APPENDIX 5 CP1 NUTRIENTS PREDICTIONS

CP1 Nutrients Prediction

Following the 2021 and 2022 Annual Reports, ECCC and CIRNAC recommended that AEM identify the source of the WBWQM over-predicting ammonia and total phosphorous levels in CP1. The following section provides the results of a desktop study conducted in 2023 to investigate whether natural attenuation in CP1 can explain the discrepancy between modelled and actual concentrations of ammonia-nitrogen and phosphorous in CP1.

Characteristics of CP1

CP1 is a large, shallow freshwater pond that receives surface contact water from site prior to treatment and discharge to the receiving environment. The shoreline of CP1 has soft substrates and strong summer winds which often causes sediment suspension throughout the open-water period. This means that dissolved oxygen can diffuse farther into the sediments, which increases the available habitat for organisms that require oxygenated sediments.

Water temperature in CP1 exhibits a typical seasonal cycle of cooler temperatures in June and September/October, with peak temperatures observed in July/August (Figure 1a). Temperatures observed from 2018 to 2023 ranged from 0.7°C to 19.4°C in CP1. Based on the data, CP1 warms quickly after ice-off in the spring and cools quickly in the fall.

Maximum summer temperatures ranged from 11.9°C in 2021 to 19.4°C in 2022. There is a range of tolerances to variations in temperature among algae and minimal temperatures at which photosynthesis can occur depends on the species.[1] Conditions in CP1 were optimal for algal growth for the majority of the open-water period (i.e., >90 days).

Field pH measurements ranged from 6.9 to 9.3 throughout the open water season from 2018 to 2023 (Figure 1b). Diurnal peaks in pH were observed in CP1, based on the continuous data logger measurements in the EWTP (Figure 2). Daytime pH reached a peak of 9.72 on 16 June 2021 and gradually declined. Diurnal pH changes aligned with turbidity measurements taken with the continuous data loggers at the EWTP. Algal photosynthesis consumes carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), producing carbon dioxide (CO_2) and hydroxide ions (OH^-) through respiration, which increases the pH of water

[1]Wetzel RG. 2001. Limnology: Lake and River Ecosystems. Third Edition. Academic Press, San Diego. USA. Pg. 1006

making the water more basic[2]. The relative rates of respiration and photosynthesis within a pond determine whether there is a net addition or removal of carbon dioxide, and therefore whether pH falls or rises. Algal blooms have been linked to pH increases above a pH of 9, which have been observed to occur regularly in the daily continuous data logger measurements recorded for CP1 throughout the open-water period. Dissolved oxygen (DO) concentrations in CP1 were generally at or near saturation (i.e., 80% to 105%) from 2019 to 2023 and field DO measurements ranged from 6.7 to 13.9 mg/L (Figure 1c). Low daily DO measurements, collected from the EWTP continuous data logger after the ice-off blooms had receded, were usually recorded in the early morning profiles (before 6 am) and after sun-down (after 10 pm). Periods of oxygen super-saturation are observed in the daylight hours, likely as a result of algal photosynthesis, while oxygen depletion was observed during the dark hours when algal respiration was likely occurring. An overall open-water average DO of 90% saturation in the daylight hours suggests a significant oxygen demand to keep the average below 100% in a shallow pond like CP1.

Conductivity in CP1 generally ranged from 1,470 to 4,450 µS/cm between June 2019 to September 2023, suggesting that micronutrients required by algae for growth and metabolism were readily available.

[2] Wallace RB, Peterson BJ, Gobler CJ. 2021. Ecosystem metabolism modulates the dynamics of hypoxia and acidification across temperate coastal habitat types. Front. Mar. Sci. 8: 1-20.

