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Ammonia Nitrogen Removal by Enhanced Algae Growth – Case Study of a Subarctic Mine Site

Pascal Marcotte
1823 Consulting Inc.
John Baechler
Agnico Eagle Mines Limited
Matthew Gillman
Agnico Eagle Mines Limited
Thomas Genty
Agnico Eagle Mines Limited

Abstract

Elevated concentrations of ammonia nitrogen is a common characteristic of mine impacted water and generally results from the dissolution of undetonated explosives (i.e., Ammonium Nitrate and Fuel Oil and emulsion explosives) by contact water. Several active water treatment technologies are commercially available to remove ammonia nitrogen, but reduction of active treatment demand by promoting natural attenuation is considered best industry practice.

In this paper, the results of laboratory-scale and full-scale trials of a semi-passive approach (i.e., enhanced algae growth) to remove ammonia nitrogen at the Meliadine mine are presented. Phosphorus was found to be the limiting factor to algae growth at the mine site. The addition of various concentrations of phosphorus was first tested at a laboratory scale. The samples were exposed to in-situ conditions, and ammonia nitrogen removal rates ranging from 40% to 93% were achieved over a period of 24 days. This paper also presents the methodology and results of an in-pond treatment during which a 50% ammonia nitrogen removal rate was observed after 68 days.

The studied mine site uses breakpoint chlorination as its primary treatment approach for ammonia nitrogen removal. The results presented in this paper show the potential of using enhanced algae growth as a pre-treatment method, subsequently reducing the quantity of chemicals required for operating the breakpoint chlorination plant. This potential requires further investigation and additional trials are currently under evaluation.

Keywords
Algae
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Corresponding Author
pascal.marcotte@1823.ca

Introduction

In Canada, hard rock miners most often use ammonium nitrate-based explosives, such as Ammonium Nitrate and Fuel Oil (ANFO) and emulsion explosives, to fragment ore bodies. At these operations, elevated concentrations of total ammonia nitrogen (hereafter referred as ammonia nitrogen) in mine contact water are common, resulting from the dissolution of explosive residues. Implementation of mitigation measures can limit this occurrence, but only to some extent (Matts et al., 2007, Marcotte et al., 2022). In most cases, water treatment is required to remove ammonia nitrogen and meet regulatory requirements. Although several active water treatment technologies are commercially available to remove ammonia nitrogen, reduction of active treatment demand by promoting natural attenuation is considered best industry practice.

Naturally occurring reactions involving nitrogen on mine sites are numerous and complex (Chlot, 2013). Among these reactions, volatilization, nitrification, assimilation and adsorption are all suspected to have a considerable impact on nitrogen species in mine water (Marcotte et al., 2021). If properly characterized and understood, water management strategies can be adapted to promote these beneficial reactions. A noteworthy case study using this approach is the Colomac mine remediation project (Chapman et al., 2007), where several nitrogen-based contaminants found in an abandoned tailings pond were removed by promoting nitrogen assimilation via enhanced algae growth. Recognizing the benefits of promoting natural attenuation, the approach used at the Colomac Mine was more recently investigated for at the Meliadine gold mine, an active mine also located in the subarctic zone of Canada. In this paper, the results of laboratory-scale and full-scale trials of this semi-passive approach are presented.

Studied Site Overview

The Meliadine gold mine, operated by Agnico Eagle Mines, is located approximately 25 km north of Rankin Inlet and 80 km southwest of Chesterfield Inlet in the Kivalliq Region of Nunavut. The mine site is located on the peninsula between the East, South, and West basins of Meliadine Lake. The current mine plan of Meliadine includes six gold deposits and relies on both open pit and underground mining practices. Underground mining operations occur in an area of continuous permafrost, with an estimated depth of the base of permafrost between 285 m and 430 m below ground. Despite the presence of permafrost, underground excavations act as a sink for groundwater via the shallow flow regime located in the active layer (seasonally thawed), and the deep flow regime beneath the base of the permafrost. This deep flow regime is characterized by high levels of Total Dissolved Solids (TDS). This saline contact water is pumped from the underground mine into dedicated saline water storage facilities. In contrast, surface contact runoff (i.e., precipitation runoff from the above-ground facilities of the mine) is characterized by low levels of TDS and is directed towards separately operated runoff collection ponds.

