Phytoremediation to improve pit lake water quality

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Abstract

The flooding of open pits is a key feature of closure plans for many metal mines. Once filled, pit lakes typically discharge to the environment. Pit lake water requiring treatment prior to discharge can represent a significant cost of long-term closure care and maintenance. We present phytoremediation technology that has been successfully used in many industries as a relatively low-cost technique to attenuate contaminants in water. Phytoremediation describes the use of plants to mitigate environmental contamination. In the context of mine pit lakes, phytoremediation is the biologically mediated removal of contaminants using photosynthesizing organisms to improve water quality. The relatively low-cost option of phytoremediation can make it an attractive alternative to conventional lime neutralisation for metal contamination resulting from metal leaching and acid rock drainage. Phytoremediation has also been investigated for treatment of other contaminants in mine water.

Metal mine pit lakes present an opportunity to use phytoremediation to treat waters affected by metal leaching and acid rock drainage. Within a pit lake, the greatest opportunity for phytoremediation of water is in the limnetic zone, which usually occupies a much greater area and volume than the littoral zone. However, other important variables may influence the potential success of phytoremediation.

Phytoremediation has been used successfully for more than a decade to treat metal-contaminated pit lake waters at the closed Island Copper Mine. We discuss how the phytoremediation program at the Island Copper Mine has been designed to treat pit lake waters to meet permit requirements and significantly reduce metal loads in the lake. Through this case study we also explore the relationships between the physical and biogeochemical characteristics of the water column and show how an understanding of this relationship is critical to planning, designing and identifying the potential success and risks of phytoremediation treatment of mine pit lakes.

1 Introduction

Phytoremediation describes the use of plants to mitigate environmental contamination. In the context of mine pit lakes, phytoremediation is the biologically mediated removal of contaminants using photosynthesizing organisms to improve water quality. The relatively low-cost option of phytoremediation can make it an attractive alternative to conventional lime neutralisation for metal contamination resulting from metal leaching and acid rock drainage (ML/ARD; Pelletier et al., 2009). Phytoremediation has also been investigated for treatment of mine water for other contaminants, including using phosphorous amendments to treat nitrate loads (Rescan, 2010) and uranium and other metal loads (Dessouki et al., 2005).

Within a pit lake, the greatest opportunity for phytoremediation of water is in the limnetic zone, which usually occupies a much greater area and volume than the littoral zone. However, other important variables may influence the potential success of phytoremediation. Evaluation of the physical structure of the water column — in addition to evaluating the source and nature of contaminants — is critical to identifying the potential success and risks of pit lake phytoremediation options. Phytoremediation has been used...
successfully for more than a decade to treat metal-contaminated pit lake waters at the closed Island Copper Mine. In this paper, we describe the phytoremediation technique used to attenuate metal concentrations in the Island Copper pit lake.

2 Engineered design of the Island Copper pit lake

Island Copper (Figure 1) was an open pit porphyry copper mine that operated from October 1971 to December 1995. At start-up, the mine had an ore reserve of 254 million (metric) tonnes, averaging 0.52% copper and 0.017% molybdenum. After receipt of agency permits, the decision to proceed with the development was made and construction of the mill, ancillary support facilities and deep-sea port began. Over the 24-year life of the mine, mineral reserves expanded to 408 million tonnes and ore production increased to 55,000 tonnes per day.

More than one billion tonnes of rock were removed from the open pit. The mine produced metal concentrates containing more than 1.3 million tonnes of copper, 31,000 tonnes of molybdenum, 31.7 tonnes of gold, 336 tonnes of silver and 27 tonnes of rhenium. By the time it closed in 1995, Island Copper was Canada’s third-largest mine and the lowest man-made depression on Earth.