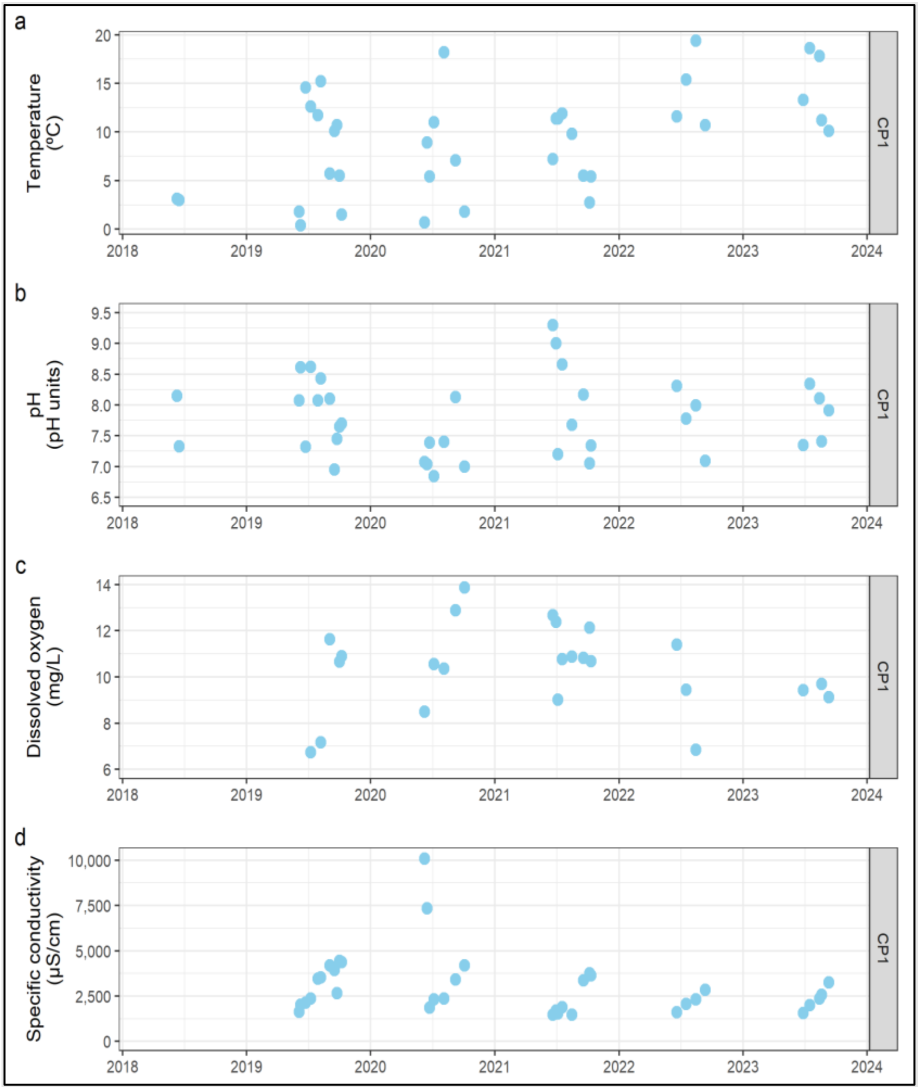

Figure 1: Field physio-chemical characteristics of CP1, 2018 to 2023.

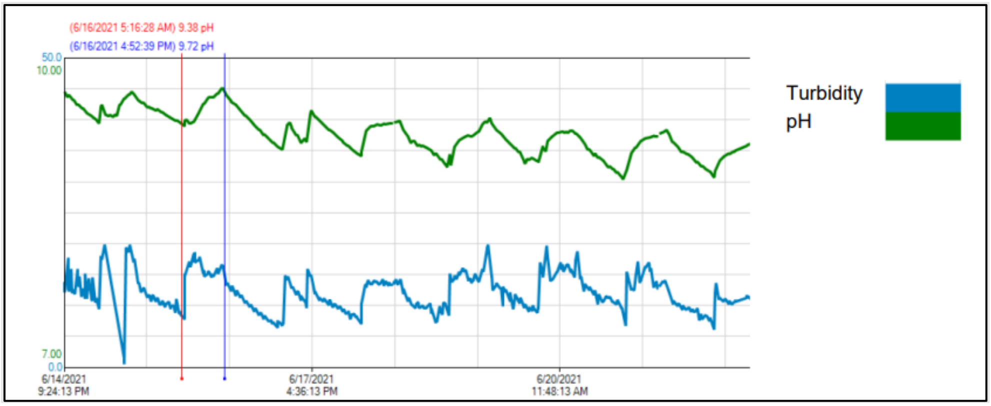

Figure 2: Example from June 2021 of diurnal cycles in pH and turbidity in CP1

Nutrient Concentrations in CP1

Nutrient uptake during algal growth is a process that removes dissolved nutrients from the water, and algal respiration and decay are major components of nutrient cycling. CP1 concentrations of nitrate + nitrite, ammonia, total Kjeldahl nitrogen (TKN), orthophosphate, and total phosphorus are presented in Figure 3.