The Meliadine mine site used exclusively emulsion explosives. Ammonia nitrogen loading from the dissolution of undetonated emulsion occurs in both the saline and surface contact water of this mine. Concentrations of ammonia nitrogen in these streams are governed by many parameters, including natural attenuation. Furthermore, a leading contributor to this natural attenuation is suspected to be algae assimilation. Algae growth can be observed every summer in both the saline water storage and surface contact water collection ponds. Consequently, ammonia nitrogen concentrations in the surface contact water collection ponds are generally well below 5 mg N/L, and do not require additional treatment. However, ammonia nitrogen concentrations in the saline contact water facilities are elevated and require further treatment. For this reason, a new water treatment plant, which relies on the breakpoint chlorination process, is currently under construction at the mine site.

2021 Laboratory-scale Trial – Results & Interpretation

Inspired by the Colomac mine remediation project, a desktop study was performed to determine the limiting constituent for algae growth in the Meliadine saline contact water (hereafter referred to as mine contact water). This study was performed by Larratt Aquatic Consulting Ltd., and identified phosphorus as the main limiting macronutrient. This study also highlighted the possibility that vitamins may also be deficient.

In a first attempt to evaluate the potential of enhanced algae growth at that mine site, a laboratory scale trial was conducted. This trial took place from July 2nd to 26th, 2021. During this trial, 19 litre pails containing mine contact water were dosed with various concentrations of phosphoric acid and vitamins, then exposed to site conditions. The testing apparatus is presented in Figure 1. Although it was initially planned to partially submerge the pails in one of the mine contact water storage facilities (to mimic site conditions and minimize temperature swings), active operation of these facilities would have jeopardized the trial. Submerging these pails in IBC totes located in a more secluded area of the mine site was ultimately selected as the preferred approach.

In total, eight nutrient addition formulas were tested: 1) no addition, 2) 0.5 mg PO_4-P/L, 3) 1.0 mg PO_4-P/L, 4) 2.0 mg PO_4-P/L, 5) 4.0 mg PO_4-P/L, 6) 8.0 mg PO_4-P/L, 7) 8.0 mg PO_4-P/L + 6.0 mg multivitamins/L and 8) 8.0 mg PO_4-P/L + 6.0 mg vitamins B12/L. Photos and in-situ parameter measurements (pH, temperature, DO, turbidity and NH_3-N) were collected at frequent intervals over a 24-day period. These tests are presented in Figure 2, while measured pH and ammonia nitrogen concentrations are presented in Figure 3.

Figure 1 Laboratory scale testing apparatus

Based on visual evidence, enhanced algae growth was most successful in pails no. 2, 3 and 4. Some algae growth was also observed in pail no. 1 and 5, but to a lesser extent. These observations are consistent with the pH and ammonia nitrogen concentrations recorded. During the first 12 days of the trial, considerable amounts of ammonia nitrogen were removed from pails no. 2, 3 and 4, followed by pails no. 1 and 5. Also during this period, an increase in pH was observed for these pails, likely due to consumption of carbon dioxide for cellular growth. At day 20, visual evidence and in-situ parameters measurement suggest that the algae bloom was over.

This laboratory scale trial demonstrated that an addition of 0.5 to 2.0 mg PO_4-P/L could improve natural attenuation of ammonia nitrogen at the mine site. This conclusion is consistent with the Colomac case study, in which an addition of 1 mg PO_4-P /L was deemed optional. However, the poor results observed in pails no. 6, 7 and 8 show that excess phosphorus may also lead to algae growth inhibition.

