wisconsin 2022

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The Cedar Lake phosphorus (P) budget was dominated by internal loading from anoxic sediment, leading to cyanobacteria blooms, particularly after periods of water column turnover (James 2014). Blooms were often greatest during turnover events in August and chlorophyll concentrations often exceeded 100 μg/L by September. Aluminum sulfate (alum) applications were implemented starting in 2017 to reduce internal P loading and suppress cyanobacteria blooms, The recommended Al doses of 130 g/m^2 in sediment areas greater than 25 ft and 100 $\frac{g}{m^2}$ for sediments located between 20 and 25 ft were based on mobile P concentrations in the upper 8-10 cm sediment layer (Fig. 1).

Figure 1. Alum dosage and application zones in Cedar Lake

These overall alum doses were split into smaller concentrations to be applied over a 15-year window at 2- to 3-year intervals. The first split dose was applied in 2017 at 20 g/m^2 in the 20-25ft depth contour and 26 g/m^2 in the > 25-ft depth zone (Table 1). The alum dose was increased

slightly in 2019. Concerns over movement and redistribution of the alum floc led to concentrating a 50 g/m^2 alum dose to sediments at depths > 25 ft. As of 2022, \sim 41 g/m² have been applied to sediments within 20-25-ft depth contour and ~ 104 g/m² have been applied to sediments located at depths > 25 ft (Table 1). Paradoxically, while mean (JUL-SEP) bottom soluble P concentrations have responded to alum

Figure 2. Trends in mean surface chlorophyll and mean bottom soluble phosphorus (SRP) before (i.e., 2010) and during the first 3 alum applications.

Mixing and turnover occurred shortly before 1 August, resulting in reoxygenation of the entire water column (Fig. 4). The lake again weakly stratified at the end of August with the reestablishment of bottom anoxia. Another mixing event in early September was accompanied by complete turnover and breakup of bottom anoxia (Fig. 4). A more detailed time series of vertical

applications by declining, mean surface chlorophyll concentrations have increased as a function of cumulative alum applications (Fig. 2). In particular, chlorophyll concentrations exhibited a peak of $\sim 100 \mu g/L$ shortly after the lake turned over in late July 2022 (Fig. 3). The lake was stratified with bottom anoxia between late May and late July 2022 (Fig. 4). There was some buildup of soluble P in the bottom water immediately above the sediment surface during peak hypolimnetic anoxia on 18 July 2022 (Fig. 5). However, the bottom soluble P concentration was \sim 77% lower at 0.193 mg/L compared to the pretreatment concentration of 0.848 mg/L on 20 July 2010. Soluble P concentrations were undetectable at depths less than 7 m in July 2022.

Figure 3. Seasonal variations in surface chlorophyll in 2022.

patterns, shown in Figure 6, indicated stratification and bottom anoxia on 18 July 2022, complete mixing and reoxygenation by 1 August 2022, re-establishment of very weak stratification with accompanying bottom anoxia by 29 August 2022, followed by another period of complete water column mixing and reoxygenation by 12 September 2022.

Patterns in soluble P concentration during these late summer polymixis events were unusual in 2022 and suggested that the relatively low soluble P concentrations that diffused through the

alum floc residing on top of the sediment were mixing throughout the water column during

Figure 4. Lake temperature and dissolved oxygen contours in 2022. Black shaded region indicates date to be collected. Red vertical bars denote turnover events.

turnover periods and completely available for algal uptake and growth (Fig. 7 and 8). For instance, after the first turnover event in late July, soluble P concentrations were elevated throughout the water column at ~ 0.022 mg/L on 1 August 2022. Temporary re-stratification in late August and redevelopment of bottom anoxia were accompanied by a slight soluble P concentration increase at the lake bottom to 0.133 mg/L, suggesting that some sediment P diffused through the alum floc layer. However, soluble P at this depth was very

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low compared to pre-treatment bottom concentrations.

Figure 5. A comparison of the vertical soluble P profile on 19 July 2010 (before alum) and 20 July

2022.

The other turnover event in early September coincided with another increase in soluble P throughout the water column.

