Pit Lake Water Quality Prediction: Insights into the Modelling of Non-Conservative Processes

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Abstract

The ability to accurately model pit lake water quality is a prerequisite to the development of defensible closure management strategies. In this paper, non-conservative processes that have the potential to influence the evolution of pit lake water quality are reviewed. Key topics examined include oxygen consumption, biogeochemical (redox) processes that may occur in the suboxic strata of stratified pit lakes, mineral precipitation, and lake primary production (algal growth) in relation to the scavenging of trace metals and their export to bottom waters via particle settling. A modelling platform (PitMod) that may be used to quantify non-conservative mechanisms is described. Bioremediation measures that may be employed to take advantage of naturally-occurring passive removal mechanisms are also discussed.

Keywords: Meromixis, bioremediation, redox, PitMod

Introduction

Pit lakes represent common features of the post-closure landscape at mining operations, often serving as focal points for water and waste management at the end of mine life. Pit lake systems are also complex, with the evolution of water quality governed by various physical (mixing), geochemical and biological mechanisms. Pit lake models must therefore be able to account for such processes to allow for the development of scientifically-defensible and cost-effective closure management strategies.

Numerous non-conservative processes have the potential to influence the evolution of pit lake water quality over time, including:

- Lake primary production (algal growth), binding of trace elements to biogenic particles, and particle settling,
- Oxygen consumption leading to development of suboxic bottom waters in stratified pit lakes,
- Suboxic redox processes that may occur in the suboxic strata of stratified pit lakes, and
- Mineral precipitation

In this paper, non-conservative processes that have the potential to influence the evolution of pit lake water quality are reviewed. The pit lake modelling software PitMod (Martin *et al.*, 2015; Dunbar, 2013) is used to illustrate how the effects of non-conservative mechanisms can be modelled. Bioremediation measures that may be employed to take advantage of naturally-occurring passive removal mechanisms are also discussed.

Description of PitMod Modelling Software

PitMod is a proprietary, one-dimensional numerical hydrodynamic model developed by Lorax Environmental Services Ltd. (Vancouver, Canada). PitMod is used for predicting the spatial and temporal distribution of temperature, density, dissolved oxygen, and water quality parameters in lakes, and incorporates physical processes similar to those found in other lake models such as DYRESM (Imerito 2007) and CE-QUAL-W2 (Wells, 2022). In addition to physical processes, PitMod is coupled to geochemical equilibrium model PHREEQC (Parkhurst and Appelo *et al.* 1999) for determinations of metal speciation, mineral precipitation, gas equilibria, and pH. Specifically, at each time step of the model, PitMod integrates the effect of all inputs governing the physical properties of the pit lake by solving a set of governing hydrodynamic equations followed by calls to PHREEQC to calculate equilibrium concentrations of all chemical species within each model layer. The output from PHREEQC includes the equilibrium concentration and speciation of all aqueous components, as well as the equilibrium concentrations of all relevant minerals. This PHREEQC output then serves as the input for the next time step in the model. PitMod can also simulate the removal of trace elements from the surface mixed layer in association with biogenic scavenging and particle settling.

Oxygen Consumption

The development of suboxia in pit lakes has important implications from the perspective of aquatic habitat as well as predicting the effects of redox processes on pit lake chemistry. Dissolved oxygen is introduced to surface waters through interaction with the atmosphere and is distributed through the water column by mixing and diffusion. Dissolved oxygen is consumed via the bacterially-mediated oxidation of organic matter (OM) (Fenchel and Blackburn, 1979). OM produced in the surface water photic zone (including phytoplankton and zooplankton) is exported to depth via the settling of organic detritus. In the absence of deep water mixing and associated replenishment of oxygen (as in stratified lakes), oxygen-consuming reactions can result in the development of anoxic bottom waters.

In PitMod, oxygen consumption is allowed to occur on both horizontal surfaces (e.g., for sediments that accumulate on pit benches) as well as within the water column. Given that pit lakes tend to exhibit low levels of algal growth, the benthic oxygen flux (units of mg/m2/d) and volumetric oxygen consumption rate (units of mg/m3/d) in PitMod are typically assumed to be representative of empirically-derived rates measured for deep oligotrophic lakes (Charlton, 1980).

