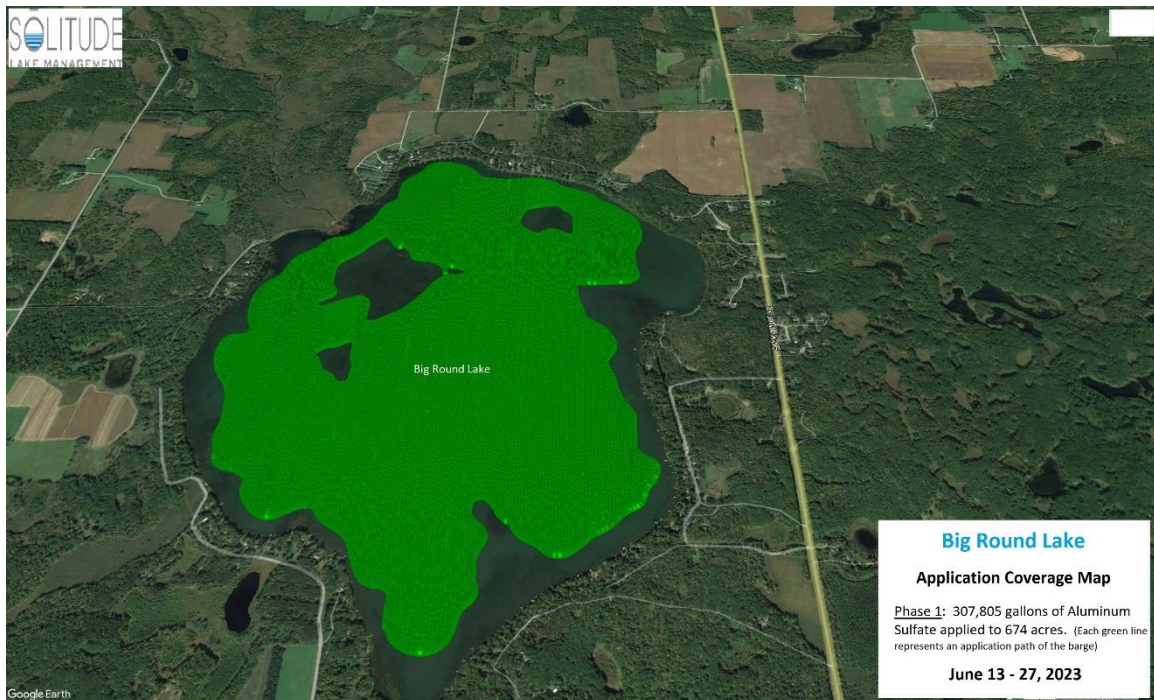


Limnological Analysis of Big Round Lake WI during Alum Application: 2023 interim report



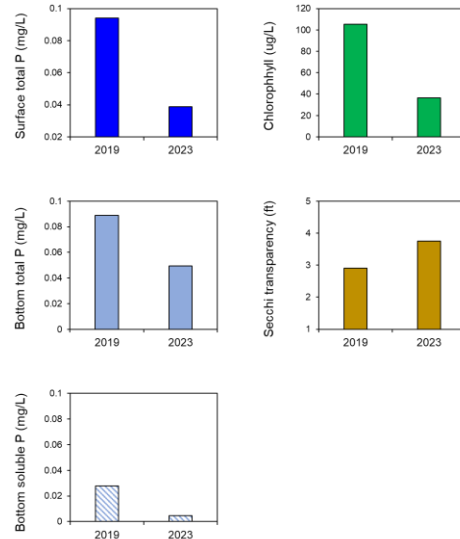
The 2023 alum application coverage map. Credit: Solitude Lake Management.

30 November 2023

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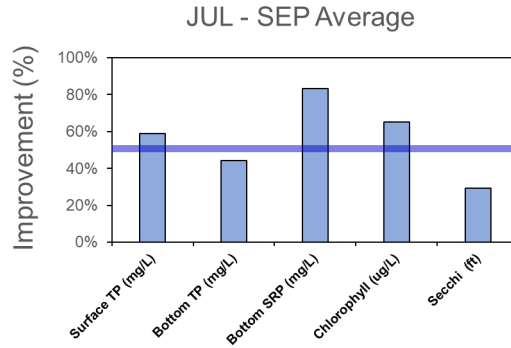
1.0 EXECUTIVE SUMMARY.

- Big Round Lake was treated with 307,805 gallons of aluminum sulfate over 674 ac (i.e., > 10-ft depth contour) between 13 and 27 June 2023. The application represented the first of four 25 g/m² Al doses to the lake.
- Prior to the 2023 alum application, stratification and bottom anoxia developed in early June 2023 with a concomitant increase in bottom soluble reactive P (SRP) to 0.094 mg/L.
- Alum application coincided with decreased bottom SRP concentrations between June and September. Despite persistent bottom anoxia, bottom SRP concentrations were usually undetectable with the exception of a very modest concentration peak of ~ 0.01 mg/L during the latter part of August.
- Chlorophyll concentrations were relatively constant at ~ 32 µg/L between June and mid-August and increased to 69 µg/L on 28 August. The late August chlorophyll bloom coincided with the modest increase in bottom SRP concentration, suggesting possible uptake for growth. However, chlorophyll declined in concentration in September and was only 19 µg/L at the end of September.
- Overall, Big Round Lake exhibited improvement in water quality during the first alum application compared to summer (JUL-SEP) limnological conditions in 2019 (i.e., before treatment). Mean summer surface total P declined by 59% to 0.039 mg/L (from 0.094 mg/L in 2019). Mean summer bottom total P and soluble P declined by 44% and 85%, respectively in 2023. Mean summer chlorophyll declined to 37 µg/L in 2023 compared to 105 µg/L in 2019, representing a 65% improvement. Secchi transparency increased from a summer mean of 2.9 ft in 2019 to 3.75 ft in 2023 (29% improvement).



Mean summer (July-September) water quality variables before (2019) and during (2023) the first alum application.

- The 2023 alum treatment also coincided with reduced summer bloom frequency exceedance. Compared to the pretreatment year 2019, blooms exceeding 30 µg/L fell from 83% to 62%, blooms exceeding 40 µg/L declined from 74% to 35%, and blooms exceeding 50 µg/L decreased from 67% to only 17%. Thus, the first year of alum application led to substantial reduction in severe cyanobacteria blooms.



Percent improvement in various limnological variable in 2023 versus 2019 pretreatment means. Horizontal blue bar denotes 50% improvement for comparison.

- Evidence of a surface Al floc layer was observed at all stations after the alum application. Concentrations of aluminum and aluminum-bound P, which represented P bound to the Al floc layer, were generally highest in the upper 2-cm sediment layer. However, concentrations were spatially variable. The WQ station and stations 10, 20, 40, and 50, located in the northern portion of the lake exhibited the highest surface aluminum and aluminum-bound P concentrations suggesting some post-application movement. This redistribution, prevalent in shallow polymictic lakes, may be caused by water column mixing and Al floc resuspension and redeposition.
- Interestingly, laboratory-derived P flux from anaerobic sediment was relatively high at a number of stations post-alum application. In particular, P fluxes were higher at the WQ station and stations 10, 50, and 70 in 2023 compared to the pretreatment year 2020. This discrepancy suggested that P flux might be spatially and temporally variable. Additional alum applications should result in uniformly lower P flux over time.

2.0 OBJECTIVES.

The objectives of these investigations were to examine lake and sediment response to the first of four partial alum applications to Big Round Lake. A 100 g/m² alum dosage to depths greater than the 10-ft contour (674 ac) was prescribed to control internal P loading. The Al dose was split into four successive 25 g/m² treatments to be applied annually between 2023-2026. Dose splitting and annual applications should maximize the binding of sediment P onto the Al floc layer in the surface sediments (Lewandoski et al. 2003, de Vicente et al. 2008a, Huser 2012, Jensen et al. 2015, James and Bischoff 2015, James 2017a) and reduce availability and direct uptake of mobile sediment P to

cyanobacteria for growth. The first partial alum application occurred to Big Round Lake between 13 – 27 June 2023.

3.0 METHODS.

In-lake monitoring

Water samples for limnological variables were collected at a centrally-located station in the deepest portion of the lake (Fig. 1). Samples were collected biweekly between June and the end of September. An integrated sample was collected over the upper 2-m for analysis of total phosphorus and chlorophyll a. An additional discrete sample was collected within 0.5 m of the sediment surface for analysis of total and soluble reactive P. Secchi transparency and in situ measurements (temperature, dissolved oxygen, pH, and conductivity at 0.5-m intervals) were also collected on each date.

Samples for total P were digested with potassium persulfate prior to analysis (APHA 2011). Samples for soluble reactive P were filtered immediately in the field using a 0.45 µm pore size syringe filter. Phosphorus was analyzed on a Perkin-Elmer UV-VIS Lambda 25 Spectrophotometer using the ascorbic acid method (APHA 2011). Samples for chlorophyll analysis were filtered onto a type A/E glass fiber filter, extracted in 90% acetone overnight in the freezer, and analyzed fluorometrically using a TD 300 fluorometer (Turner Designs).