The reduction in ammonia concentration between 8 June 2020 and 23 June 2020 was attributed to dilution of the pond water as the ice melted. This was also observed in concentrations of other water quality parameters such as TDS, potassium, and nitrate; however, samples taken 5 July 2020 and 4 August 2020 continued to show a decrease in ammonia concentrations, while TDS remained reasonably stable, suggesting other processes were removing ammonia from the system, such as assimilation by algae and sedimentation losses, or nitrification/denitrification. Ammonia concentrations were elevated in June 2020 relative to subsequent years, suggesting higher under-ice concentrations of ammonia in 2020.

In May 2023, ammonia nitrate + nitrite samples collected early in the season were low compared to early spring samples collected in 2020, but for ammonia were elevated relative to concentrations reported for the remainder of the open-water period in 2023 (Figure 3a,b). These concentrations coincide with algae blooms observed in CP1 in 2023. The reduction in ammonia concentration from May to June in 2023 is likely the result of a combination of dilution as the ice melted and algal assimilation during the bloom event.

From 2018 to 2023, concentrations of orthophosphate and total phosphorus (TP) ranged from <0.01 to 0.20 mg-P/L, and <0.01 to 0.32 mg-P/L respectively (Figure4a,b). Phosphorus concentrations are observed to decrease sharply each open water season, yielding dissolved inorganic nitrogen (DIN) to phosphorous ratios well over 16:1, which is considered to be a marker of phosphorous limitation in aquatic systems[3] (Redfield, 1934). The release of phosphorus accumulated below ice in CP1, or from the year-round input of treated STP effluent, along with abundant DIN supply, warming temperatures, and increase in light supply as the ice melts creates ideal conditions for algal growth in the spring, leading to the algal blooms observed in CP1.

[3] Redfield, A. C. (1934). On the Proportions of Organic Derivatives in Sea Water and their Relation to the Composition of Plankton.