Figure 1 Island Copper before, during and after flooding

A unique feature of the operational closure plan was the 1996 decommissioning of the open pit by flooding it with seawater from adjacent Rupert Inlet and capping it with fresh water to create a 355-metre-deep lake covering 174 hectares. As part of the mitigation plan, this lake provided a receiving environment for acid rock drainage from the mineralised rock deposited around the rim of the pit during operations. The rapid development of meromixis was expected to result in the long-term development of anoxic conditions deep in the lake. These conditions would cause metals to precipitate as insoluble metal-sulphides, providing a means of treatment for injected ML/ARD. Table 1 lists the physical characteristics of the Island Copper pit lake and the water inputs to the lake.
The site receives high rainfall (an average of 1.9 m/yr from 2009 to 2013), little snow (less than 15% of precipitation) and has relatively cool summers and mild winters, resulting in a long growing season ideal for vegetation growth. Construction of the upland waste rock dumps began in the early 1970s and land reclamation in the 1990s. Land reclamation included a nominal half-metre soil reclamation cap, contouring and planting of the waste rock dumps with woody vegetation. This cover was designed to reduce erosion and was not intended to limit or reduce infiltration of meteoric water into the stockpiles. The grading and vegetation cover were designed to maintain an aesthetic quality consistent with the surrounding landscape. Today, approximately 88 million tonnes of waste rock stored over 44 hectares of land have waters reporting to the pit lake for remediation. The approximate annual quantity and quality ML/ARD reporting to the surface and middle layers of the pit lake from 2009 to 2013 are shown in Table 2.

### Table 1  Island Copper pit lake dimensions and approximate water inputs

<table>
<thead>
<tr>
<th>Basic parameter</th>
<th>Approximate value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal dimensions of pit lake</td>
<td>Approximately 1 by 2 km, oval</td>
</tr>
<tr>
<td>Major rock type in walls</td>
<td>Andesitic pyroclastic, quartz feldspar porphyries, Bonanza volcanic, minor sulphides</td>
</tr>
<tr>
<td>Surface area of pit lake</td>
<td>1.74 million m²</td>
</tr>
<tr>
<td>Perimeter of pit lake</td>
<td>5,600 m</td>
</tr>
<tr>
<td>Maximum depth of pit lake</td>
<td>355 m</td>
</tr>
<tr>
<td>Total volume of pit lake (five-year average)</td>
<td>243 million m³</td>
</tr>
<tr>
<td>Annual direct rainfall to pit lake</td>
<td>1.9 m/yr, equivalent to 3.4 million m³/yr</td>
</tr>
<tr>
<td>Mine water directed to pit lake</td>
<td>4.3 million m³/yr</td>
</tr>
<tr>
<td>Run-in water from pit walls</td>
<td>1.1 million m³/yr</td>
</tr>
<tr>
<td>Lake evaporation (from regional estimates)</td>
<td>1.0 million m³/yr</td>
</tr>
</tbody>
</table>

**Note:** Five-year averages use 2009 to 2013 data.

### Table 2  Key characteristics of mine water reporting to the pit lake

<table>
<thead>
<tr>
<th>Variable</th>
<th>To surface</th>
<th></th>
<th>To middle layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>North catchment</td>
<td>Other</td>
<td>Southeast catchment</td>
</tr>
<tr>
<td>Total annual flow (five-year average; million m³)</td>
<td>2.0</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td>pH</td>
<td>6.64–8.08</td>
<td>3.69–8.32</td>
<td>4.30–7.83</td>
</tr>
<tr>
<td>Conductivity (µs/cm)</td>
<td>726–1,220</td>
<td>187–2,840</td>
<td>1,210–2,302</td>
</tr>
<tr>
<td>Sulphate (mg/l)</td>
<td>293–638</td>
<td>44.0–1,960</td>
<td>653–1,621</td>
</tr>
<tr>
<td>Dissolved zinc (mg/l)</td>
<td>0.646–4.22</td>
<td>0.191–23.2</td>
<td>0.564–11.1</td>
</tr>
<tr>
<td>Dissolved copper (mg/l)</td>
<td>0.0107–0.201</td>
<td>0.00823–3.78</td>
<td>0.00323–2.52</td>
</tr>
<tr>
<td>Dissolved cadmium (mg/l)</td>
<td>0.00396–0.0234</td>
<td>0.00085–0.120</td>
<td>0.0027–0.0541</td>
</tr>
</tbody>
</table>