Laboratory-derived rates of P release from sediment

Sediment cores were collected at the WQ sampling station and 7 additional stations in Big Round Lake (Fig. 1) for determination of diffusive P flux from sediment under controlled laboratory conditions (James 2017b). Cores were carefully drained of overlying water in the laboratory and the upper 10 cm of sediment were 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 each lake was filtered through a glass fiber filter (Gelman

A-E), with 300 mL then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. They were placed in a darkened environmental chamber and incubated at a constant temperature of ~20 °C to reflect summer conditions. The Eh environment in the overlying water was controlled by gently bubbling nitrogen-CO₂ (anaerobic) through an air stone placed just above the sediment surface in each system. Bubbling action insured complete mixing of the water column but 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. 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 2011). Rates of P release from the sediment (mg/m² d) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m²) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

Evaluation of sediment P characteristics

The objectives of this task were to quantify vertical variations in sediment textural characteristics and mobile P fractions involved in sediment internal P loading to the overlying water column. Sediment cores were sectioned at 2-cm intervals over the upper 10 cm for analysis of sediment physical-textural characteristics and P fractions. Sediment sections were analyzed for moisture content, sediment density, organic matter content, loosely-bound P, iron-bound P, labile organic P, and aluminum-bound P. Subsamples were dried at 105 °C to a constant weight and burned at 550 °C for determination of moisture content, sediment density, and organic matter content (Håkanson and Jensson 2002). Phosphorus fractionation was conducted according to Psenner and Puckso (1988) and Hjieltjes and Lijklema (1980) for the determination of ammonium-chloride-extractable P (1 M NH₄Cl; 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 and labile organic P). Sediment total aluminum was analyzed via inductively-coupled plasma atomic absorption spectrophotometry using EPA method 6010D after digestion according to EPA method 3050B.

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface under anaerobic conditions that result in desorption of P from bacterially-reduced iron compounds (i.e., Fe^{+3} to Fe^{+2}) in the sediment and diffusion into the overlying water column (Mortimer 1971, Boström 1984, Nürnberg 1988). The sum of these fractions are referred to as redox-sensitive P (i.e., redox-P; the P fraction that is active in P release under anaerobic and reducing conditions). In addition, labile organic P (LOP) can be converted to soluble P via bacterial mineralization or hydrolysis of bacterial polyphosphates to soluble phosphate under anaerobic conditions (Gächter et al. 1988; Gächter and Meyer 1993; Hupfer et al. 1995). The sum of redox-P and LOP is collectively referred to a biologically-labile P. This fraction is generally active in recycling pathways that result in exchanges of phosphate from the sediment to the overlying water column and potential assimilation by algae.

4.0 RESULTS.

Lake limnological response

Local precipitation (measured at Amery, Cumberland, and Luck WI) more than 1 inch occurred in late March, mid-April, and late May 2023 (Fig. 2). A two-week period of drought occurred in early June. A total of only 3 storm events that were 1-inch or more of rain fell between late June and late July and the month of August exhibited drier conditions. Daily precipitation exceeded 1 inch and 2 inches during two storm events in late September, respectively. Monthly precipitation at Amery in 2023 was well below the long-term average in May, June, and August, and near average in July and September (Fig. 3).

Big Round Lake stratified rapidly in early June with the development of bottom anoxia (Fig. 4). Alum application was initiated on 13 June, after this strong stratification period. Bottom anoxia persisted during the alum treatment and continued through mid-September. However, the vertical extent of bottom anoxia was confined to only ~ 0.5 m above the sediment-water interface.

Total and soluble P concentrations increased in the bottom waters in conjunction with the development of hypolimnetic anoxia in early June, indicating internal P loading prior to the alum application (Fig. 5). Bottom concentrations increased to a peak 0.18 mg/L TP and 0.09 mg/L SRP during this period. The alum application coincided with a decline in bottom SRP concentrations. By early July, bottom SRP was undetectable, suggesting binding and deposition as the newly-formed Al floc settled through the water column to the sediment surface. However, bottom SRP concentration increased slightly between late July and late August. Although very modest in concentration, this internal P load could have been available for algal uptake. Thus, the alum application was very effective in scavenging bottom P to the settling floc and reducing apparent internal P loading. However, some very modest internal P loading occurring later in the summer suggesting that the Al floc may have started to become saturated with P (i.e., binding sites were filling). By comparison, Big Round Lake exhibited relatively high bottom SRP concentration between late July and early August 2019 (i.e., before the first alum application, Fig. 5).

Surface concentrations of total P were much lower in 2023 compared to the pretreatment summer of 2019 (Fig. 6). Immediately prior to and during the early stages of alum application in early June 2023, surface total P was modestly high at ~ 0.04 mg/L, coinciding with a high chlorophyll concentration of 35 µg/L (Fig. 7). Surface total P concentrations declined in July in conjunction with the alum application and were < 0.04 mg/L. In contrast, chlorophyll remained moderately high during this same period, ranging between 25 µg/L and 37 µg/L (Fig. 7). Both surface total P and chlorophyll increased in mid- to late August 2023, coinciding with very modest increases in hypolimnetic bottom P (Fig. 5), suggesting possible assimilation of internal P loading that was not completely

sequestered by the Al floc located on the sediment surface. Surface total P and chlorophyll concentrations increased to nearly 0.05 mg/L and 69 µg/L in late August (Fig. 6 and 7), respectively. However, this algal bloom was short-lived and concentrations of both surface total P and chlorophyll declined in September. In contrast, surface total P and chlorophyll increased to August maxima of 0.15 mg/L and 207 µg/L during the pretreatment summer of 2019 (Fig. 6 and 7).

Secchi transparency was improved during the first alum application year of 2023 (Fig. 8). Secchi depth ranged between 2.6 ft and 4.9 ft between mid-July and September 2023. In contrast, transparency was much lower during the July through September period of 2019, ranging between 1.5 ft and 2.6 ft (Fig. 8).

Regression relationships between surface chlorophyll and total P indicated that the alum application had a positive impact on P limitation of algal growth (Fig. 9). Much more severe P limitation of algal growth occurred during the summer of 2023 compared to 2019. Lower P-limited chlorophyll concentrations in 2023 also translated into great Secchi transparency compared to the pretreatment year 2019 (Fig. 9).

Mean summer (JUL-SEP) limnological response variables improved substantially in 2023 versus 2019 in conjunction with the alum treatment (Fig. 10 and Table 1).

Compared to 2019, mean surface total P and chlorophyll declined by nearly 60% and 65%, respectively (Fig. 11), to 0.039 mg/L and 36.6 µg/L in 2023. Mean summer bottom total P and soluble P

declined to 0.05 mg/L and not detectable, respectively during the 2023 alum treatment, representing a 44% and 83% improvement (Fig. 11). Secchi transparency

Table 1. Summary of changes to Big Round Lake water quality after the first alum treatment in 2023.			
Variable	2019 (Pre Al)	2023 (Alum)	Percent improvement (Pre Al versus 2023)
Surface TP (mg/L)	0.094	0.039	59%
Bottom TP (mg/L)	0.089	0.050	44%
Bottom SRP (mg/L)	0.028	0.005	83%
Chlorophyll (ug/L)	105.2	36.64	65%
Secchi (ft)	2.9	3.75	29%

improved by 29% in 2023 versus 2019 to 3.75 ft.

A comparison of monthly means (pretreatment 2019 versus 2023) indicated that the severity of water quality impairment in Big Round Lake was reduced during the 2023 alum treatment, particularly in August and September (Fig. 12). In addition, the percent of the summertime that chlorophyll blooms exceeded 30 $\mu\text{g/L}$, 40 $\mu\text{g/L}$, and 50 $\mu\text{g/L}$ were reduced in conjunction with the 2023 alum application (Fig. 13).

Seasonal increases in summer lakewide P mass declined substantially in 2023 in conjunction with the alum treatment (Fig. 14). The pretreatment lakewide summer P mass increase was 14.5 kg/d in 2019. After the alum application in 2023, it was only 3.7 kg/d.

Sediment characteristics and diffusive phosphorus flux

Vertical patterns in sediment moisture content for sediment cores collected at the water quality station suggested the 2023 alum floc layer was located at the sediment surface (Fig. 15). Since the Al floc layer is only slightly denser than water at 1.01 to 1.02 g/cm^3 , relatively high shear stress and turbulence would be required to induce mixing and incorporation into the original much denser sediment surface layer (James 2017).

Moisture content of the sediment, a surrogate of density, was highest in the upper 2-cm sediment layer of sediment collected after the 2023 alum treatment, suggesting the Al floc layer was residing on top of the original sediment interface (Fig. 15). The aluminum and aluminum-bound P concentrations were highest at 11.1 mg/g and 0.470 mg/g, respectively, within this sediment surface layer (Fig. 16). The Al:P binding ratio was also lowest in the surface sediment layer at the water quality station, suggesting P binding to the Al floc layer in 2023. This ratio was $\sim 29:1$ in the 0-2-cm layer, indicating binding sites were being filled in the Al floc layer. As binding sites are filled with P over many years, the Al:P ratio should decline to $\sim 12:1$ to $15:1$ (Rydin et al 2000).

Other stations exhibited peaks in aluminum and aluminum-bound P (Fig. 17 and 18), primarily within the surface sediment layer. However, concentrations were variable

Table 2. Variations in aluminum and aluminum-bound P concentrations in the surface sediment layer at various stations in Big Round Lake in 2023.				
Station	Al floc layer (cm)	Al (g/m ²)	Al-bound P (g/m ²)	Al:P ratio
WQ	2	11.1	0.384	29
10	2	11.6	0.308	38
20	2	14.9	0.305	49
30	2	7.6	0.120	63
40	2	9.9	0.307	32
50	4	25.0	0.708	35
60	2	9.0	0.097	93
70	2	8.3	0.134	62

spatially with stations 10, 20, 40, and 50, and WQ exhibiting the highest surface concentration peaks, while stations 30, 60, and 70 surface concentration peaks were lower (Table 2). Even though alum was precisely and evenly applied over the entire area, post-application movement is possible and had been well documented in other lakes treatment with alum (Egemose et al. 2009, Egemose et al. 2013, Huser 2017). Post application movement of the very low density newly-formed Al floc can occur via wind and wave activity and other turbulent processes. Additional application in 2024, 2025, and 2026 should result in more even distribution over the target area.