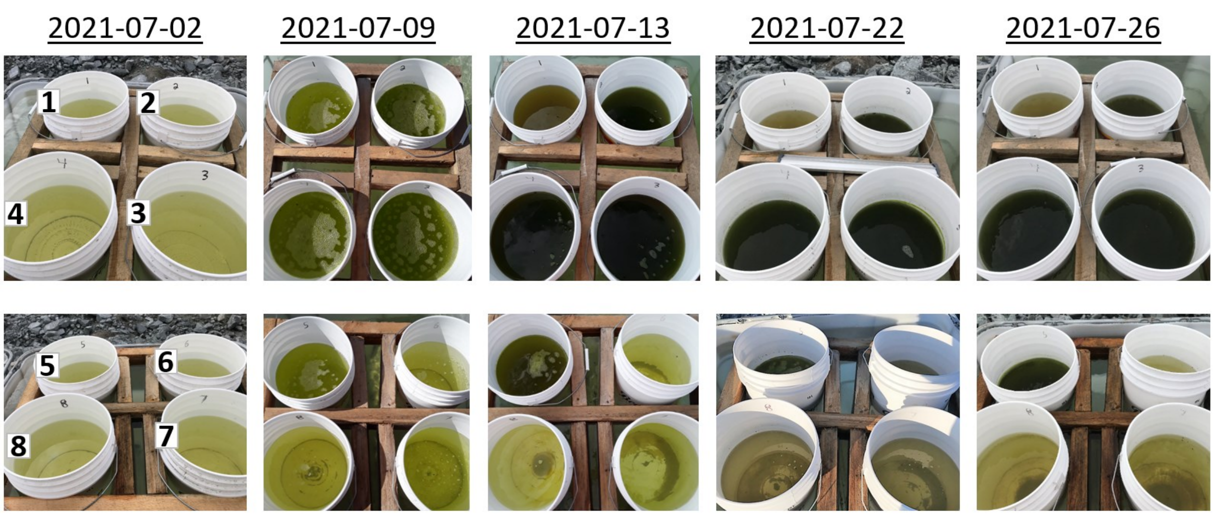


Figure 2 Photos taken during the laboratory scale trial

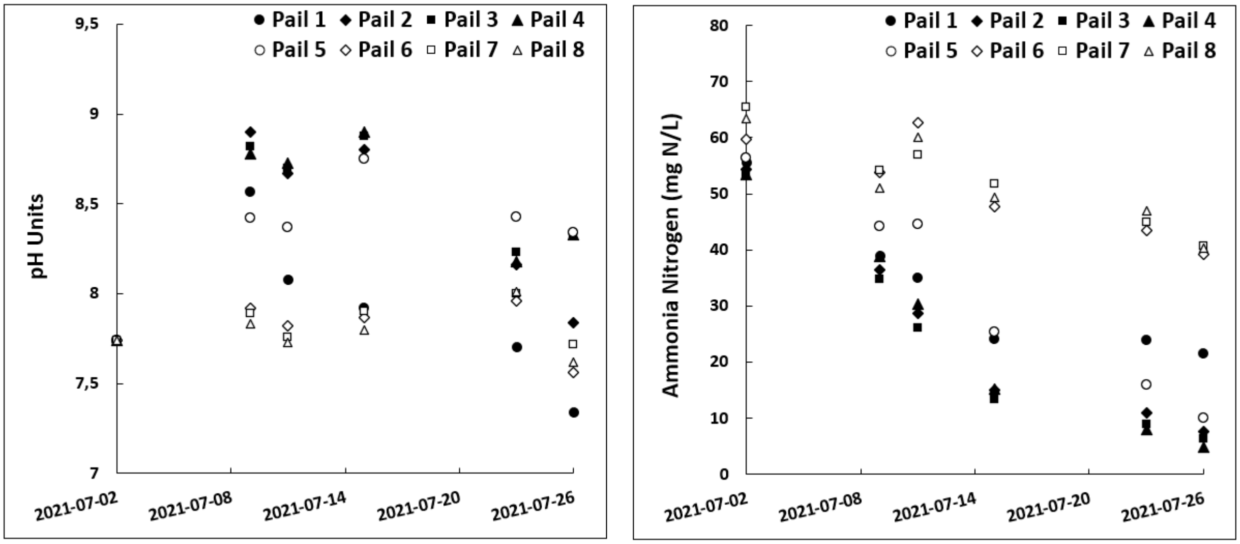


Figure 3 pH and ammonia nitrogen measurement during the laboratory scale trial

2022 Full Scale Trial – Results & Interpretation

Building upon the results achieved in 2021, a full-scale trial was also performed at the mine site. This trial took place from July 11th to September 7th, 2022. For this trial, 3650 m^3 of mine contact water was pumped into a lined pond, resulting in an average water depth of 1.3 m. During the water transfer, approximately 1 mg PO_4-P/L was added to this pond, by adding 11.5 kg of monoammonium phosphate (MAP). Precautions were taken to avoid excessive precipitation of calcium phosphate (i.e., dissolving the MAP in a small amount of fresh water first, then gradually dosing the solution in the stream of transferred water) . Around the same time, an apparatus was also deployed to allow easy sampling of the water column. In-situ parameter measurements at various depths (pH, temperature, conductivity, DO, turbidity, NH_3-N) and photos were taken every three days, while external analysis (water quality and phytoplankton) were performed at the pond surface on T=0 day, T=18 days and T=41 days.