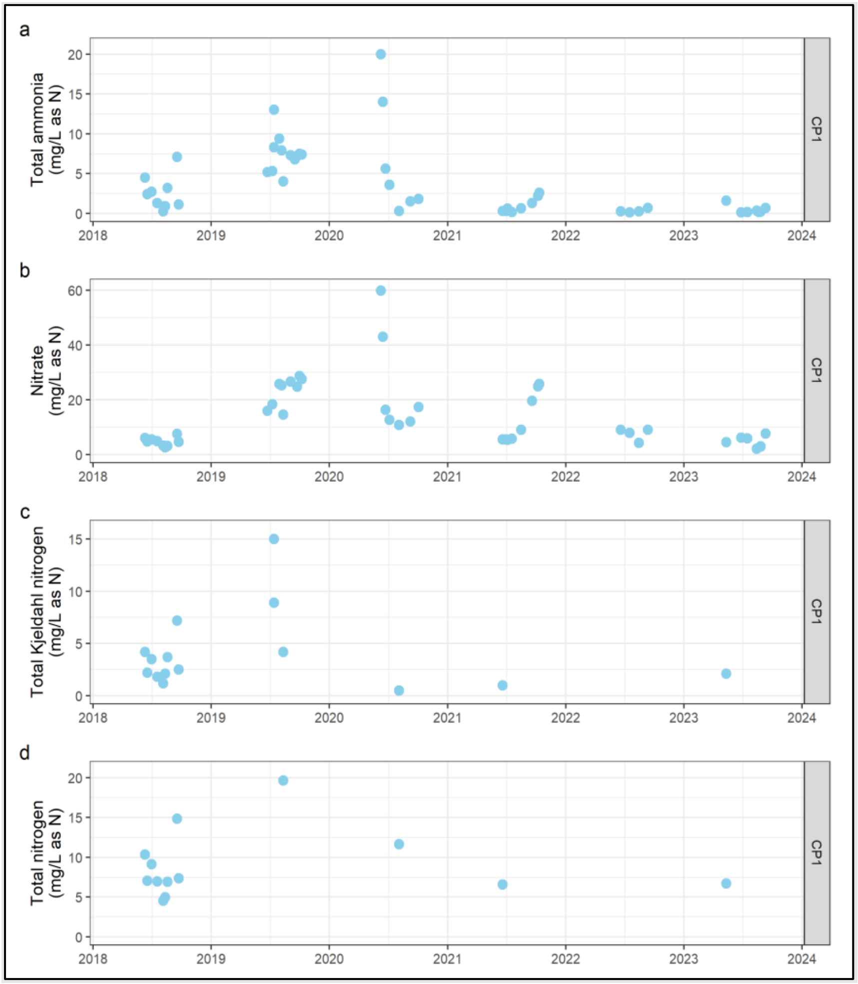

Figure 3: Concentrations of ammonia, nitrate, total Kjeldahl nitrogen and total nitrogen in CP1, 2018 to 2023.

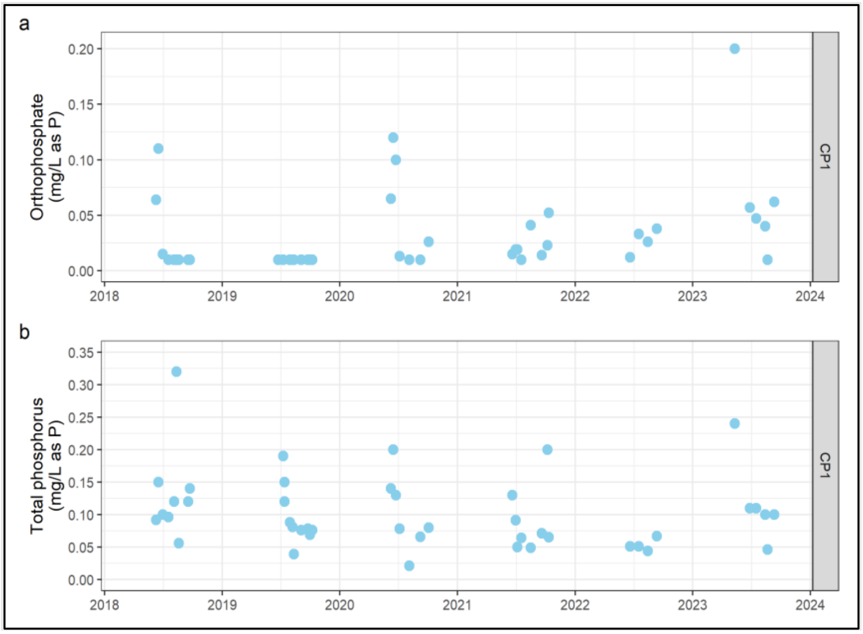

Figure 4: Concentrations of orthophosphate and total phosphorous in CP1, 2018 to 2023.

Nutrient Assimilation Pathway

The nutrient assimilation pathway in CP1 is regulated by the local conditions in the pond. Water temperature in CP1 exhibits a typical seasonal cycle of cooler temperatures in June and September/October, with peak temperatures observed in July/August. Water temperature quickly reached the critical temperature for photosynthesis for diatoms in the spring and warmed to temperatures conducive to algal productivity by July and August. Micronutrients (as indicated by TDS concentrations) required by algae for growth and metabolism appeared to be readily available and there is sufficient inorganic phosphorus (i.e., orthophosphate) available for algal production and growth in the early spring, immediately after ice melt. Dissolved oxygen concentrations, based on field measurements, were generally at or near saturation suggesting a significant oxygen demand to keep the average value below 100% and sufficient oxygen concentrations to support aerobic microbial processes. The strong summer winds, common in the area throughout the open-water period also allow for complete water column mixing in CP1, which prevents anoxic pockets from forming in the pond.