Laboratory-derived anaerobic diffusive P fluxes were unexpectedly high at most stations in 2023 and, in many cases, higher than pretreatment fluxes measured in 2019-2020 (Fig. 19). This result was unusual and may suggest that diffusive P fluxes are highly variable in Big Round Lake, making comparisons difficult, at least for 2023. For instance, the rate of P flux measured at station 50 in 2020 (i.e., before alum) was 2.11 mg/m² d. While I expected P fluxes to decline, the rate was paradoxically higher at 4.38 mg/m² d at this same station after the 2023 alum treatment. These apparent discrepancies may be explained by a few factors. First, the potential seasonal variability in diffusive P flux might not have been adequately captured since only one core was examined at each station. Second, perhaps there were interannual variations that were not detected. For example, P fluxes at station 50 and other stations may be higher one year and lower another year depending on mobile P concentrations at the sediment-water interface.

Finally, there may be micro-localized variations in P flux due to differences in sediment. In contrast, other recently alum-treated lakes in the region (i.e., Long Lake; East Balsam Lake; Cedar Lake; Half Moon Lake in Eau Claire) have exhibited substantial reductions in laboratory-derived diffusive P flux during and immediately after alum application.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The 2023 Al application to Big Round Lake represented the first of four 25 g/m² treatments that will be applied annual between 2023 and 2026. Compared to the pretreatment year, 2019, mean summer (i.e., JUL-SEP) limnological response variables were much improved in 2023 in conjunction with the first 25 g/m² alum application. With the exception of some very minor bottom soluble P concentration increases in August, the first alum application in 2023 largely suppressed hypolimnetic P accumulation throughout the summer despite bottom anoxia. Relative to 2019, mean summer surface total P declined by 59% to 0.039 mg/L (from 0.094 mg/L in 2019). Mean summer bottom total P and soluble P declined by 44% and 85%, respectively in 2023. Mean summer chlorophyll declined to 37 µg/L in 2023 compared to 105 µg/L in 2019, representing a 65% improvement. Secchi transparency increased from a summer mean of 2.9 ft in 2019 to 3.75 ft in 2023 (29% improvement).

The overall alum application strategy was to split the estimated 100 g/m² Al dose into four 25 g/m² applications to 1) improved P binding efficiency and capacity onto the Al floc by subjecting consecutive annual low dose applications to sediment P, thereby, saturating binding sites on the Al floc with P and 2) suppress cyanobacteria blooms during the application process. Many cyanobacteria form resting stages as akinetes or spores that reside in the sediment and germinate under optimal environmental conditions. These resting stages may directly assimilate sediment P in excess of growth requirements and develop extensive blooms when germinated and mixed into the water column (Istvanovics et al. 1993, 2000; Pettersson et al. 1993; Perakis et al. 1996; Cottingham et al. 2015). Thus, controlling sediment P with consecutive annual alum treatments represents an application strategy designed to limit cyanobacteria access to sediment P in

Big Round Lake. The 2nd consecutive alum application at 25 g/m² over 674 ac is scheduled for June 2024.

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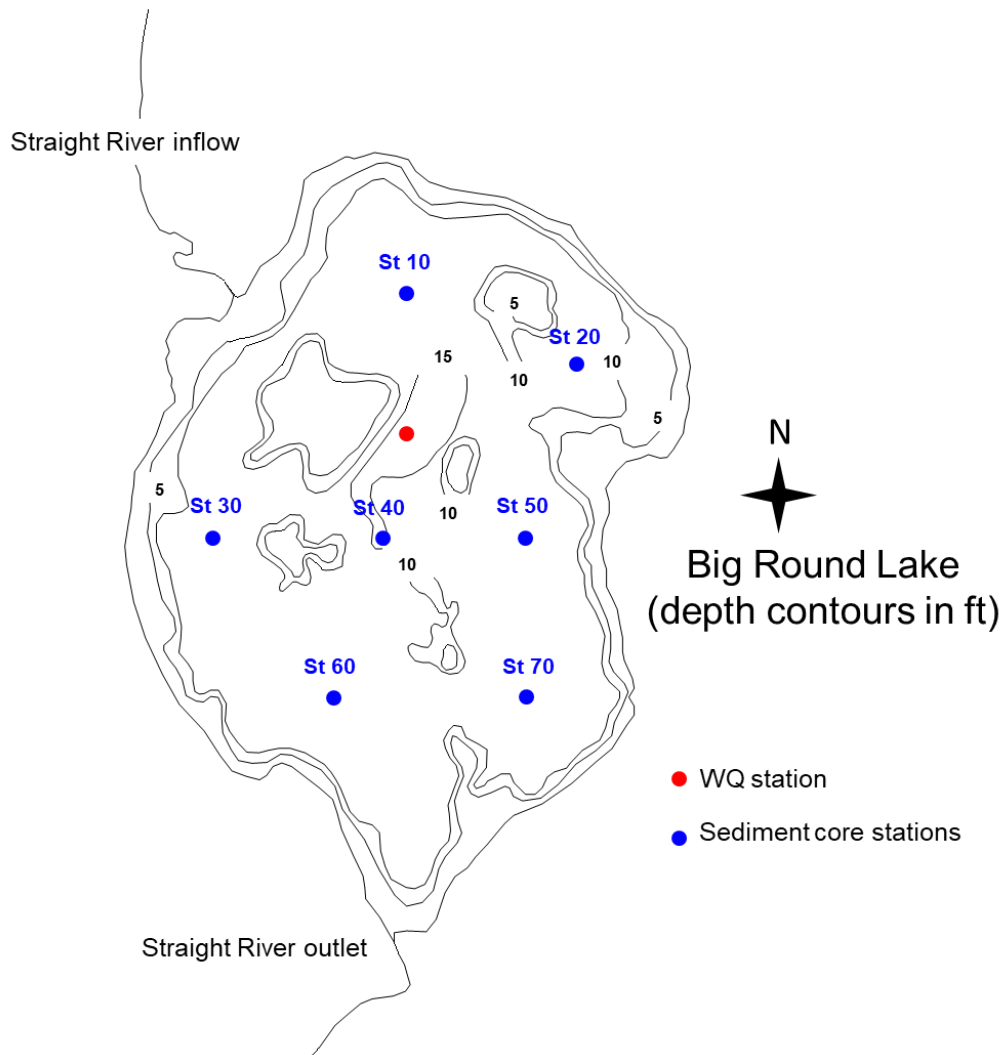


Fig. 1. Bathymetric map of Big Round Lake showing the water quality station and various sediment coring locations.
Fig. 2. Straight River above Big Round Lake at 250th Ave showing bridge construction and boom line.

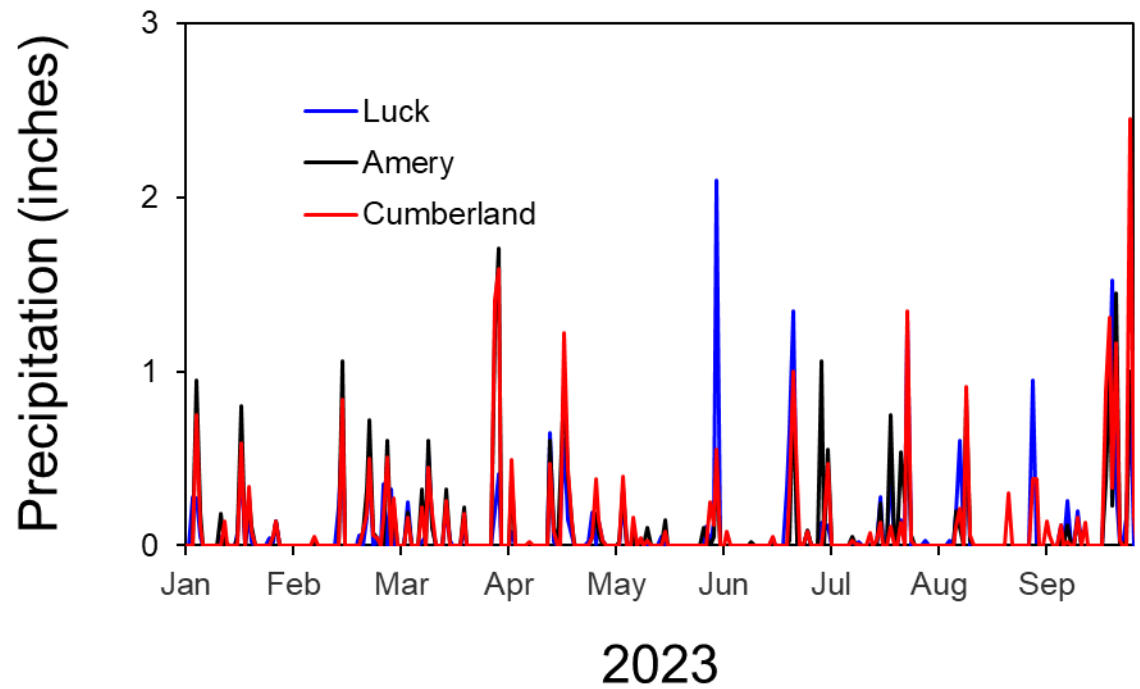


Fig. 2. Variations in seasonal precipitation measured at Luck, Amery, and Cumberland Wisconsin Wisconsin.