Drone photos of the 2022 full scale trial are presented in Figure 4, while in-situ parameter measurements are presented in Figure 5. On the drone photo taken right after the water and phosphorus were added (T=0 day), sediments at the bottom of the pond can be seen. In contrast, the opacity of the water is much higher at T=2 days, and the presence of green foam can be observed. This indicates that enhanced algae growth was already occurring after less than 48 hours. The water opacity and green tint remained strong throughout the whole duration of the trail, as shown at T=29 days (Figure 4). However, the green foam was only observed at T = 2 days.

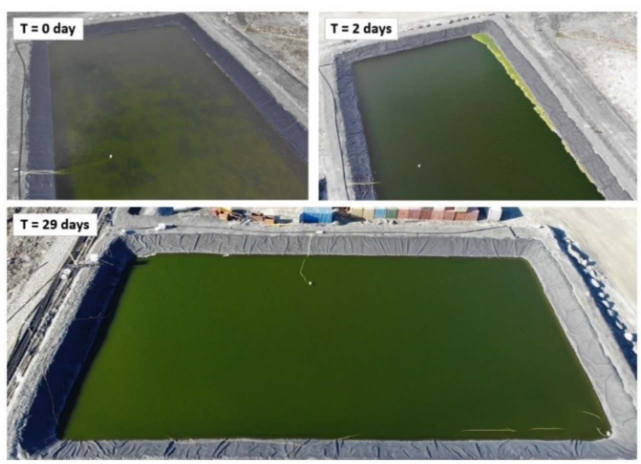


Figure 4 Drone photo of the 2022 full scale trial

In Figure 5, a sharp decrease in the ammonia nitrogen concentration can be observed over the first 12 days of the trial. During this period, turbidity increased steadily, while pH increased by more than one unit in the initial two days of the trial. These observations are consistent with the 2021 laboratory trial results, and suggest that ammonia nitrogen removal by enhanced algae growth is occurring.