Indeed, total and soluble P, averaged for the entire water column, exhibited abrupt concentration increases followed each turnover event (Fig. 8). This pattern suggested that soluble P mass in the lake was not conserved (i.e., remained the same) after mixing, but rather additional SRP sources were entrained

into the water column. One possibility is that mixing over the sediment surface during turnover can increase the rate of diffusive P flux (Hondzo et al. 2005). This soluble P was apparently 100% available for algal uptake, resulting in a large, sustained cyanobacteria bloom between late August and September 2022 (Fig. 9).

Figure 6. Vertical profiles of water temperature (upper panels) and dissolved oxygen (lower panels) in 2022.

Why has cumulative alum additions to Cedar Lake coincided with lower hypolimnetic P concentrations, yet greater availability of soluble P for algal uptake, and increasingly severe cyanobacterial blooms as of 2022? These patterns have led to several conclusions and hypotheses. First, although the alum is binding P (e.g., Fig. 5), there is still some "leakage" and diffusion through the alum floc into the hypolimnion. This observation is not unusual because the entire dose has not yet been applied. However, this soluble P seems to be entirely available for algal uptake and growth. Even though concentrations are much lower in the bottom waters after the alum treatments, they are still high enough to stimulate large blooms.

Second, after soluble P diffuses through the alum floc, there are apparently no other controls such as iron precipitation to remove the soluble P back to the sediment. Cedar Lake had a relatively low iron:phosphorus (Fe:P) ratio in the anoxic hypolimnion for the alum applications. Thus, some of the internal P load that accumulated in the hypolimnion was mixed to the surface during turnover events, stimulating algal blooms. Iron did precipitate some of the internal P load back to the sediment before treatment, but a portion remained in the water for algal uptake.

Figure 7. Vertical profiles of soluble P in 2022.

Third, cumulative alum applications seem to have exacerbated this pattern of available soluble P, rather than controlling it. Although hypolimnetic P has declined, soluble P still mixes into the surface waters. With cumulative alum applications soluble P availability has increased. These observations suggested that the alum applications have may have indirectly completely removed iron from precipitating P from the water column. Thus, once soluble P mixes into the water above the alum floc, it is available for algal uptake.

One mechanism that could explain this phenomenon is that the sulfate biproduct of aluminum sulfate has diffused into the sediment after each application and ultimately reacted with iron to form iron sulfide (FeS). Sulfate is converted to S, HS⁻, and H₂S by bacteria under anaerobic conditions in the

Figure 8. Seasonal changes in water-column weighted P in 2022. Red vertical lines denote turnover events.

sediment. These sulfur products can react with reduced iron $(Fe²⁺)$ in the sediment to form FeS, an inert solid that becomes permanently buried and removed from any further reaction with soluble P (Caraco et al. 1993, Fig. 10). An outcome of iron removal as FeS could be a further decline in soluble iron diffusing from sediment into the water column to precipitate P during turnover and reoxygenation. For instance, the 50 g/m^2 alum application to the 25-ft depth contour in 2021 could have temporarily increased the sulfate concentration in the lake severalfold, leading to enhanced diffusion into the sediment and conversion of mobile Fe to FeS (Fig. 11).

Figure 9. Total P (upper), soluble P (middle), and chlorophyll (lower) contours in 2022. Black shaded region indicates date to be collected. Red vertical bars denote turnover events.

Another difficulty in managing internal P loading in Cedar Lake is the polymictic (i.e., it can completely turnover several times during the summer) behavior. Since it can turn over completely in late July and August during peak

summer, internal P loading must either be completely suppressed by alum or there needs to be

some iron in sufficient concentration to precipitate out any soluble P during these turnover events. Otherwise, any soluble P that diffuses through the alum floc becomes completely available for cyanobacterial uptake and growth. Addition of iron to increase the Fe:P ratio in the hypolimnion of Cedar Lake would help to control soluble P that has diffused through the alum floc from availability to cyanobacteria until the alum additions are sufficient enough to suppress internal P loading.

Figure 10. Conceptual diagram of the role sulfate may play in consuming iron and lowering the Fe:P ratio in the hypolimnion.