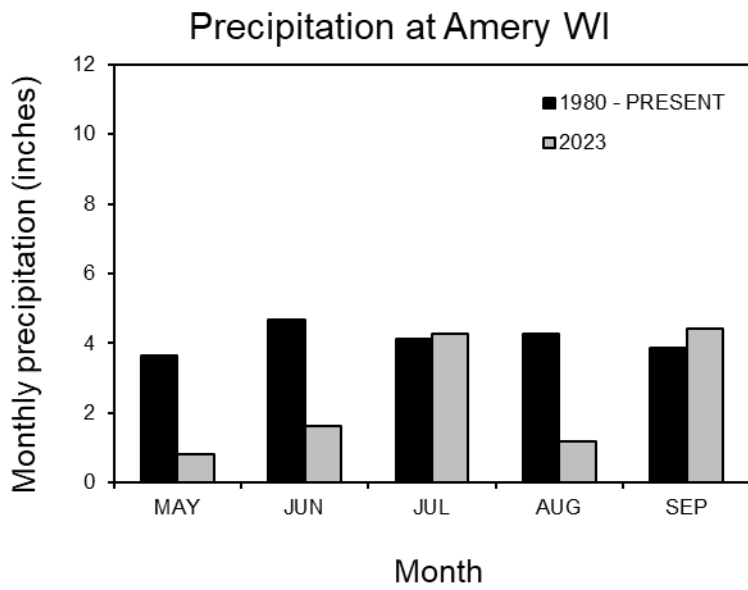


Fig. 3. Monthly variations in precipitation measured at Amery Wisconsin.

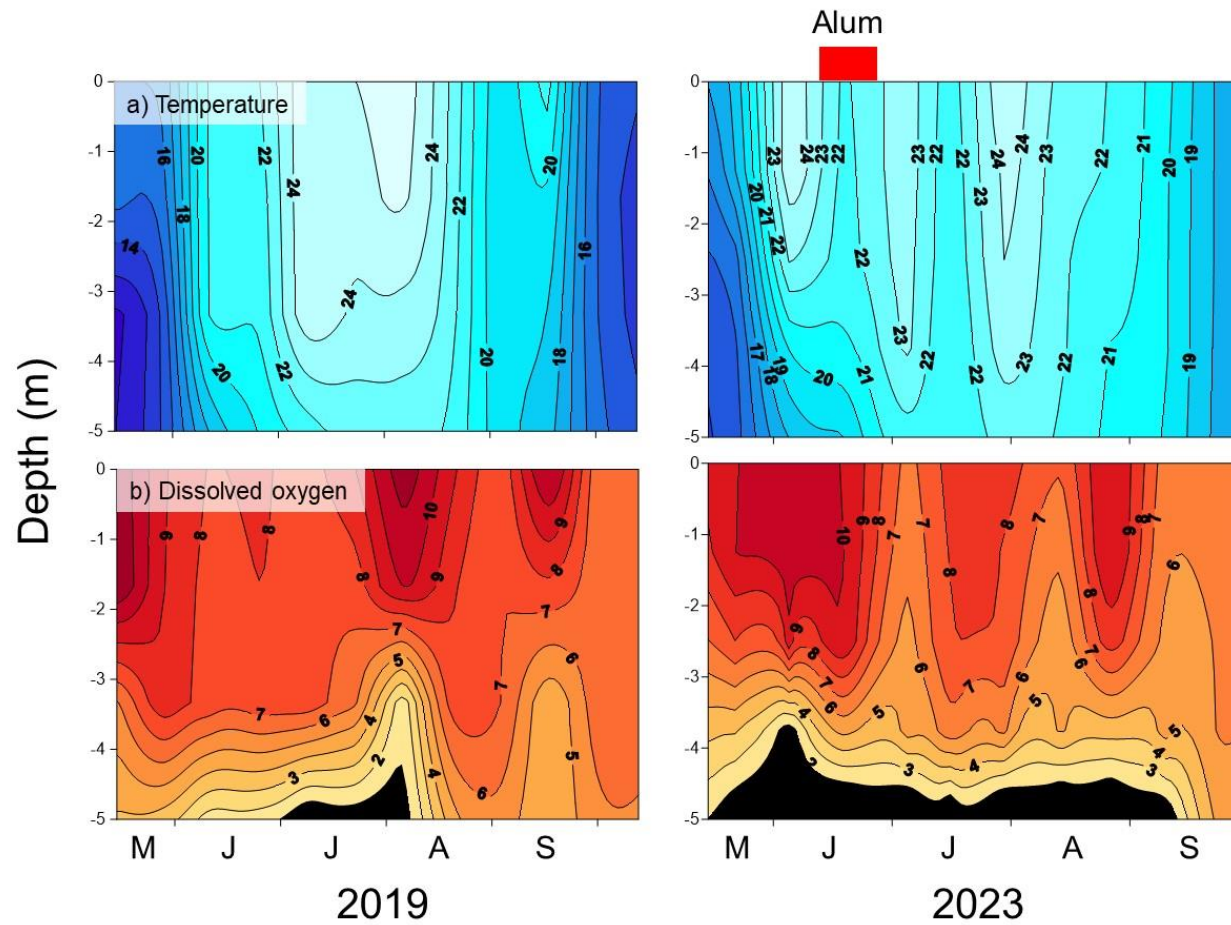
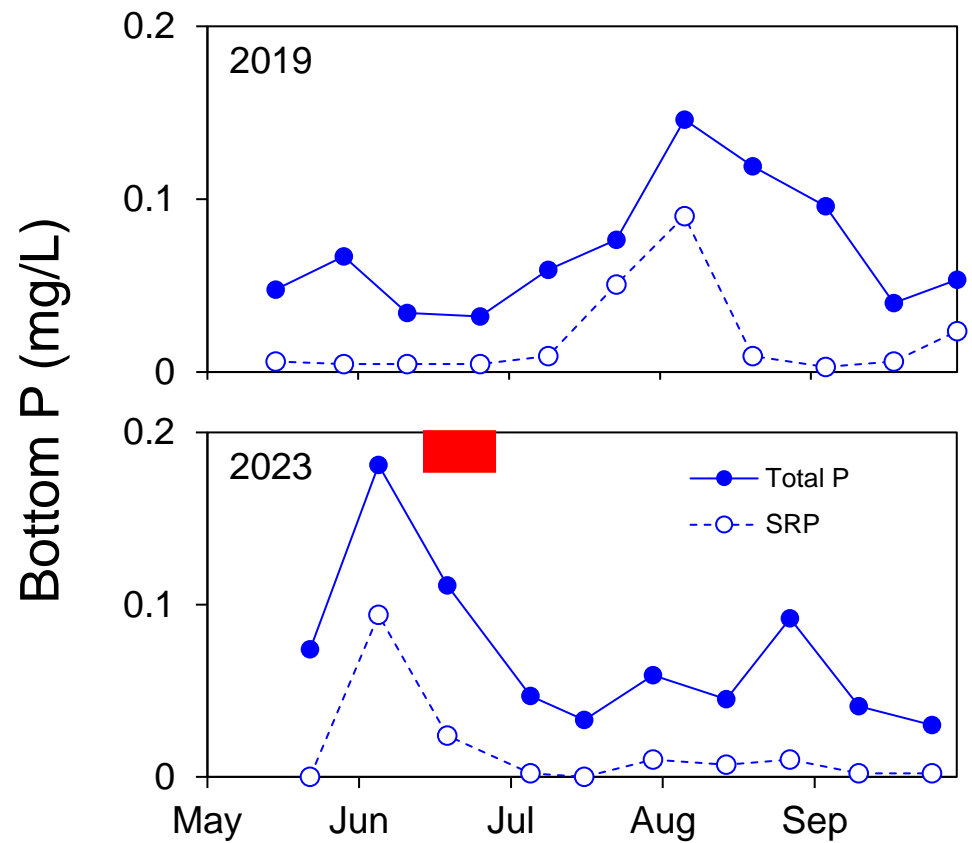


Fig. 4. Seasonal and vertical variations in water temperature (upper panels) and dissolved oxygen (lower panels) at the Big Round Lake sampling station in 2019 (pre-alum application) and 2023 (1st alum application). Black bottom area in the lower panel represents the period of hypolimnetic anoxia.

Fig. 5. Seasonal variations in bottom total and soluble phosphorus (P) in 2019 (pre-alum application, upper panel) and 2023 (1st alum application, lower panel). Horizontal red bar denotes the period of the first alum application in 2023.