**Note:** Estimates are from 2009 to 2013. Ranges are from quarterly sampling.
Because the pit lake was intended as a water treatment facility, near-shore habitat features were intentionally left out its design. The surface of the lake receives direct precipitation (3.4 million m$^3$/yr), run-in from the pit walls (1.1 million m$^3$/yr), drainage from the catchment north of the lake (2.0 million m$^3$/yr), and mine drainage inputs from other sources (0.8 m$^3$/yr). The lake normally has open water year-round owing to the mild climate, and evaporation loss at the surface is estimated at 1.0 million m$^3$/yr based on regional data from Environment Canada (2015). There is no evidence of significant groundwater input to the pit lake. Water from the southeast catchment (1.5 million m$^3$/yr) is injected into the lake’s middle layer through the south injector system (SIS). The SIS was installed after flooding to convey drainage from waste dump areas to a depth of about 220 m. The system has a capacity in excess of 800 l/s. The SIS (Figure 2) consists of a 36-inch high-density polyethylene (HDPE) pipe approximately 380 m long extending from an elevation of approximately 3 m below sea level (−3 m amsl) to approximately −220 m amsl. The end of the SIS pipe is equipped with a multiport diffuser, through which the SIS drainage discharges at the bottom of the middle layer of the pit lake. In addition, a 40-metre section of 63-inch HDPE pipe, installed from −3 m up to +5 m amsl, penetrates the surface of the pit lake and provides a deaeration chamber for the injected flow. Another approximately 75-metre section of 36-inch HDPE pipe connects the deaerator to the SIS settling pond to the south, which in turn is fed by ditches and piping from the northeast areas of the property.

The pit lake design takes advantage of the strong density contrast between seawater and freshwater to create a meromictic lake. The lake is now a three-layer system, with each layer having distinct physical and chemical characteristics (Table 3). The strong salinity contrast between the top and middle layers forms the density gradient between them (the pycnocline). Although there is a temperature difference between these two layers, it is the salinity contrast that provides the water column stability between the two layers. The
elevation of the pycnocline at the Island Copper pit lake is of importance in determining which layer can discharge to Rupert Inlet. The diffuse discharge to the inlet is also important in eliminating salt loads from the top layer, thereby preventing salt build-up and water column instability.

In February 2005, the middle layer lifting (MLL) system was commissioned to control the pycnocline elevation. The Island Copper MLL system is an example of the maintenance of the physical water column structure of a pit lake through designed manipulation. Before the commissioning of the MLL system, the pycnocline was rising at a rate of approximately 0.5 m/year, mostly during the rainy winter period. The pycnocline’s rise was caused by upward displacement from the injection of mine drainage at depth. The concept of the MLL system is simple. Water from the upper portion of the middle layer is “pumped” to the surface at a rate slightly greater than the rate at which mine water is injected at depth through the SIS (Figure 2). The action of the MLL system counteracts the upward displacement of the pycnocline, and in fact results in a lowering of the pycnocline over time. The system is described in Pelletier et al. (2009).

Figure 3 shows four density profiles of the pit lake measured in 2013, expressed as $\sigma_t$ units. The salinity contour plot of Figure 4 shows the typical fluctuations in water level, the clearly defined pycnocline, and the drop in pycnocline elevation since the MLL was commissioned.

