PART V: PREDICTIVE MODELING OF FUTURE PIT LAKES

CHAPTER 11

Modeling Pit Lake Water Quality: Coupling of Lake Stratification Dynamics, Lake Ecology, Aqueous Geochemistry, and Sediment Diagenesis


INTRODUCTION

Evolution of water quality in pit lakes, including master state variables such as redox (oxidation-reduction) potential and pH, is initially determined by the quality of surface and subsurface inflows and how the inflow waters interact with pit mineralogy. However, as the volume of inflows relative to the lake volume decreases (as would be expected as the pit fills), the physical, chemical, and biological processes in the lake itself begin to impact, or even dominate, lake water quality. For example, physical processes such as energy transport in the water column affect stratification and mixing, which in turn control the transport of many species to different regions of the lake; biological and microbially mediated lake processes include primary production and the metabolism of organic matter; geochemical processes include the buffering of pH, in circumneutral waters by dissolved inorganic carbon, or under acidic or alkaline conditions by precipitation and dissolution reactions of mineral phases.

There are many feedbacks between these different processes. For example, diagenesis in sediments involves microbially mediated redox reactions driven by the availability of organic matter; the resulting release of nutrients to the water column drives further primary production (organic matter production), and the release of alkalinity may neutralize water column acidity. Another feedback example is the way in which sorption of phosphate to surfaces of amorphous Al and Fe minerals (the solubility of which is pH dependent) may limit phosphate concentrations and hence curtail autochthonous organic matter production. External factors, such as climate, combined with the interactions between the internal processes and lake bathymetry influence the overall lake water quality, including the generation, distribution, and fate of contaminants. The impacts on water quality of all of these lake processes must be balanced against the impact of inflowing waters. For example, the geochemical characteristics of inflows may counteract alkalinity generation within the lake. Alternatively, it can be considered that lake processes may ameliorate poor water quality of inflowing water.

An essential method to test these authors’ understanding of what drives the overall water quality in pit lakes and to quantify the relative contribution of inflows versus lake processes is the use of numerical models that adequately describe and quantify the conceptual models and, most importantly, allow the multitude of processes to progress at the appropriate time and length scales. Such models may also be used to investigate the response of pit lake water quality to remediation
measures, such as nutrient or organic carbon addition to stimulate alkalinity generation from sediments (e.g., Wendt-Pothoff et al. 2002) or to remove metals from the water column (e.g., Cruset et al. 2003). A comparison of numerical simulation results with carefully conducted field and laboratory observations allows the conceptual models to be rigorously tested under controlled scenarios.

Subsurface water quality is typically assumed to be dominated by geochemical processes, and models such as PHREEQC (Parkhurst and Appelo 1999) have been used successfully to predict inorganic chemical concentrations in the subsurface environment (Proctor et al. 2000). In contrast, density stratification, dissolved oxygen (DO) dynamics, nutrient concentrations, and primary productivity in drinking water reservoirs and lakes have been successfully modeled over the last few decades using a variety of stratification and/or nutrient-phytoplankton-zooplankton (NPZ) models. However, these models pay scant attention to geochemical cycling occurring in lakes (Ramsey et al. 2006). When modeling the long-term water quality of pit lakes, the significance of this geochemical cycling simply cannot be ignored. As will be shown in this chapter, stratification and biological cycling cannot be ignored in attempts to predict remediation outcomes. Up to now, there has been no available model that combines geochemical process descriptions of suitable complexity to resolve the issues of concern within mining influenced waters with the limnological process descriptions of the classic lake stratification and NPZ models.