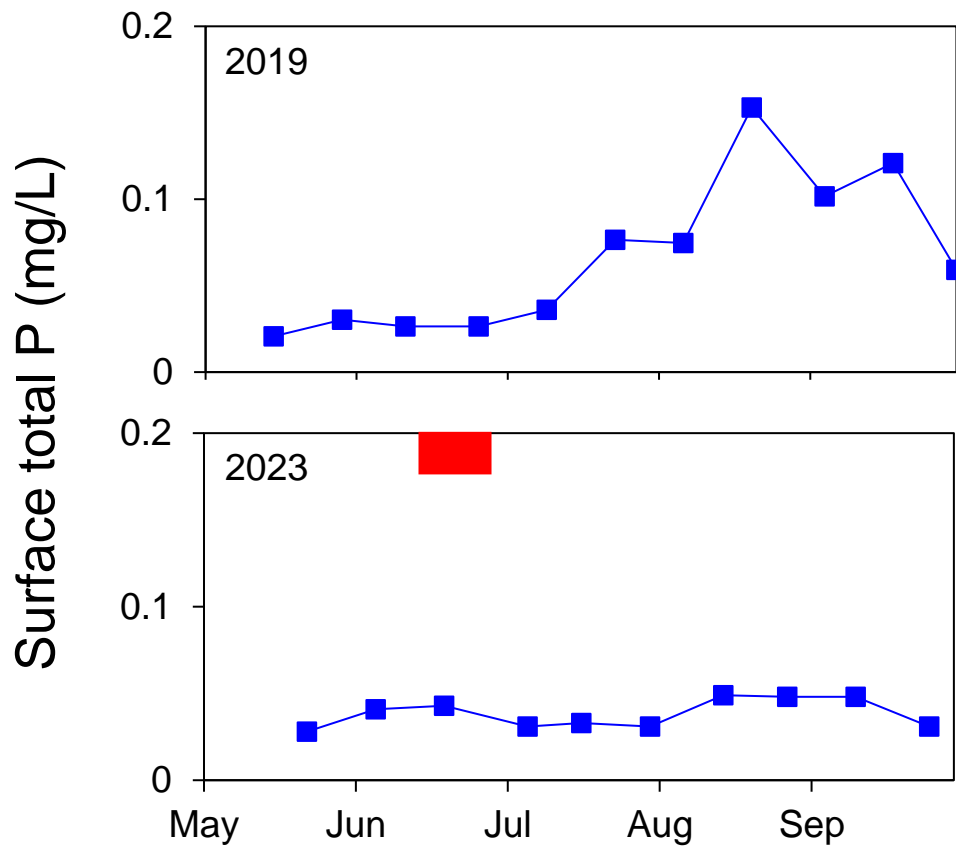
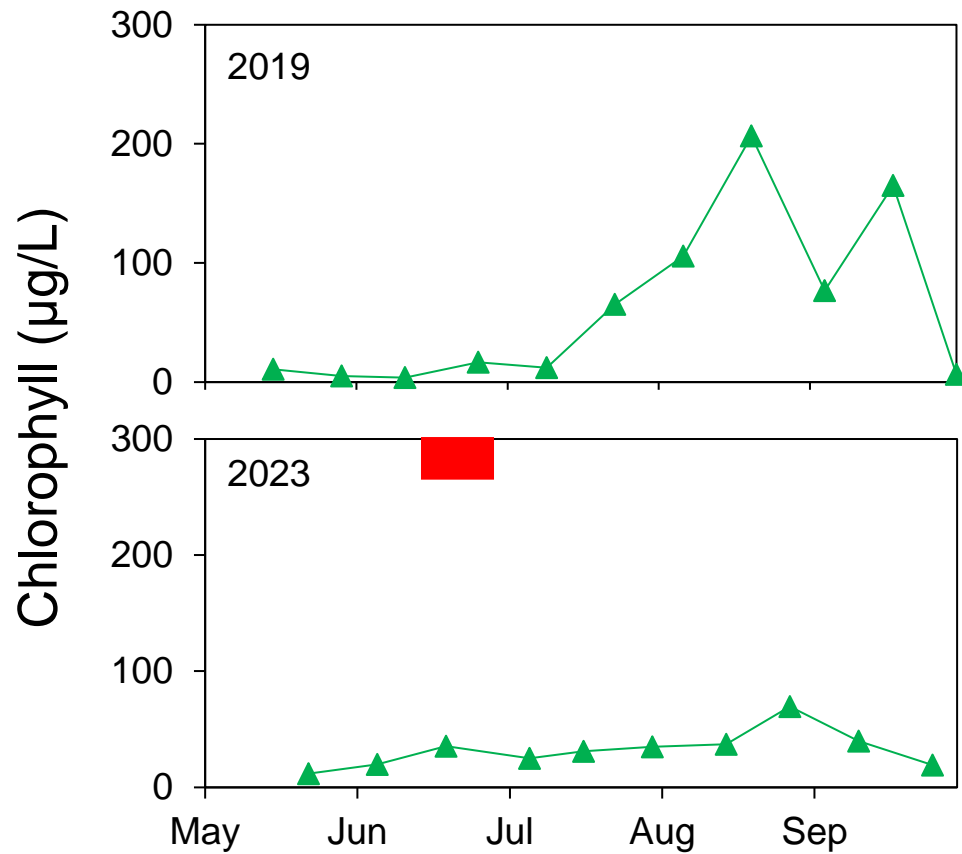


Fig. 6. Seasonal variations in surface (upper 2-m integrated depth) total phosphorus (P) in 2019 (pre-alum application, upper panel) and 2023 (1st alum application, lower panel). Horizontal red bar denotes the period of the first alum application in 2023.

Fig. 7. Seasonal variations in surface (upper 2-m integrated depth) chlorophyll in 2019 (pre-alum application, upper panel) and 2023 (1st alum application, lower panel). Horizontal red bar denotes the period of the first alum application in 2023.



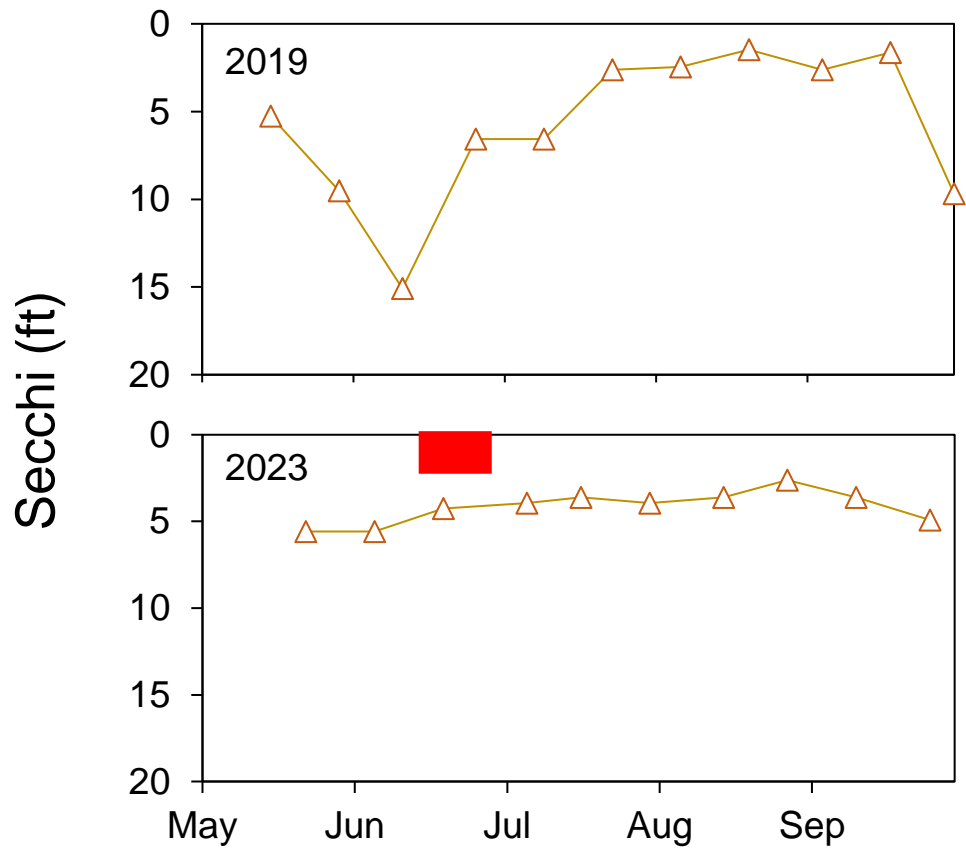


Fig. 8. Seasonal variations in Secchi transparency in 2019 (pre-alum application, upper panel) and 2023 (1st alum application, lower panel). Horizontal red bar denotes the period of the first alum application in 2023.

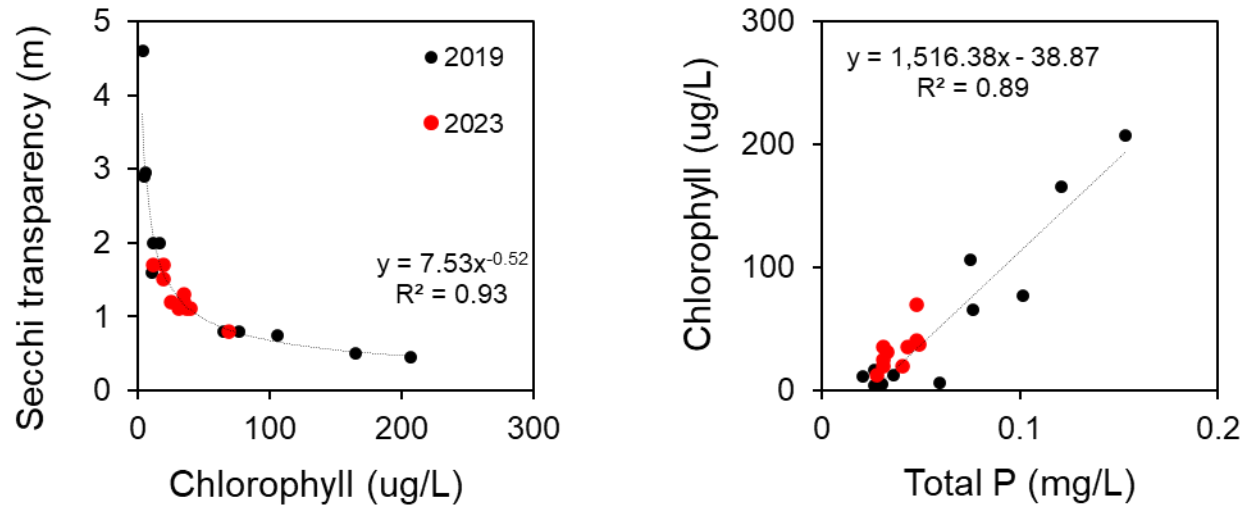


Fig. 9. Relationships between limnological trophic state variables.