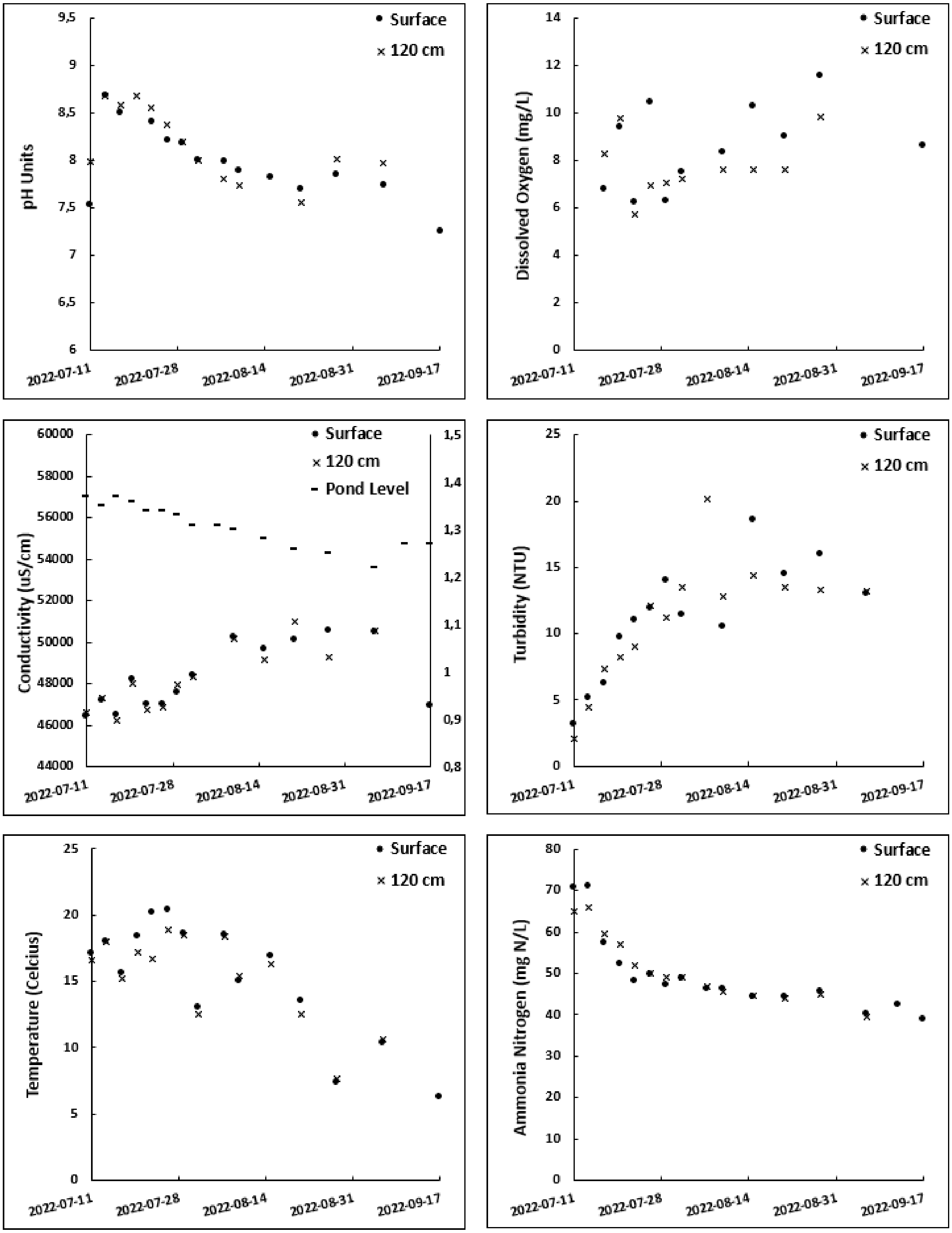


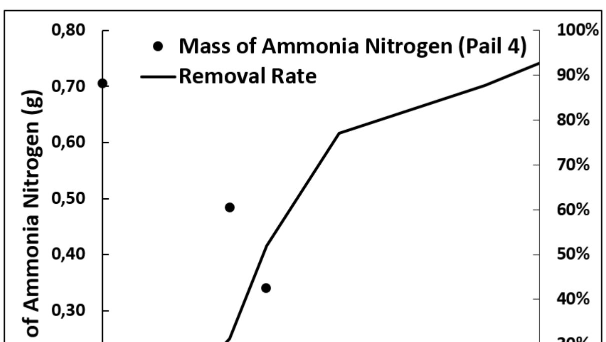
Figure 5 In-situ parameters measurements of the 2022 Full Scale Trial