METHODS
Model Description

In 2003–2006, an established NPZ model for lake aquatic ecology, the Computational Aquatic Ecological Dynamic Model or CAEDYM.v2 (e.g., Romero et al. 2004), which can be coupled to one-dimensional (1-D) or three-dimensional (3-D) lake, or two-dimensional (2-D) river, hydrodynamic models, was significantly revised to include aqueous speciation and solubility equilibria, as well as kinetically controlled reactions, in both the water and sediment. The newly developed geochemistry module is applied to determine the dynamics of pH, major ions, metals, and other critical water quality parameters in mine lakes. The kinetic descriptions within the sediment were adapted from CANDI. CANDI is an early-diagenesis model that describes the breakdown of deposited organic matter (Boudreau 1996). CANDI has typically been applied to marine systems (e.g., Haeckel et al. 2001; König et al. 2001; Luff and Moll 2004). An important feature of the new model (CAEDYM.v3) was the ability to investigate feedback between geochemical, ecological, and diagenetic processes. The conceptual description of these processes, including feedback between components, is shown for the water column (Figure 11.1) and the sediment (Figure 11.2). The model was coupled to the 1-D (laterally averaged) hydrodynamic model DYRESM for application to Lake Kepwari in Western Australia.

Aqueous speciation and solubility equilibrium control were accounted for by solving the mass-action expressions for the simulated components, which included Al, Ca, Mg, Na, K, Fe(II), Fe(III), Mn(II), Mn(IV), SiO_2 (silica), Cl, DIC (dissolved inorganic carbon), SO_4 (sulfate), PO_4 (phosphate), NO_3 (nitrate), CH_4 (methane), and H_2S (hydrogen sulfide). The mass-action expressions were solved according to the numerical method of Barrodale and Roberts (1980), as discussed in Parkhurst and Appelo (1999) and in the CAEDYM documentation (Hipsey et al. 2007). Mineral phases for the validation work were limited to those that were significant in the mine lake geochemistry and which were expected to interact with diagenetic processes. These mineral phases include gibbsite, iron hydroxide, and iron sulfide. The mass-action constants from the WATEQ4F database (Nordstrom et al. 1990) were used for speciation. In addition, all
dissolved phase geochemical variables can be set to be subject to diffusion in the sediment as in Boudreau (1996).

Unlike other diagenetic models that have incorporated the CANDI approach, the implemented code accounted for both labile and refractory dissolved organic carbon (DOC_{L} and DOC_{R} respectively) as well as labile and refractory particulate organic carbon (POC_{L} and POC_{R} respectively). Depending on the nature of the investigation, the model may be configured to use either a static or dynamic model for organic matter diagenesis. The organic matter breakdown pathway of the static model is conceptually summarized in Figure 11.1 and uses semiempirical parameterizations for sediment-water flux rates of dissolved components. The dynamic diagenesis model discretizes the sediment profile in layers, and in each layer simulates the hydrolysis of the complex organic matter pools (POC_{V}, POC_{A}, DOC_{V}, and DOC_{A}) and terminal metabolism of low-molecular-weight DOC_{L} by oxidants (O_{2}, MnO_{2} [manganese dioxide], Fe(III), and SO_{4}^{2-} [sulfate]), the release and transformation of nutrients [NH_{4}^{+} [ammonium], PO_{4}^{3-} [phosphate], NO_{3}^{-} [nitrate]], and reduced by-products (Mn(II), Fe(II), NH_{4}^{+}, H_{2}S, CH_{4}, FeS [iron sulfide]). A complete list of reactions is available in work by Boudreau (1996). The reactions were implemented identically to CANDI, but the generic organic matter term was replaced by DOC_{L} in the breakdown equations, and the POC_{V}, POC_{A}, POC_{L}, and DOC_{A} breakdown steps were included using the same reaction rates for all cases except nitrification. For nitrification, a rate of 0.05 day^{-1} was used and no denitrification was allowed to occur below pH 5 because acidity has been found to limit denitrification (Devlin et al. 2000). Note that for brevity, the results shown here are of the more simple static sediment module to allow detailed examination of water column processes and interactions.