Table 3  **Physical and chemical characteristics of the pit lake**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Top layer</th>
<th>Middle layer</th>
<th>Bottom layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (five-year average; m)</td>
<td>6.5</td>
<td>215</td>
<td>130</td>
</tr>
<tr>
<td>Volume (five-year average; million m$^3$)</td>
<td>11.4</td>
<td>217</td>
<td>14.8</td>
</tr>
<tr>
<td>Sampling depths (m)</td>
<td>0, 2</td>
<td>10, 30, 100, 200</td>
<td>300, ~338</td>
</tr>
<tr>
<td>Five-year ranges (2009–2013)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.17–9.76</td>
<td>6.52–7.81</td>
<td>6.46–7.81</td>
</tr>
<tr>
<td>Salinity (PSU)</td>
<td>5.5–7.4</td>
<td>19.5–24.7</td>
<td>26.1–28.8</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>4.51–25.1</td>
<td>10.7–13.7</td>
<td>13.1–13.2</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/l)</td>
<td>8.48–15.8</td>
<td>&lt;0.04–1.91</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Hydrogen sulphide (mg/l)</td>
<td>&lt;0.1–1.61</td>
<td>&lt;0.1–2.7</td>
<td>0.7–8.8</td>
</tr>
<tr>
<td>Dissolved zinc (mg/l)</td>
<td>&lt;0.0008–0.247</td>
<td>&lt;0.0008–0.0414</td>
<td>&lt;0.0008–0.0096</td>
</tr>
<tr>
<td>Dissolved copper (mg/l)</td>
<td>0.0012–0.0124</td>
<td>&lt;0.00005–0.00079</td>
<td>&lt;0.00005–0.00118</td>
</tr>
<tr>
<td>Dissolved cadmium (mg/l)</td>
<td>0.0000024–0.00476</td>
<td>&lt;0.00002–0.000336</td>
<td>&lt;0.00002–0.000050</td>
</tr>
</tbody>
</table>

*Note: Estimates are from 2009 to 2013. Ranges are from quarterly sampling.*
Figure 3  Seasonal water density profiles of the Island Copper pit lake water column

Figure 4  Upper 10 m of the Island Copper pit lake water column, showing changes in surface and pycnocline elevations over time
3 Phytoremediation at the Island Copper pit lake

As discussed earlier, the Island Copper pit lake receives ML/ARD at the surface and at depth, which contributes to the lake’s total metal load. As part of the phytoremediation program, weekly nutrient amendments are made to the lake’s surface. Commercial-grade fertiliser is purchased in batches of approximately 24,000 l of liquid fertiliser comprising 8,130 kg of ammonium polyphosphate (10-34-0) and 22,870 kg of urea ammonium nitrate (28-0-0). The mixture is delivered to the site by tanker truck and stored in a steel tank. Each delivery of fertiliser lasts approximately three to four months under the current fertilisation schedule. The liquid fertiliser is applied to the surface of the lake from the stern of a purpose-built motorboat with an integrated 434 l fertiliser tank. The fertiliser is mixed into the surface waters through the propeller wash of the boat. This procedure is repeated over a number of transects, for a total of approximately 2,150 l of fertiliser per week. In total, approximately 2% of the lake’s surface area is fertilised by boat; however, sampling at multiple locations immediately after fertilisation shows that nutrient concentrations are uniform within the mixed layer. Based on the principle of a well-mixed surface layer, testing is underway to automate injection of fertiliser to the surface of the pit lake without the use of a boat. In either case, the weekly application rate is equivalent to 382 mg N/m² and 63 mg P/m². Lake fertilisation is suspended during July and August, when metal loads to the lake are low because of the dry conditions. A monitoring program evaluates the evolving ML/ARD and the effects of the fertilisation program on water quality, primary production, and the overall biogeochemical performance of the pit lake.

3.1 Biological response to nutrient amendments

Phosphorous is typically the limiting nutrient for phytoplankton populations in natural lakes. Nitrogen is abundant in the atmosphere as nitrogen gas, and some phytoplankton (cyanobacteria) can use this form of nitrogen and are thus never limited by nitrogen in surface waters. Consequently, these organisms can often out-compete other phytoplankton species when nitrate and other forms of nitrogen are at low concentrations. The forms of nitrogen most utilised by phytoplankton are nitrate and ammonia. Nutrient amendments to the pit lake provide nitrogen and phosphorus in a ratio of 6:1 by weight. Although this is slightly less than the Redfield ratio (Redfield, 1958), it has proven effective for the Island Copper pit lake system.

Nutrient amendments from 2009 to 2013 produced an average nitrate concentration in the top layer of 0.0188 mg/l (as N) and ranged from below the instrument detection limit to 0.122 mg/l. Surface concentrations were slightly greater in winter than in summer because of the suspension of lake fertilisation in July and August. The average ammonia concentration in surface waters ranged from below the detection limit (0.0050 mg/l) to 0.107 mg/l (as N) from 2009 to 2013. Urea concentrations were as high as 0.339 mg/l (as N) in surface waters.