Signs of algae growth after 12 days were less pronounced. The ammonia nitrogen removal rate significantly decreased beyond 12 days, with turbidity plateauing in the 15 NTU range, and pH decreased closer to its initial value. Recorded water temperature also decreased after 15 days, but this parameter is not suspected to be the cause of the reduced algae growth, since natural occurring algae blooms have been observed onsite at water temperatures near 0 °Celsius. Dissolved oxygen remained high throughout the water column during the whole trial duration, with the highest values recorded near the end of the trial (when the water temperature was colder). An upward trend was also observed in the conductivity of the mine contact water during the trial, while a downward trend was observed in the pond level. Both observations are likely explained by more evaporation than precipitation during the trial.

Although only in-situ readings observed at surface and 120 cm depth are presented in Figure 4, trends observed at 30 cm, 60 cm and 90 cm were similar. The absence of substantial differences in the water quality at these various depths suggest that algae bloom of that magnitude reaches at least 1.2 m depth.

Ammonia nitrogen removal rates achieved in the 2021 laboratory scale trial and 2022 full scale trial are presented in Figure 6. To eliminate the effect of evaporation, the total mass of ammonia nitrogen was calculated using the ammonia nitrogen concentrations and water levels. For both trials, the removal rate started to plateau around day 12. The removal rate observed at T=12 in the 2021 trial was 77%, compared to 32% observed during the 2022 trial. However, the biomass productivity observed at T=12 in 2021 was only 0.82 g NH_3-N/m^2/day, compared to 2.08 g NH_3-N/m^2/day in 2022. The difference in depth to surface ratios used for these trials, as well as the shading from the rim of the pails, could explain this difference.

By the end of each trial, the removal rate observed were respectively 93% after 24 days, and 50% after 68 days. In total, 125 kg of ammonia nitrogen were removed during the 2022 trial. In chemical products alone, the cost of treating ammonia nitrogen by breakpoint chlorination is estimated at \$140/kg NH_3-N. Meanwhile, approximately \$50 worth of phosphorus was used during the 2022 trial.



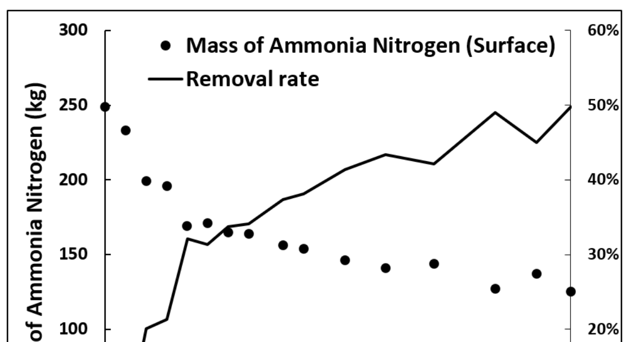


Figure 6 Ammonia nitrogen removal rate achieved during the 2021 laboratory scale trial (left) and 2022 full scale trial (right)

Although removal rate reduction during scale up of an algae treatment has been documented elsewhere (Sutherland et al. 2020), the difference between the removal rate observed in the 2021 and 2022 trials required further investigation. Table 1 presents the external water quality analysis performed on both trials.