![Figure 11.1](image-url)  
**FIGURE 11.1** Schematic of the revised CAEDYM.v3, indicating interactions between the geochemical, nutrient, and biological cycles. Note that the sediment module shown is simplistic; details of the sediment module are given in Figure 11.2.
Model Validation — Lake Kepwari

Parallel to model development, lake monitoring was conducted to provide the detailed validation data required to increase the authors’ confidence in the developed model. Lake Kepwari, formerly known as Mine Lake WOSB, is a coal pit lake located 160 km south-southeast of Perth, Western Australia (Figure 11.3). Since the cessation of mining in the pit in 1997, the slopes and overburden piles surrounding the pit have been landscaped and revegetated, and coal seams exposed during mining were covered and/or submerged.

The region has a Mediterranean climate with hot, dry summers (12°C to 29°C) and cool, wet winters (4°C to 15°C). The majority of the rainfall occurs between May and September, and the average annual potential evaporation is estimated to be between 1,450 and 1,650 mm.

After dewatering of the WOSB pit ceased in 1997, the void started to fill with groundwater and precipitation. Between 1999 and 2005, the lake was rapidly filled by winter diversion of the adjacent ephemeral Collie River South Branch (Figure 11.4). Prior to the first river diversion, the lake volume was 10% of the final lake capacity of approximately 24 GL. Since 2005, the lake has been at capacity volume. Ongoing annual river diversion is planned to replace loss to evaporation. An earlier water balance with forward prediction (Varma 2002) estimated a groundwater inflow of up to 0.6 GL per year if the lake volume was less than about 20 GL, no groundwater recharge if the volume was above 20 GL, and annual surface runoff to the lake of 2 to 50 ML. The current volume of annual groundwater discharge or recharge to the void is unknown, as is surface water inflow.
**FIGURE 11.3** Lake Kepwari, showing bathymetry using 10-m depth contours. The Lake Diagnostic System (LDS) was located at the center of the lake; water samples were typically collected close to the LDS and from station S.

**FIGURE 11.4** The Lake Kepwari void was filled with a diversion of the Collie River South Branch. The riverine diversion was pH 7, and the lake pH increased during diversion periods. However, after diversion was completed each year, the lake pH gradually dropped until the following winter diversion.

**Field Sampling**

A Lake Diagnostic System (LDS; Precision Measurement Engineering, Carlsbad, California) was installed at the deepest point of the lake (Figure 11.3) from March 2004 to March 2006. The LDS measured wind speed, wind direction, air temperature, relative humidity, and short-wave and net radiation, at a sample rate of 15 seconds. The LDS also sampled water column temperature via 20 thermistors over a depth of 60 m. Water column profiles of temperature, conductivity, DO, oxidation–reduction potential, pH, and photosynthetically active radiation, with depth resolutions ranging from 2 cm to 2 m, were measured approximately every 2 to 6 months from
May 2004 to May 2005. Geochemical, nutrient, and organic carbon sampling was also performed on seven occasions between March 2004 and July 2005.

RESULTS
Largely without calibration, the numerical model prediction of Lake Kepwari water quality over an annual cycle closely reproduced the patterns of stratification and overturn observed in the lake (Figure 11.5), as well as evapoconcentration as indicated by the conservative tracer chloride (Figure 11.6). The model also reproduced major temporal and spatial patterns for nonconservative species, with only NH₄ and DOC (Figure 11.6) and pH and Al (Figure 11.7) shown here for brevity. A sensitivity analysis indicated that even though the lake is now at full capacity, surface and groundwater inflows may still be important factors in the long-term evolution of the lake water quality. The model also allowed the importance of geochemical processes for lake water quality to be tested, for example, solubility equilibrium control of pH by Al hydroxide phases (Figure 11.7). The modeling study of Lake Kepwari thus demonstrated the capability of the model to reproduce the main features of the current water quality in the lake and highlighted the need for testing against data sets, which include well-constrained water and mass balances for the lake.