From 2009 to 2013, total phosphate in surface waters ranged from 0.0020 mg/l to a peak of 0.142 mg/l in May 2009. Dissolved phosphate concentrations at the surface are generally close to or below the best available detection limit (<0.002 mg/l) for the first half of the year, indicating near-complete utilisation of this nutrient by phytoplankton cells. As with nitrate, dissolved phosphate concentrations in surface waters peak in the wet period. From 2009 to 2013, the peak concentration of dissolved phosphate was 0.0180 mg/l in November 2010. Ortho-phosphate was typically below the analytical detection limit (<0.001 mg/l) because of its preferential consumption by phytoplankton. Diatoms are not ideal candidates for the pit lake treatment system, as they often have a low surface-area-to-volume ratio and a high sinking rate (low residence time in the top layer). Although silicic acid is a required macronutrient for diatoms, this nutrient is not used as a component of the fertiliser to avoid the dominance of diatoms in the phytoplankton.

Figure 5 shows Secchi depths and chlorophyll a concentrations measured in the top and middle layers of the lake from 2009 to 2013. Chlorophyll a concentrations at the surface ranged from below detection (August and September of most years) to 142 µg/l (April 2013), and averaged 16.1 µg/l. The low chlorophyll concentrations measured in August and September coincide with the period when fertiliser was not applied to the pit lake. In the middle layer (100 m depth), chlorophyll a measurements ranged from below detection
to 12.6 µg/l, and averaged 5.2 µg/l. The presence of any measurable biomass in the middle layer is caused by phytoplankton cells sinking out of the productive top layer and eventually settling to the lake bed.

The stimulation of phytoplankton growth by fertilisation increases the pH of surface waters by reducing the concentration of dissolved carbon dioxide, which is consumed through photosynthesis. The pH in the top layer of the pit lake trends approximately with chlorophyll in the top layer. The observed pattern follows that of increased primary productivity. In the top layer, the pH from 2009 to 2013 ranged from 7.17 to 9.76 and averaged 8.73.

The phytoplankton biomass found in the top and middle (10 m) layers of the pit lake is primarily composed of the chlorophytes *Coccomyxa granulata* and *Oocystis cf. parva* in the winter, spring and summer months and by the chlorophyte *Ankistrodesmus falcatus* and the diatom *Chaetoceros muelleri* in the fall. The same trends in phytoplankton abundance are observed in the middle layer, with the predominant species *O. parva* dominating the assemblages from February through October. *C. granulata* is a mostly solitary cell, 3 to 4 µm in diameter, which sometimes forms spherical colonies (Caljon, 1983). It is a “spring-summer species” that tolerates a wide range of salinities. *A. falcatus* is a needle-like, mostly solitary cell that is 2 to 6 µm in diameter and 25 to 100 µm long (Prescott, 1982). This species is most commonly found in acidic water with high temperatures. *O. parva* can generally tolerate a wide variety of habitats (Wehr and Sheath, 2003), including bogs. Its small cells, 4 to 7.5 µm in diameter, can occur as a single cell or as families surrounded by a mother cell (Prescott, 1982). Colonies can be up to 43.9 µm in diameter (Prescott, 1982). Based on these characteristics, the phytoplankton species that colonise the Island Copper pit lakes are well suited to the ambient water quality conditions. Overall, the biological composition of the pit lake appears to be dominated by chlorophytes.

The effect of the observed production of these small phytoplankton species is to provide adsorption surfaces for the removal of dissolved metals in the top layer. The lake has met its discharge permit limits, which are based on dissolved metal concentrations in the top layer. Figure 6 shows concentrations of the particulate fraction of zinc from 2009 to 2013 in the top layer and in the upper portion of the middle layer, immediately below the upper pycnocline (at a sampling depth of 10 m). Particulate zinc in the top layer primarily represents the fraction of zinc adsorbed to phytoplankton cells and available for downward export to the lower layers. In the top layer, particulate zinc concentrations are at their highest when phytoplankton
biomass is high and there is a high metal load to the surface of the lake. At Island Copper, this occurs from early winter until the late spring of each year. In the summer months, before significant metal loading to the surface occurs, particulate zinc is low because of the limited metal loads for the biological system to treat despite the season’s generally low primary production. Similar responses to biological treatment in the top layer are observed for particulate copper and cadmium (Fisher and Lawrence, 2006; Pelletier et al., 2009). In contrast to the top layer, particulate zinc, copper and cadmium concentrations at a depth of 10 m do not correspond closely to chlorophyll a measurements because of the relatively low metal concentrations present in the middle layer. These low metal concentrations have been present since 2006, when biogeochemical processes caused metal-sulphide precipitation. This is discussed in the following section.