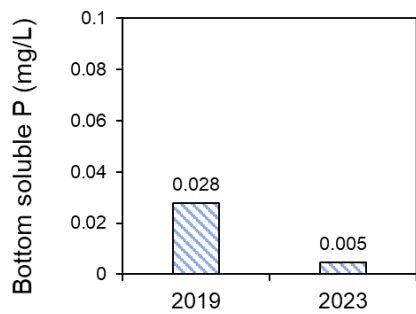
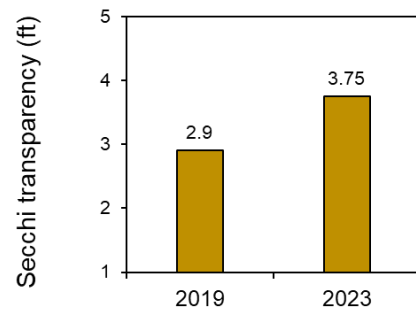
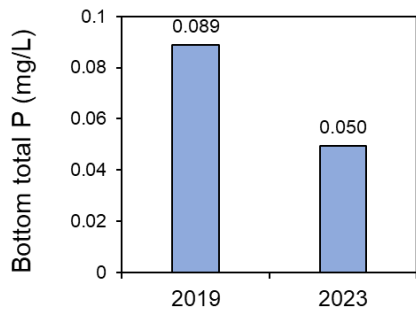
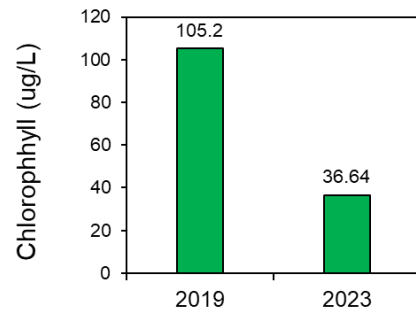
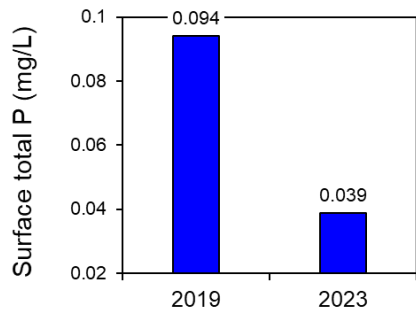


Fig. 10. Variations in mean summer (JUL-SEP) limnological response variables (surface total P, Bottom total and soluble P, chlorophyll, and Secchi transparency) in 2019 (pre-alum application) and 2023 (1st alum application).

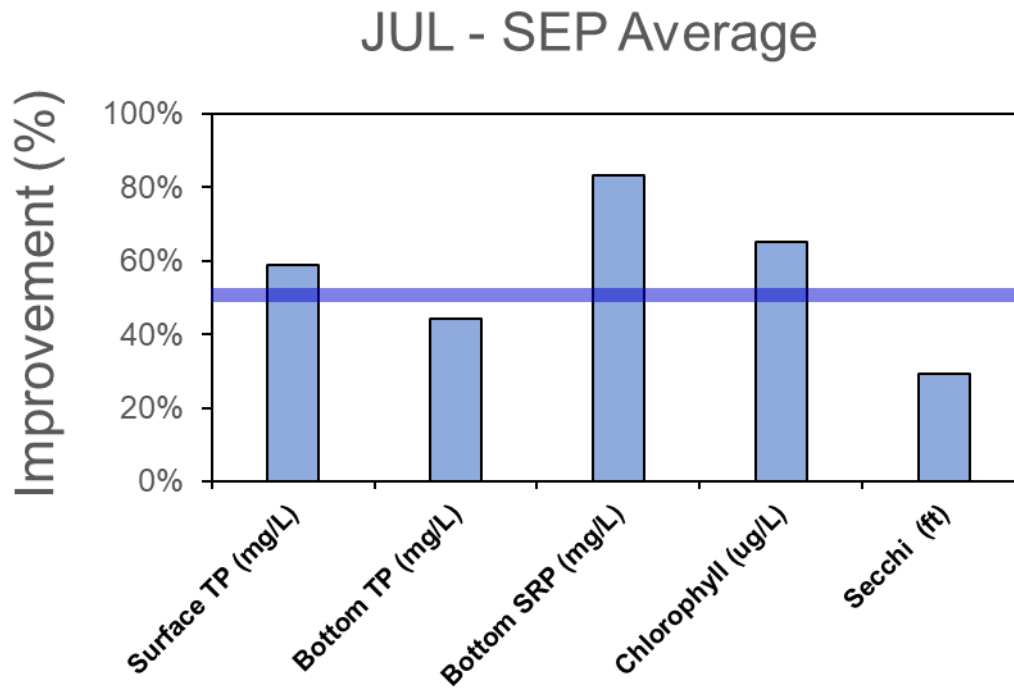
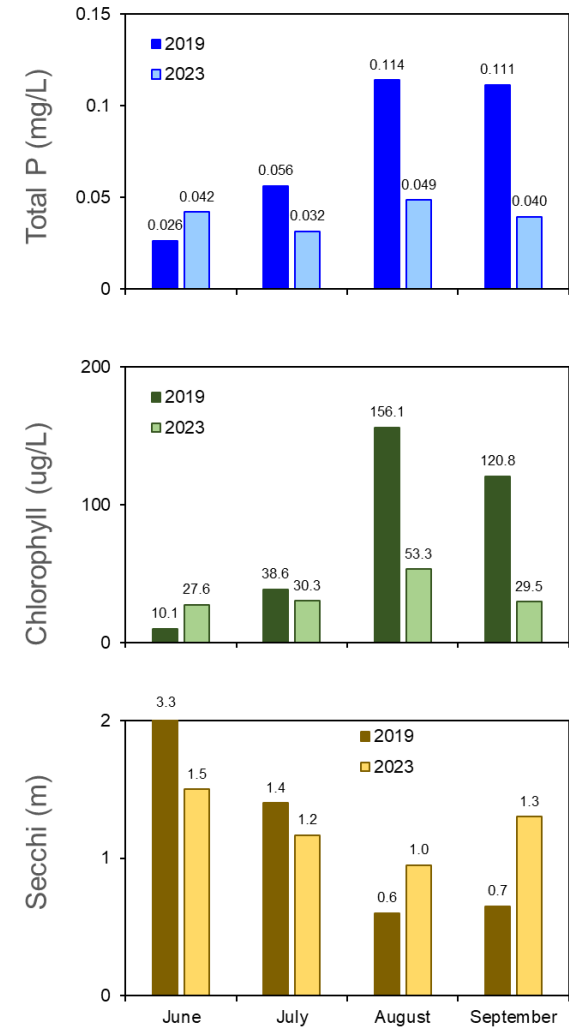


Fig. 11. Percent improvement in summer (JUL-SEP) limnological response variables in 2023 in conjunction with the first alum treatment. Percent improvement was calculated as the change or difference between 2019 versus 2023 summer means.

Fig. 12. Comparisons in monthly surface total phosphorus (upper panel), chlorophyll (middle panel), and Secchi transparency (lower panel) in 2019 (pre-alum application) and 2023 (1st alum application).



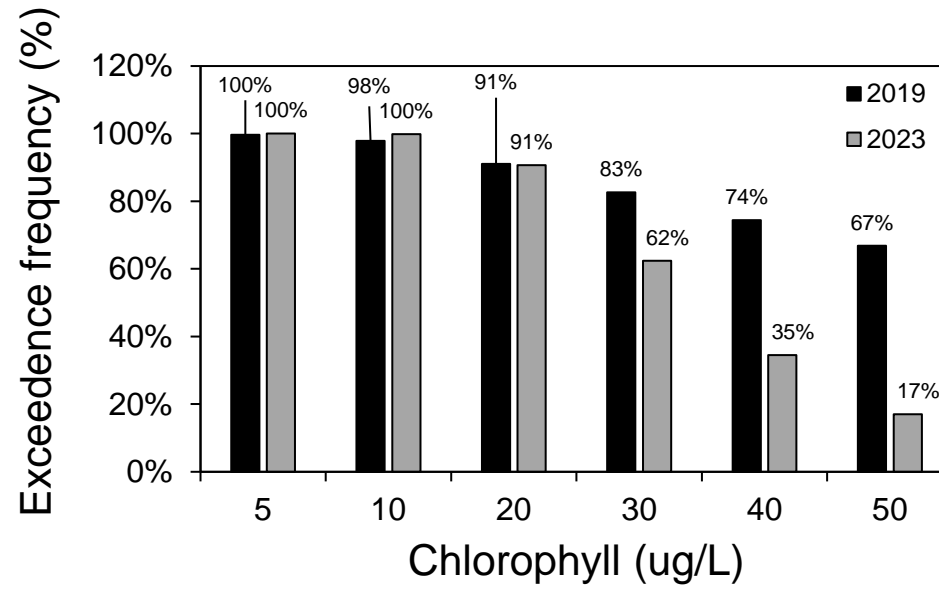


Fig. 13. Percent of the time in the summer that chlorophyll exceeded 5 µg/L, 10 µg/L, 20 µg/L, 30 µg/L, 40 µg/L, and 50 µg/L in 2019 (pre-alum treatment) and 2023 (1st alum application).