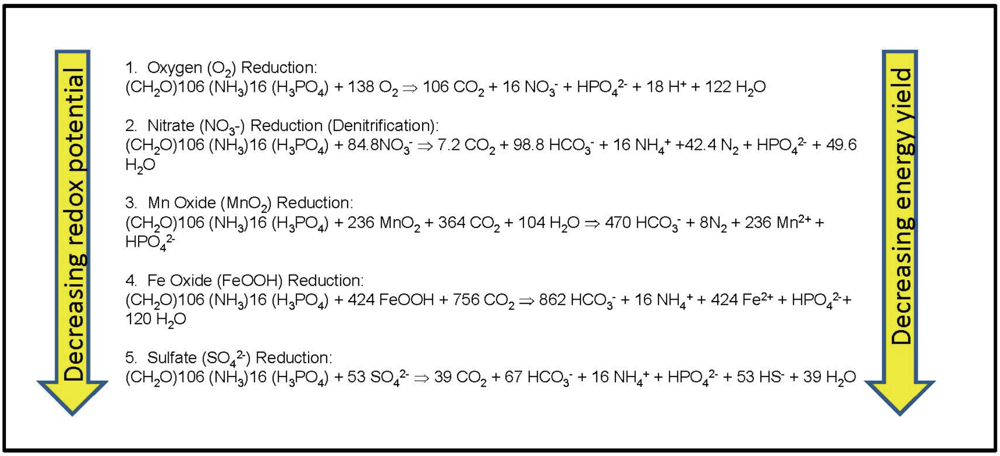
Biogeochemical Processes in Suboxic Waters

Pit lakes have a tendency to develop permanently stratified water columns (meromixis), which can have profound influences on the chemical and biological processes that occur in both the water column and sediments. In particular, the restricted exchange of constituents across the pycnocline can result in the depletion of dissolved oxygen in lake bottom waters. Under conditions of suboxia, redox-related mechanisms can greatly influence the behaviour of trace elements and other parameters. Biogeochemical processes relevant to suboxic lake strata include:

- Nitrate reduction
- Ammonia generation
- Reductive dissolution of Fe+Mn oxyhydroxides, and liberation of sorbed trace elements.
- Sulfate reduction
- Metal sulfide precipitation
- Alkalinity generation

To account for such processes, PitMod includes an algorithm that allows for redox reactions to proceed from oxygen reduction to sulfate reduction, based on the aqueous concentrations of the various electron acceptors and their respective energy yields (fig. 1). For Fe(III) and Mn(IV) reduction, the inventory of Fe and Mn oxide concentration can be specified in PHREEQC. In this regard, the availability of Fe and Mn oxide particles can represent a large uncertainty in redox predictions, given that the inventory of these constituents in the water column is governed by complex processes such as pit wall weathering and pit wall erosion rates.

Other key biogeochemical processes simulated by PitMod include alkalinity generation in response to suboxic redox reactions (Sigg *et al.* 1991) and metal sulfide precipitation. Alkalinity generation has relevance to the neutralization of acidity that may be introduced to the pit lake via pit wall runoff or input of acidic source waters from waste management facilities. Of additional importance for bioremediation is the reduction of sulfate, which liberates dissolved hydrogen sulfide (H2S) (fig. 1). Many trace elements (e.g., Fe, Co, Ni, Zn, Cd, and Pb) react rapidly with dissolved sulfide to precipitate as insoluble sulfide minerals (Balistrieri *et al.* 1994). Consequently, the precipitation of metal sulfides, and their subsequent settling to the lake bottom, can provide an effective, and largely permanent,



1. Oxygen (O_2) Reduction:
$(CH_2O)106\ (NH_3)16\ (H_3PO_4) + 138\ O_2 \Rightarrow 106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 18\ H^+ + 122\ H_2O$

2. Nitrate (NO_3-) Reduction (Denitrification):
$(CH_2O)106\ (NH_3)16\ (H_3PO_4) + 84.8NO_3^- \Rightarrow 7.2\ CO_2 + 98.8\ HCO_3^- + 16\ NH_4^+ + 42.4\ N_2 + HPO_4^{2-} + 49.6\ H_2O$

3. Mn Oxide (MnO_2) Reduction:
$(CH_2O)106\ (NH_3)16\ (H_3PO_4) + 236\ MnO_2 + 364\ CO_2 + 104\ H_2O \Rightarrow 470\ HCO_3^- + 8N_2 + 236\ Mn^{2+} + HPO_4^{2-}$