![Figure 6](image)

**Figure 6** Particulate zinc concentrations in the pit lake top layer

### 3.2 Biogeochemistry of pit lake

The in situ phytoremediation is designed to treat lake surface waters for discharge to Rupert Inlet, and to export organic carbon to depth to induce metal removal through biological sulphide generation. Pelletier et al. (2009) discuss the success of metal-sulphide precipitation in the sulphidic zone of the lower layers of the lake.

The biogeochemical zonation in the pit lake is delineated into three redox zones (oxic, transition and sulphidic). These zones differ from the physical delineation separating the pit lake into layers (top, middle and bottom) based on water density described in Table 3. The main driver behind the redox potential of the water is related to the bacterially mediated oxidation of organic matter, which is coupled with the reduction of a redox indicator species. Redox reactions occur in a predictable sequential order (i.e. the redox ladder) based on the energy yields known as Gibbs Free Energy (Table 4).
Phytoremediation to improve pit lake water quality

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Redox reaction

Aerobic respiration
Denitrification
Manganese reduction
Ferric reduction
Sulphate reduction
Methanogenesis

Chemical equation
CH$_2$O(s) + O$_2$(aq) → CO$_2$(g) + H$_2$O(l)
CH$_2$O(s) + 0.8NO$_3^-$ + 0.8H$^+$ + 0.8H$_2$O(l) → CO$_2$(g) + 0.4N$_2$(g) + 1.4H$_2$O(l)
CH$_2$O(s) + 2MnO$_2$(s) + 4H$^+$ → CO$_2$(g) + 2Mn$^{2+}$(aq) + 3H$_2$O(l)
CH$_2$O(s) + 2αFe$_2$O$_3$(s) + 8H$^+$ → CO$_2$(g) + 4Fe$^{2+}$(aq) + 5H$_2$O(l)
CH$_2$O(s) + 0.5SO$_4^{2-}$(aq) + 0.5H$^+$ → CO$_2$(g) + 0.5HS$^-$ + H$_2$O(l)
CH$_2$O(s) → 0.5CO$_2$(g) + 0.5CH$_4$(g)

$\Delta G^\circ$ (kJ mol$^{-1}$)

−519
−510
−503
−297
−124
−85

Notes:
1. $\Delta G^\circ = \Sigma \Delta G^f_{\text{products}} - \Sigma \Delta G^f_{\text{reactants}}$.
2. $\Delta G^f_{\text{CH}_2\text{O}}$ = −129 kJ mol$^{-1}$ (Charlson and Emerson, 2000).
3. $\Delta G^f_{\text{O}_2}$ = 16.37 kJ mol$^{-1}$ (Weast, 1983).
4. All other $\Delta G^f$ values from Drever (1997).
5. MnO$_2$ is pyrolusite and αFe$_2$O$_3$ is hematite.

In oxic environments, oxygen is preferentially reduced to water as organic matter is oxidised (oxic zone). Once oxygen is depleted, consumption of nitrate (i.e. denitrification) ensues. Denitrification is not discussed in detail here because of the interferences caused by the nutrient amendment program and phytoplankton metabolism. Manganese and iron are subsequently reduced from insoluble oxides and hydroxides to soluble metals. We refer to the zone over which manganese and iron are reduced as the “transition zone,” located between saturated oxic and sulphidic waters. The reduction of sulphate to hydrogen sulphide (sulphide) occurs once all the available manganese and iron have been reduced.