Table 1 External analysis results for the 2021 and 2022 trials

Parameters	Units	2021 Laboratory Scale Trials Pail 1 T = 0	Pail 1 T = 24	Pail 4 T = 24	2022 Full Scale Trials Surface T = 0	Surface T = 18	Surface T = 42
Conventional and Nutrients							
pH	Units				7.71	7.55	6.79
Conductivity	umho/cm				48000	49000	51000
Total Dissolved Solids	mg/L				31300	31300	29800
Total Suspended Solids	mg/L	39	51	170	24	17	35
Total Alkalinity (as CaCO3)	mg /L	160	72	34	92	25	10
Total Inorganic Carbon	mg C/L	35	17	9	17	5	3
Total Organic Carbon	mg C/L	31	43	80	13	23	20
Dissolved Organic Carbon	mg C/L	31	38	54	12	15	18
Total Phosphorus	mg P/L	0.36	0.30	1.8	0.88	0.26	0.25
Orthophosphate	mg P/L	0.12	0.021	0.22	0.60	0.13	0.060
Total Ammonia Nitrogen	mg N/L	53	23	7.7	71	52	47
Nitrite	mg N/L	2.17	0.960	0.106	1.64	1.32	0.466
Nitrate	mg N/L	102	123	122	90.3	88.4	89.6
Nitrate + Nitrite	mg N/L	104	124	122	92.0	89.8	90.1
Total Kjeldahl Nitrogen	mg N/L	56	29	19	68	48	51
Dissolved Silicon	mg/L	<5.0	<0.1	<5.0	3.7	<5.0	<5.0
Major Ions							
Dissolved Calcium (Ca)	mg/L	1790	2100	2100	1200	1140	1200
Dissolved Magnesium (Mg)	mg/L	932	1020	1010	946	908	953
Dissolved Potassium (K)	mg/L	309	357	346	321	304	311
Dissolved Sodium (Na)	mg/L	7000	7830	7660	7790	7630	7830
Dissolved Chloride (Cl-)	mg/L	13000	16000	17000	16000	15000	16000
Dissolved Sulphate (SO4)	mg/L				1800	1900	2000
Dissolved Fluoride (F-)	mg/L				0.10	0.13	0.11
Metals							
Total Copper (Cu)	mg/L	0.017	0.026	<0.025	<0.025	0.0053	<0.025

Residual orthophosphate in the T=18 days and T=42 days samples of the 2022 trial were lower than the T=24 days sample for pail 4 in 2021. Therefore, phosphorus limitation may explain the lower algae growth observed in the 2022 trial. However, additional field results suggest otherwise. In the last two weeks of the 2022 trial, 19 L aliquots of pond water were collected and spiked with various concentrations of phosphorus. These aliquots we exposed to site conditions (in pails next to the pond), but in-situ readings for these aliquots (at all phosphorus concentrations) kept trending in a similar matter than the in-situ readings of the pond itself.

Both the dissolved organic carbon and the dissolved inorganic carbon were also lower in the 2022 samples than in 2021. An attempt was made to spike aliquots of mine water with various concentrations of Na_2CO_3, but once again, in-situ readings for these aliquots kept trending in a similar matter than the in-situ readings of the pond itself.

Silicon is an essential micronutrient for diatoms. However, the detection limits found in Table 2 for silicon are such that it's difficult to compare the 2021 and 2022 trials. Nevertheless, the average ratio of N:Si in diatoms is 15:16 (Brzezinski, 1985). Therefore, silicon is limiting if found in lower concentrations than dissolved inorganic nitrogen (ammonia nitrogen, nitrite, nitrate). This is the case for all samples presented in Table 2. Silicon limitation was likely preventing diatom growth during both the 2021 and 2022 trials.