Experiments can be conducted to test these hypotheses. For instance, replicate sediment cores collected from various locations would be incubated in the laboratory under anaerobic conditions until some soluble P accumulates in the overlying water (Fig. 12). The systems would then be switched to aerobic conditions by gently bubbling air into the overlying water. If iron control is absent or modest, soluble P will not precipitate back to the sediment. Instead, soluble P concentrations will remain about the same in the overlying water (Fig. 12). Iron, as ferric chloride (FeCl3) would be added to a second set of laboratory sediment systems before the start of incubation. These systems would similarly be incubated under anaerobic conditions then switched to aerobic conditions. The added iron should accumulate in the water as Fe^{2+} under

Figure 11. Estimated change in lake sulfate concentration after the 2021 alum application of 50 g/m² to the 25-ft depth contour.

anaerobic conditions, then chemically oxidize to $Fe³⁺$ when the system is bubbled with air. The oxidized iron should precipitate the soluble P that diffused through the alum floc and concentrations in the overlying water should then decline. If so, the results would suggest that Cedar Lake has low iron and supplemental iron addition is needed to help remove soluble P that is leaking through the alum floc.

Ferric chloride has been used extensively in wastewater treatment as well as in-lake treatments to control internal P loading (Smolders et al. 2001, Engstrom 2005, Kleeberg et al. 2013). The goal is to add enough iron to overcome iron-consumption processes (i.e., sulfate reduction and chelation with dissolved organic carbon) and completely bind soluble P entering the lake water from the watershed and sediment at a 5:1 ratio (Kleeberg et al. 2013). This iron dosage can be estimated as;

Fe dose $(g/m^2) = ((P_{\text{watershed}} + P_{\text{internal}}) \times 5 \text{ Fe:P ratio}) + \text{OC-Fe} + \text{S-Fe}$

Where:

 $P_{\text{watershed}} + P_{\text{internal}} =$ the annual P loading from the watershed and sediment,

Fe:P ratio $=$ the desired molar Fe:P ratio in the hypolimnion to control any P that has accumulated,

OC-Fe = Fe that is removed from recycling by binding to dissolved organic carbon. This is probably important in Cedar Lake,

S-Fe = Fe that is removed from recycling by reacting with S to form FeS.

Kleeberg et al. (2013) provide methods for calculating this dose. They suggest that the (Pwatershed + Pinternal) be multiplied by a specific number of years needed for control. The F:P ratio of 5 will ensure all accumulated P in the hypolimnion will be removed via precipitation.

A preliminary estimate of iron needs for Cedar Lake is shown in Table 2. For the estimate I used annual watershed P loading from James (2014) and current internal P loading estimated from P mass balance in 2022. I suggest multiplying the sum of these P loads by 5 years of control (but this term can be adjusted). I estimated Fe consumption processes by organic carbon based on the organic matter in the upper 10-cm sediment layer. For consumption of Fe by S I estimated a sulfate reduction rate using 2010 water chemistry data. The estimated Fe dose needed is 76 g/m² over the 20-ft depth contour.

The 76 g/m² Fe dose for Cedar Lake is relatively modest compared to the 241 g/m^2 dose estimated for Lake Groß-Glienicke Germany (Kleeberg et al. 2013). Ultimately, 500 g/m^2 Fe was added to this lake (Wolter 2010). In contrast, ~ 150 g/m² Fe was added to Lake Plötzensee Germany (Heinrich et al. 2021). The high Fe addition to Lake Groß-Glienicke was very effective in retaining P in the sediment. In contrast, the added Fe was ultimately consumed in Lake Plötzensee and

the lake is back to pretreatment levels. They suggested consumption of Fe by S was underestimated in the dose calculation for Lake Plötzensee and that multiple iron applications would probably be needed to maintain sufficient Fe for retaining P.

For Cedar Lake, Fe amendments may likely provide additional control of hypolimnetic P during the on-going alum treatments. The Fe dose should be enough to overcome consumption processes by sulfate and organic carbon and high enough to provide an Fe:P ratio of 5:1 for maintaining complete precipitation of soluble P during turnover (i.e., add as much as is affordable). A couple of weaknesses in the Cedar Lake Fe dose calculation are the estimates of Fe consumption via sulfate reduction binding with organic carbon. These consumption rates may need to be adjusted based on further literature search. It is important to note that the Fe dose estimate for Cedar Lake may not be a "permanent" fix for the low Fe:P ratio as the iron is consumed over time. The goal is that the alum at full strength will completely suppress internal P loading and additional iron will not be needed.

Moving forward, I suggest considering an Fe amendment to the lake to increase the Fe:P ratio. I also suggest that poly-aluminum chloride be considered for the remaining alum application and any future maintenance applications to avoid input of sulfate to the lake and consumption of Fe.

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