![Temperature stratification cycles in Lake Kepwari from October 2003–October 2005. The top panel shows DYRESM output, and the bottom panel shows LDS field data. Temperature stratification occurs from October to May each year. Note that the riverine diversion occurs in June-July when the lake is isothermal, and therefore its signature is rarely detectable.](image-url)
DISCUSSION
The strength of the developed model is the tight coupling between the inorganic geochemical cycles and the biological nutrient cycles, as highlighted in the scenario simulations shown in Figure 11.8. When gibbsite dissolution was not included in the model setup (Figure 11.8, panel A), the pH in the lake increased with time. At low pH there is an inhibition of nitrification and therefore an accumulation of NH$_4$ in the bottom waters. As the pH increases, under the "no gibbsite" scenario, the NH$_4$ concentrations in the bottoms waters decrease. This could have a significant impact on primary productivity in the lake. When gibbsite solubility is included in the model setup, the lake is maintained at around pH 5. Al concentrations decrease, and the inhibition of nitrification at lower pH causes the accumulation of NH$_4$ (Figure 11.8, panel B). Finally, in Figure 11.8, panel C, the addition of alkalinity (whether internal or external) is included, which counteracts the acidity source of the gibbsite. As a result, the pH increases, the Al completely drops out of solution, and the NH$_4$ concentrations decrease. These results illustrate the usefulness of the model, particularly under possible remediation scenarios. For example, one of the most common remediation methodologies is the addition of alkalinity, either in inorganic form or

FIGURE 11.6 Model output (lines) compared to field data (symbols) for Cl, NH$_4$, and DOC. Solid lines indicate depth and volume averaged surface water concentrations, and dashed lines indicate depth and volume averaged bottom water concentrations. Triangles show measured bottom water concentrations, and circles show measured surface water concentrations.
through the promotion of biological alkalinity generation. The model allows exploration of the impact of alkalinity addition on geochemical cycling. Ultimately, this process understanding will enhance remediation efficiency.

The generic process descriptions in the developed model can be applied to almost any aquatic system irrespective of the pH. Examples of systems that can now be modeled include the effect of artificial destratification on algal blooms associated with Fe reduction and PO$_4$$_3$$_3$ release; treatment of eutrophic waters or drinking water by addition of AI or Fe salts to remove organic matter and/or phosphorous; and the removal of heavy metals through addition of nutrients to stimulate primary production (organic matter scavenging) and/or sulfate reduction (metal sulfide precipitation). The model also allows study of the response of water quality to altered groundwater and surface water inflow under various climate change scenarios.

Although the initial test field site was a coal mine pit lake, the model is based in sophisticated process description and parameterization. This approach and modeling capability allows immediate application to pit lakes of widely varying water quality. The authors now require a comprehensive validation exercise of model predictions against high-quality data sets from pit lakes because it is essential to increase our confidence in the simulation results. In particular, there is a need for testing model performance against long-term data sets from systems with well-constrained groundwater inflow, sediment fluxes and aquatic food web data, as well as hydrodynamic and geochemical state variables. As with all models, there is also the need to quantify, given the available data, the uncertainty in model simulation results and, alternatively, the minimum data.
required to obtain a result to within a given degree of certainty. The result will be an improved tool for management and remediation of acidic mine lakes, including design optimization for future field and laboratory campaigns.

The model described previously in this chapter would optimally be used in conjunction with the sampling protocol for monitoring required for long-term prediction of water quality in pit lakes. This protocol is currently being developed by the authors, funded by ACMER and a number of industry partners.

In summary, the essential tools for investigating the impact of different closure strategies on future pit lake water quality are

- A sound conceptual knowledge of the system, including current and future water balances;
- A good quality data set (measured and/or modeled) on external sources of contaminants, possible pit configurations/bathymetry, and meteorological conditions; and
- Numerical lake modeling tools, as described in this chapter, to test different closure scenarios.
REFERENCES