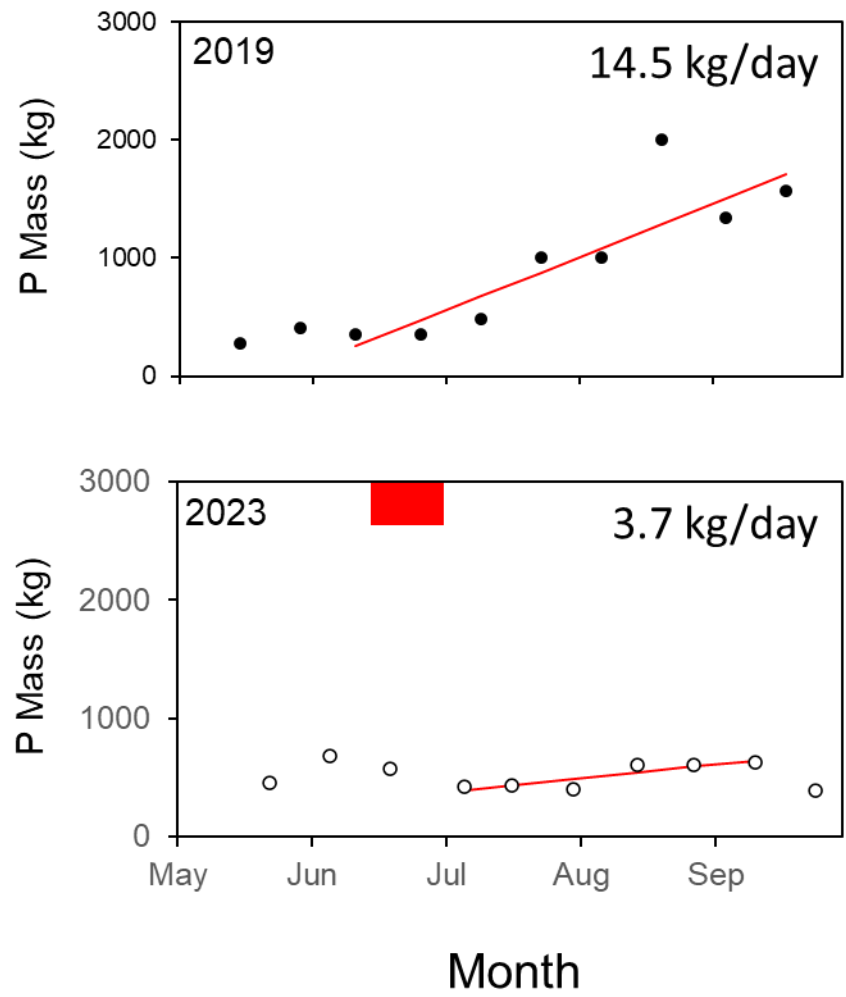


Fig. 14. Changes in lakewide total phosphorus (P) mass in 2019 (before alum treatment, upper panel) and 2023 (during the 1st alum application, lower panel). Horizontal red bar denoted the period of alum application in 2023.

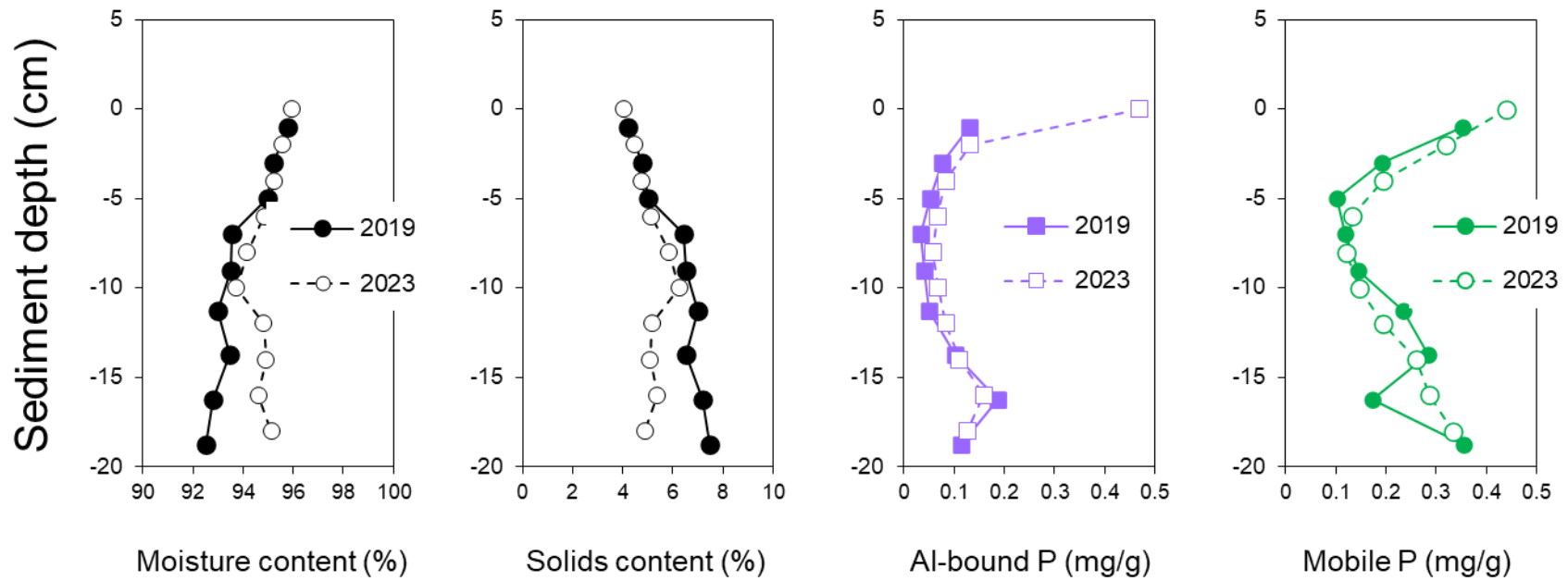


Fig. 15. Sediment vertical profiles showing changes in moisture content, solids content, aluminum-bound P, and mobile P (i.e., the sum of the loosely-bound and iron-bound P fractions) in 2019 (before alum treatment) and 2023 (during the 1st alum application).

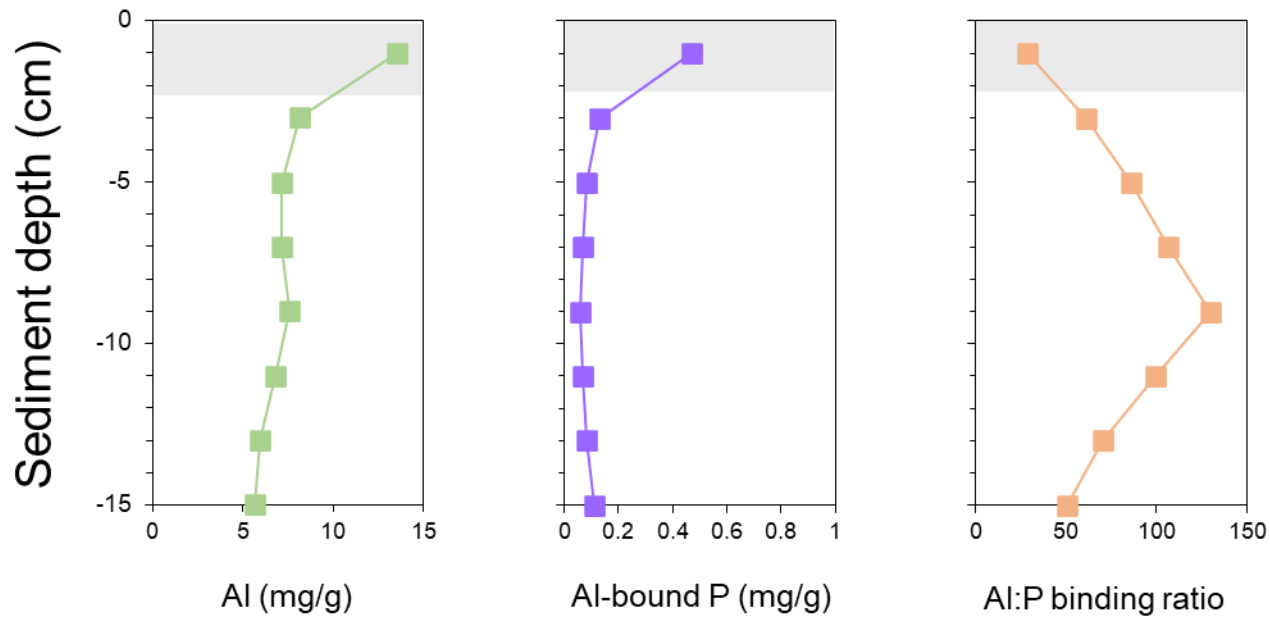


Fig. 16. Variations in sediment aluminum, aluminum-bound P, and the Al:P binding ratio for sediment collected at the WQ station in Big Round Lake in 2023. The gray area denotes the probably location of the Al floc Layer. The Al:P binding ratio represents the mass of P bound per mass of Al. An Al:P binding ratio of ~ 12:1 to 15:1 can be achieved over time as sediment P diffuses upwadrd into the Al floc.