4. Fe Oxide (FeOOH) Reduction:
$(CH_2O)106\ (NH_3)16\ (H_3PO_4) + 424\ FeOOH + 756\ CO_2 \Rightarrow 862\ HCO_3^- + 16\ NH_4^+ + 424\ Fe^{2+} + HPO_4^{2-} + 120\ H_2O$

5. Sulfate (SO_4^{2-}) Reduction:
$(CH_2O)106\ (NH_3)16\ (H_3PO_4) + 53\ SO_4^{2-} \Rightarrow 39\ CO_2 + 67\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 53\ HS^- + 39\ H_2O$

Figure 1 *Redox reactions associated with the re-mineralization (oxidation) of organic matter, represented as* $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$*, showing the relationship to redox potential and energy yield.*

removal mechanism of trace elements from the water column (Green *et al.* 1989; Achterberg *et al.* 1997).

Mineral Precipitation

Within PitMod, coupling to PHREEQC allows for mineral precipitation. At each time step in the model, equilibrium concentrations and speciation of all aqueous components, as well as saturation indices (SI) for relevant minerals, are calculated. In this step, mineral precipitation is allowed to occur to maintain SI = 0. In the progressive neutralization of acidic drainage, for example, PitMod can account for pH buffering afforded by minerals such as K-jarosite [$KFe_3(SO_4)_2(OH)_6$], schwertmanite [$Fe_8O_8(OH)_6(SO_4)\cdot nH_2O$], bausaluminite [$AL_4(OH)_{10}SO_4$] gypsum ($CaSO_4\ 2H_2O$), gibbsite [$Al(OH)_3$], ferrihydrite [$Fe(OH)_3$] and calcite ($CaCO_3$). For pit lakes, the inclusion of mineral precipitation has particular relevance for systems where acidic inflows (e.g., acidic pit wall runoff) are neutralized by alkaline water sources within the pit lake (e.g., groundwater inflows, surface runoff).

Metal Scavenging by Biogenic Particles

In lake environments, the dominant vertical transport mechanism for trace elements is particle settling. Settling particles, especially organic aggregates (e.g., algal particles), play a dominant role in the binding and transfer

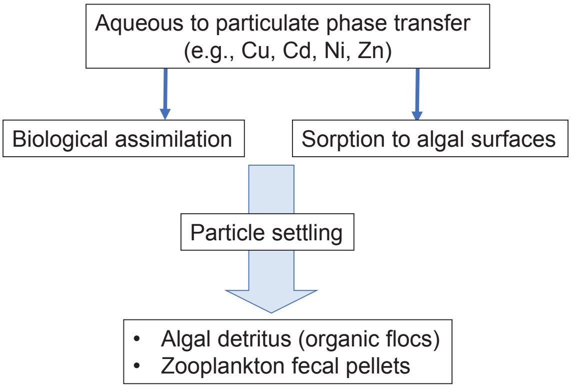


Figure 2 *Schematic illustrating uptake/assimilation of trace elements by biogenic particles followed by particle settling.*

of trace elements to lake bottom waters, thereby regulating the concentrations of dissolved species in surface waters (Sigg, 1985). This scavenging mechanism can be viewed as a two-stage process: 1) phase transfer from dissolved to particulate phase (via assimilation by algae or adsorption to cell surfaces); and 2) particle settling, which may include the sinking of organic aggregates or zooplankton faecal pellets (fig. 2). In general, pit lakes tend to be oligotrophic, exhibiting low rates of in situ primary production (algal growth). However, algal production and associated metal scavenging can be enhanced through fertilizer addition (discussed below).

PitMod includes functionality to allow for metal removal from the surface layer in response to the processes highlighted in fig. 2. Removal fluxes have been specifically developed for Cu, Ni, Zn, Co and Cd given the tendency to these elements to associate with biogenic particles as well as the availability of information for these elements in the primary literature. Removal rates (expressed as mg/m^2/d) were developed based on empirical data for lakes of varying levels of metal contamination (e.g., Nriagu *et al.* 1981; Kubota *et al.* 1974). Upper rates for metal removal were additionally informed by data for in pit bioremediation studies designed to foster eutrophic conditions in response to fertilizer addition (e.g., Dessouki *et al.* 2005).