Formation of nitrate was observed during the 2021 trial, suggesting that the observed ammonia nitrogen removal rate may be the result of a combined effect from nitrification and assimilation. After 24 days, pail no. 1 contained an additional 22 mg NO_3-N/L, while pail no. 4 contained an additional 21 mg NO_3-N/L. This conversion of ammonia nitrogen to nitrate alone may have contributed to as much as 73% of the overall ammonia nitrogen removal observed in pail no. 1, and 46% in pail no. 4. This phenomenon wasn't observed during the 2022 trial, and may explain the difference between both years. Nitrifying bacteria require the following conditions to thrive: sufficient surface area for biofilm development, absence of toxicants (mainly copper), > 4 mg DO/L, > 0.2 mg P/L, a pH between 6.5 and 8.5, and an alkalinity above 80 mg $CaCO_3$/L (WEF, 2010). When comparing results from the 2021 and 2022 trials, and assuming that algae biomass could provide sufficient surface area for biofilm development, all conditions for nitrifying bacteria to thrive are met. One noticeable difference between the water quality of the 2021 and 2022 trial is the initial alkalinity (160 versus 92 mg $CaCO_3$/L). It is possible that alkalinity in the 2022 trial may have limited nitrification after some time. Additional trials at various concentrations of alkalinity, orthophosphate, silicon, dissolved organic carbon and dissolved inorganic carbon are required to fully understand the limitations observed in 2022.

Finally, phytoplankton analyses were also performed on the 2021 and 2022 trials. The species that contributed the most to the samples biomass are presented in Table 2. Beneficial flagellated green algae were the most common algae in all samples presented in this table. Some were found at the palmelloid stage, suggesting salt or nitrogen stress. Bacteria were also found in very high numbers for most samples, representing an important component of the total biomass. Although diatoms are also present in most samples, they are not as common as the green algae. This is likely due to silicon limitation, as discussed above.

Table 2 Phytoplankton contributing the most to the samples biomass in 2021 and 2022

Taxa*	2021 Laboratory Scale Trials			2022 Full Scale Trials		
	Pail 1 T = 0	Pail 1 T = 24	Pail 4 T = 24	Surface T = 0	Surface T = 18	Surface T = 42
Diatoms						
Nitzschia sp. sm	28	231	616	7700		
Nitzschia sp. lrg		1386	3696	16324	308	
Green Algae						
Brachiomonas cf. submarina					4620	924
Chlamydomonas sp. A lrg	364	6160	75152	6160	12 012	616
Chlamydomonas sp. B sm	70	3157	24024	8624	6776	1848
Chlamydomonas palmelloid stage	280	693	3080		4620	1540
Dunaliella cf. salina					6468	12936
Dunaliella sp. B sm	508	4158	38808	6160	25564	12628
Others						
Bacteria - all types	Dominant	Dominant	N/A	Very high	Very high	Very high

*Blank data = not seen in any fields.

Conclusion and Future Considerations

Although several active water treatment technologies are commercially available to remove ammonia nitrogen, reduction of active treatment demand by promoting natural attenuation is considered best industry practice. A noteworthy case study documenting this approach is the Colomac mine remediation project, where enhanced algae growth was used to remove several nitrogen-based contaminants in a tailings pond (Chapman et al., 2007). This approach was more recently investigated at the Meliadine gold mine, also located in the subarctic zone of Canada.

The laboratory scale trial performed in summer 2021 yielded ammonia nitrogen removal rates up to 93%, after 24 days. This trial also proved that phosphorus was a limiting macronutrient in the mine water, and the addition of 0.5 to 2.0 mg P/L was optimal to enhance algae growth. In a subsequent trial performed in a full scale lined pond during summer 2022, 1 mg P/L was added to 3650 m^3 of mine water. After 68 days, 50% of the ammonia nitrogen was removed. Nutrient deficiency during this trial is suspected. Nevertheless, 125 kg of ammonia nitrogen was removed during the 2022 trial. In chemical products alone, the cost of treating ammonia nitrogen by breakpoint chlorination is estimated at \$140/kg NH_3-N. Meanwhile, approximately \$50 worth of phosphorus was used during the 2022 full scale trial. These results show the potential environmental and economic benefits of applying this approach at larger scales, and additional trials are currently under evaluation.

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