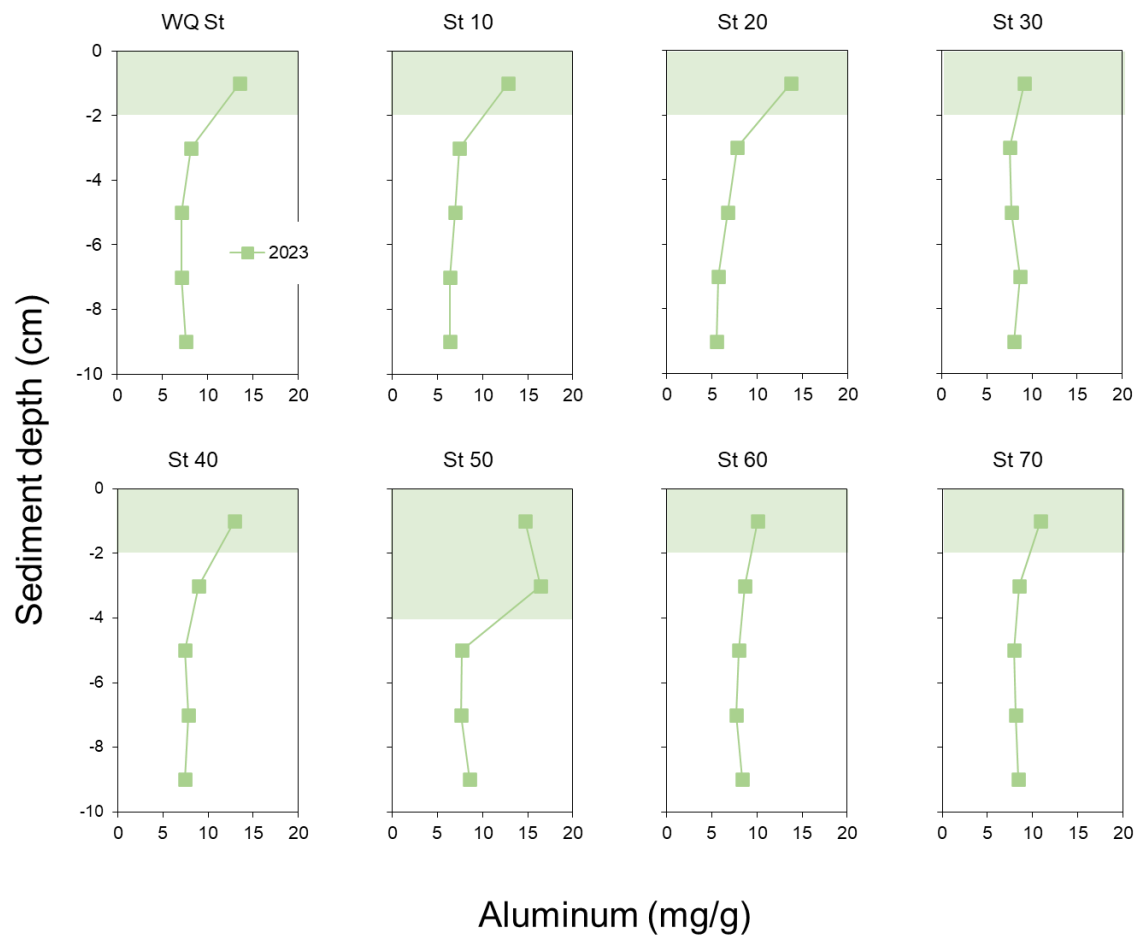


Fig. 17. Spatial variations in sediment core vertical profiles of aluminum in 2023 (i.e., during the 1st alum application). Green shaded areas denote the location of the Al floc.

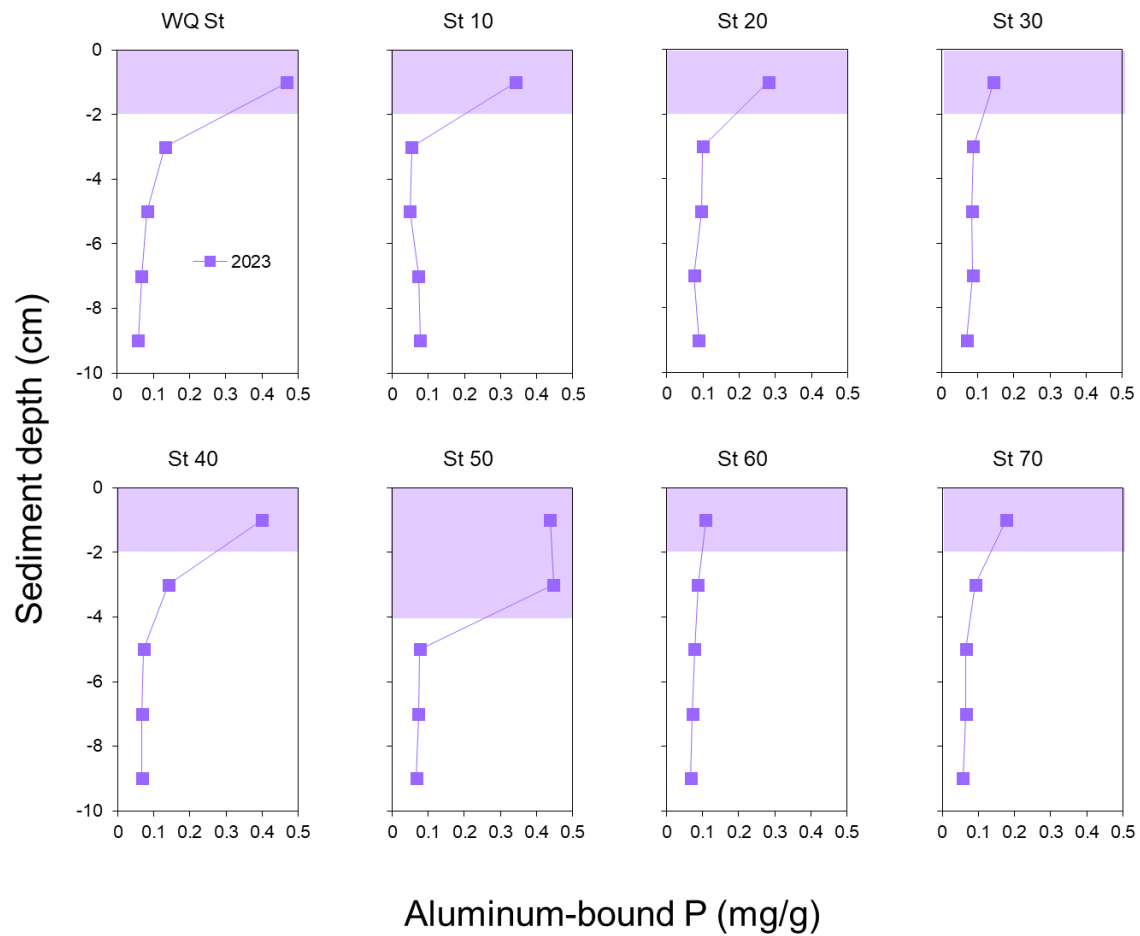


Fig. 18. Spatial variations in sediment core vertical profiles of aluminum-bound P in 2023 (i.e., during the 1st alum application). Lavender shaded areas denote the location of the Al floc.

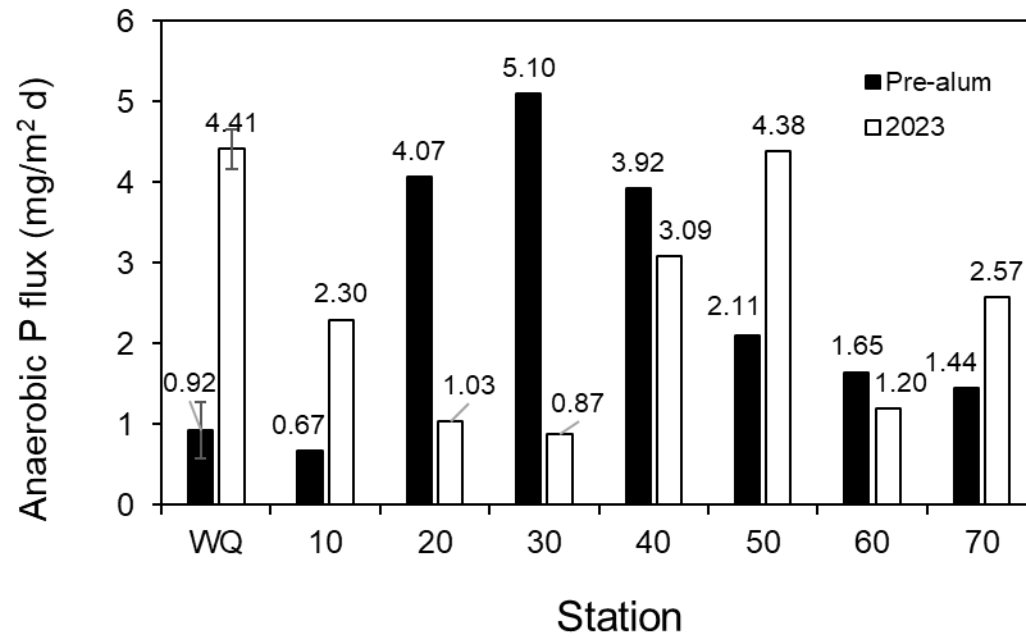


Fig. 19. Laboratory-derived anaerobic diffusive P flux at various stations measured in 2019 (before alum treatment) and 2023 (during the 1st alum application).