In PitMod, metal export terms are applied to the uppermost 10 m of the water column, since metal scavenging will be primarily associated with biogenic processes in the photic zone (zone of active algal production). For colder climates that exhibit seasonal ice formation, the export terms are only applied during the ice-free period (June through October), as algal growth will greatly diminish during ice-covered periods.

Opportunities for In Pit Bioremediation

The *in-situ* bioremediation of pit lakes involves the addition of nutrients and/or organic matter to create conditions conducive to the removal of target parameters (Martin *et al.* 2003). The addition of organic matter as liquid or solid amendments provides a direct source of organic matter to the pit lake. In contrast, lake fertilization (e.g., addition of phosphorus fertilizer) adds organic carbon indirectly by stimulating photosynthetic production. Pit lakes tend to be oligotrophic in nature, whereby algal production is typically limited by available phosphorus. In this regard, algal productivity can be effectively stimulated through phosphorus addition. For every mole of phosphorus added, algae fix ~106 moles of carbon via photosynthesis (Redfield 1958). The efficiency in this process translates to the ability to treat large volumes of water at relatively low cost.

Key processes relevant to metal removal in response to lake fertilization are illustrated in fig. 3, which illustrates the links between nutrient addition, algal growth, particle concentration, particle flux and export of metals to the lake bottom via particle settling. In this regard, in-pit bioremediation can be viewed as a means to enhance naturally occurring lake processes as illustrated in fig. 2.

Bioremediation as modelled by PitMod demonstrates that with lake fertilization and the achievement of meso-eutrophic conditions, concentrations of dissolved Cd, Cu, Ni and Zn can be reduced to near-background levels (Martin 2023). These results highlight the potential merits of in pit bioremediation in reducing the concentrations of trace metals prior to the onset of pit lake

***Table 1** Metal removal rates applied in PitMod for pit lakes of varying trophic status.*

Parameter	Oligotrophic mg/m^2/d	Mesotrophic mg/m^2/d	Eutrophic/ Bioremediation Scenario mg/m^2/
Zn	0.03	2.4	12
Ni	0.003	2.0	10
Cu	0.013	1.6	8.0
Co	0.003	0.5	2.7
Cd	0.0007	0.1	0.32

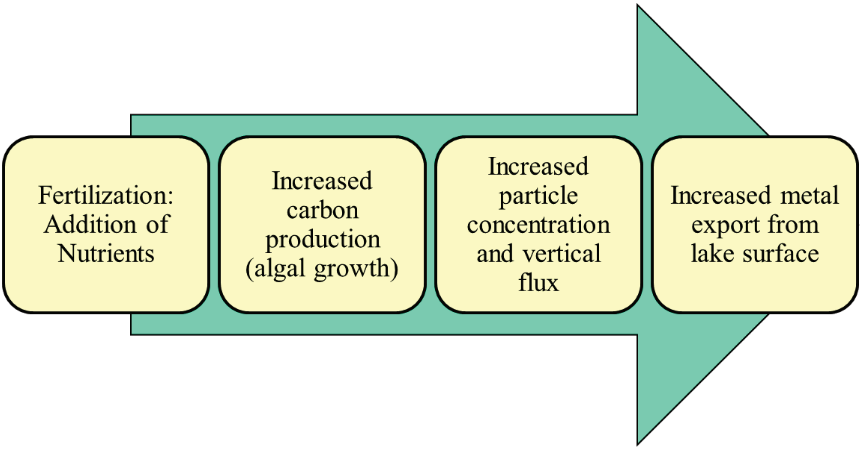


***Figure 3** Schematic illustrating linkages between lake fertilization, algal growth and export of metals from lake surface layer via particle settling.*

discharge to the environment. Further, since many pit lakes tend to develop meromictic density structures, any metals removed from the surface layer and sequestered to the pit bottom can be assumed to remain at depth. In other words, the flux can be assumed to be uni-directional (permanent metal removal from the surface layer).

Conclusions

Non-conservative processes, such as oxygen consumption, suboxic redox processes, mineral precipitation, and metal scavenging by biogenic particles, have the potential to greatly influence the behaviour and concentration of mine-related constituents in pit lake systems. While such processes are complex, modelling platforms (e.g., PitMod) are available to describe such mechanisms in meaningful ways. In turn, being able to model non-conservative processes offers mine managers opportunities more effective ways to optimize closure water management, minimize post-closure treatment requirements, and enhance environmental protection of downstream systems.

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