The sulphidic zone is characterised by the presence of reduced species (dissolved manganese and iron and sulphide), as well as by the absence of oxygen and manganese and iron (hydr)oxides. Insoluble metal-sulphides can precipitate and accumulate in the bottom sediments in a sulphidic environment. In strongly reducing environments, methanogenesis, the lowest rung on the redox ladder, will ensue. The high sulphate (naturally occurring in the seawater initially added to the pit) concentration likely prevents the onset of methanogenesis in the Island Copper pit lake. Table 5 lists the redox couples associated with each redox reaction in Table 4.

### Table 5

<table>
<thead>
<tr>
<th>Oxidised member</th>
<th>Reduced member</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ (oxygen)</td>
<td>H$_2$O (water)</td>
</tr>
<tr>
<td>Mn$^{4+}$ (manganese IV)</td>
<td>Mn$^{2+}$ (manganese II)</td>
</tr>
<tr>
<td>Fe$^{3+}$ (iron III)</td>
<td>Fe$^{2+}$ (iron II)</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (sulphate)</td>
<td>HS (sulphide)</td>
</tr>
<tr>
<td>C$^0$ (carbon)</td>
<td>CH$_4$ (methane)</td>
</tr>
</tbody>
</table>

The redox potential of the water is also modified by the upwards diffusion of reduced species into zones located higher on the redox ladder. Reduced species diffusing into an increasingly oxic environment may react with oxidised species. As a result, oxidised species can be reduced and reduced species can be oxidised.
As a result of nutrient-enriched primary production at the surface, the concentration of organic matter in the Island Copper pit lake is highest in surface waters and gradually decreases with depth. Aerobic surface waters (oxic zone) overlay anoxic waters dominated by reduced species. The transition zone is situated directly beneath the oxic zone and is characterised by a suboxic to anoxic environment and a steady increase in dissolved manganese and iron. The sulphidic zone is located beneath the transition zone. The majority of the pit lake volume is classified as sulphidic. This biogeochemical model of the Island Copper pit lake is summarised in Figure 7. The idealised model focuses on the dominant biogeochemical processes and excludes the physical transport processes caused by the MLL system, downward erosion of the pycnocline caused by wind-induced turbulent currents, turbulent mixing at the side walls caused by breaking internal waves of the pycnocline, diffusion across the pycnocline, convective mixing and rainwater dilution.

Figure 8 shows the redox indicator species in the pit lake plotted against depth. Redox indicator profiles are plotted for two distinct sampling events (June and December 2013) to highlight the contrast between the geochemical characteristics observed during the summer and winter months. The overall conceptual model of the pit lake does not change from summer to winter; however, the concentrations of the redox indicator species do change significantly, with a notable increase in sulphide concentrations in the winter. Total organic carbon (TOC) is plotted in Figure 8 alongside the redox indicator species. Near the surface, high loads of TOC indicate a high adsorption potential for metals. During the fall and winter, the TOC in the surface declines; however, TOC at depth increases. Bacteria oxidise the TOC in the water by reducing the redox species.

The key characteristics of the Island Copper pit lake biogeochemical model are:

- The upper portion of the pit lake (above 2 m) is oxic.
- The anoxic zone, below depths of 2–10 m, can be classified as sulphidic and constitutes the majority of the pit lake volume.
- The main mechanism of metal removal in the surface oxic waters is likely adsorption onto organic matter, although there is also potential for mineral precipitation (e.g. [hydr]oxides).
- Dissolved iron and manganese concentrations increase at depths below 200 m, likely because of the reductive dissolution of oxides. The potential for iron and manganese to precipitate as sulphides is lower than that of other metals in solution.
- The likely mechanism for dissolved metal removal from the anoxic zone is mineral precipitation:
  - Mineral precipitation in the anoxic zone is dictated by the redox state of the water, which is a function of the organic matter delivered from the fertilisation program.
  - The formation of sulphates, hydroxides and possible carbonates is a mechanism for dissolved metal removal.
  - As the lower zones progress towards an increasingly sulphidic state, the potential for metal removal in these zones via metal-sulphide precipitation remains high.
Phytoremediation to improve pit lake water quality

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Figure 7  Conceptual model of pit lake biogeochemistry
**Figure 8**  Island Copper pit lake redox species with depth
3 Discussion

The Island Copper pit lake can be divided into physically distinct and stable layers as a result of meromixis. The top layer is approximately 6 m thick, brackish and well mixed. The middle layer is saline and occupies approximately 90% of the pit lake volume. The bottom layer’s salinity is the closest to seawater, indicative of remnant floodwater from Rupert Inlet. The injection of ML/ARD in the middle layer causes an upward displacement of the pycnocline, and this effect is actively managed using the innovative MLL system, which requires no external power.