Ammonia enters CP1 through surface contact water (i.e., rain and snowmelt that has come into contact with the mine infrastructure) and remains in the system through internal recycling, with minor input through nitrogen fixation (based on the presence of only one low-abundance taxon capable of nitrogen fixation in the algal taxonomy of a July 2022 sample).

Field pH measurements in CP1 ranged from 6.9 to 9.3, suggesting that once ammonia enters CP1 through surface contact water it remains in the protonated form of the ammonium ion and that little ammonia is being lost to volatilization (i.e., returning to gaseous forms of nitrogen). The expectation is that ammonia removal is occurring primarily though ammonia consumption by algae/photosynthetic bacteria and not through ammonia volatilization or nitrogen gas evolution. Ammonia volatilization requires a pH of around 9.2. The algae blooms in CP1 have increased pH to above 9 during certain parts of the day, although the proportional losses to volatilization are likely much less than those observed through ammonia assimilation by algae. Once taken up by algae, ammonia can be incorporated into biomass and recycled within the system (through ammonification and nitrification), until it is converted from nitrite/nitrate to nitrogen gas (denitrification), or it is trapped in particulate forms that are deposited to the sediment.

The 2023 sample results support ammonia assimilation by algae being an important factor in the reduction of early open-water ammonia concentrations in CP1. The ammonia concentrations in samples collected early in the season were elevated relative to concentrations reported for the remainder of the open-water period in 2023 (Figure 2a,b). These elevated concentrations of ammonia also coincided with an algae bloom observed in CP1 in 2023. The subsequent reduction in ammonia concentration from May to June in 2023 and lack of visible algal blooms for the remainder of the open-water period suggests that it is likely that ammonia was assimilated into algal biomass during the bloom event, which eventually settled out of the water column with senescence of the bloom.

If nitrification and denitrification are paired and occur spatially close to each other, the nitrate produced in nitrification can be quickly converted to nitrogen gas rather than being assimilated into algal biomass, which reduces the chance for algae to continue to form blooms. However, unlike nitrification, denitrification is an anaerobic process and is unlikely to be occurring in the oxygen-rich water column in CP1 during the open-water season. The sediment-water interface in CP1 is also likely oxygenated as a result of frequent wind-driven mixing in the top layers of the sediment but it is expected that the sediment rapidly becomes anoxic within a few centimetres into the sediment profile. As such, it is likely that denitrification is occurring in the sediments in CP1. Denitrification is carried out by a diverse group of bacteria that are often chemoorganotrophs that must be supplied with some form of organic carbon[4]. The soft sediments in CP1 contain a surplus of organic carbon for these bacteria and are not limiting this process. However, it is unclear based on the available dataset what biochemical processes may be occurring in the sediment and the degree of denitrification that may be occurring is unknown.

It should also be noted that a large proportion of the biochemical processes that occur in the nitrogen cycle are governed by bacteria, not by algae[5][6], and currently there is no information available on the bacterial processes occurring in CP1. Bacteria are responsible for converting N_2 into biologically available nitrogen (includes aerobic, anaerobic, phototrophic and chemotrophic forms), nitrification is carried out exclusively by aerobic bacteria, and denitrification is carried out exclusively be anaerobic bacteria, while the role of algae in the nitrogen cycle is large, related to assimilation of dissolved inorganic nitrogen forms into biomass.

Conclusion

The investigation into the nutrient dynamics in CP1 highlights the intricate relationship between nutrients and algae in aquatic ecosystems, and while the ammonia removal mechanism is still unclear in CP1, data shows that natural attenuation by algal growth plays a dominant role in this process.

[4] Lam P, Kuypers MMM. 2011. Microbial nitrogen cycling processes in oxygen minimum zones. Annu. Rev. Mar. Sci. 3:317-345.
[5] Lam P, Kuypers MMM. 2011. Microbial nitrogen cycling processes in oxygen minimum zones. Annu. Rev. Mar. Sci. 3:317-345.
[6] Bernhard A. 2010. The Nitrogen Cycle: Processes, Players, and Human Impact. Nature Education Knowledge. 3(10): 25