The pit lake can also be divided into three zones to distinguish between dominant geochemical processes. The zone closest to the surface is oxic and characterised by detectable levels of oxygen. The oxic zone extends from the surface to depths of between 2 and 10 m. Below the oxic zone is the transition zone, the position of which varies seasonally. In June, the transition zone extends to below the 10 m interval, whereas in December the zone is truncated in response to elevated sulphide concentrations. Beneath the transition zone, the sulphidic zone extends to the bottom of the pit lake. Although the pit lake is characterised by three distinct redox zones, a clear delineation between the zones is not easily discernable because of mixing processes. Sulphide is detectable within the oxic zone and the transition zone. Therefore, metal attenuation results can be further segregated into two zones: oxic surface waters and sulphidic waters.

Two attenuation mechanisms likely control metal concentrations in the oxic surface waters: metal adsorption by phytoplankton cells and secondary mineral precipitation. The pit lake appears to undergo slight seasonal cycles in biogeochemical redox zonation and, therefore, metal attenuation mechanisms within the pit lake. The largest variations are observed in the oxic upper layers. During the summer, the metal concentrations are lowest in the surface oxic zone. This corresponds to lower observed rainfall when compared to December rainfall and, therefore, lower metal loadings, as well as lower observed sulphide concentrations.

During the winter months, the highest metal concentrations are observed in the oxic layer. This corresponds to an increase in metal loadings from ML/ARD as a result of heavy rainfall. The primary mechanism for removal of metals in waters in the surface oxic zone is likely metal adsorption onto organic matter.

The primary mechanism for the removal of metals in the sulphidic zone is likely the result of metal-sulphide precipitation. The concentration of sulphides in the lower layers of the pit lake have increased since pit flooding, and this has resulted in the development of a sulphidic zone where soluble metal concentrations are low and concentrations of hydrogen sulphide are high. Sulphide mineral precipitation is the most important geochemical factor for the attenuation of metals at depth in the pit lake. The process is anticipated to continue to assist in metal sequestration to the lake bed.

4 Conclusions

Phytoremediation at Island Copper pit lake has been successful in treating metal loads from ML/ARD. The designed system takes advantage of the compartmentalised physical characteristics and geochemical zonation of the meromictic lake and integrates treatment of surface waters using nutrient amendments, with the resulting phytoplankton biomass providing a carbon source for microbial oxidation occurring in the majority of the lake’s water volume. The system has required an engineered manipulation of the physical structure of the water column using an innovative system to control the pycnocline elevation. The phytoremediation techniques at Island Copper have been successful because of the integrated approach to linking the physical and biological systems operating in the pit lake.

Having been flooded with seawater and capped with freshwater, the Island Copper pit lake represents an extreme case in the continuum of meromixis. Although few other lakes may have such a strong density contrast between layers, the Island Copper case shows that an integrated physical and biological pit lake design can provide a long-lasting and effective treatment system. The site-specific conditions at Island Copper resulted in challenges for water management, but these same conditions allowed for innovative management solutions integrating physical and biological systems into a semi-passive treatment design. Proximity to the sea was a challenge to mining but facilitated flooding the pit to create a meromictic pit lake.
The challenge of managing ML/ARD in a high-precipitation environment was tempered by the exploitation of isolated layers of the lake where contaminants could undergo in situ treatment. The downward flux of primary production from the top layer fuelled and continues to fuel this in situ treatment in the isolated lower layers, and links the physical and biological systems.

The converse is likely true, in that ignoring the inter-relation between the physical and biological characteristics of a pit lake or future pit lake might lead to unintended or non-optimal results.

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**References**


