

Prediction of Long Term Water Quality in Acidic Pit Lakes

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1 INTRODUCTION

Stewardship of the post-mining environment relies, amongst other things, on our ability to predict the long-term fate and transport of contaminants. Ideally, if remediation is deemed necessary, scenarios should be tested numerically prior to scale-up. Pit lakes exemplify post-mining environments that must be appropriately managed for optimal benefits to local communities. Yet the potential benefits are dependent on our ability to predict, and possibly manipulate, long term water quality in the lakes. However this predictive capability requires a detailed understanding of the biogeochemical cycling of contaminants in the post-mining environment. Our understanding of metal and nutrient cycling in pH neutral conditions is reasonably advanced, based on the past 100 years of limnological, hydrological and catchment research. However many post-mining environments are highly acidic, and the impact of acidity on biogeochemical cycling is poorly understood. In particular our understanding of the interactions between groundwater and surface inflows, meteorological forcing, lake stratification cycles and local geochemical conditions is limited, in part due to the lack of appropriate numerical models that bring all of these controls together.

In acidic pit lakes, high levels of dissolved species consist predominantly of Fe and SO₄, coming from iron sulphide oxidation, and Al, coming from accelerated mineral weathering processes at low pH (Eary, 1999). Addition of alkalinity leads to precipitation of Fe(III) and Al out of solution as (oxy)hydroxides or hydroxysulphates; these reactions are however associated with proton release. Precipitation of Fe and Al thus constitute “buffering systems” which must be overcome before the pH will increase. Compilations of data from multiple mine lakes indicates grouping into the “Fe” and “Al” buffering systems (e.g. Klapper and Schultz, 1995), which maintain pH at approximately <3.8 and 3.2 - 4.2 respectively, with the more normal carbonate buffering system coming into play at pH > 6. The buffering capacity is critical for the long term remediation potential of pit lakes, and must be described in any lake water quality model. Our understanding of how the three major buffering systems interact, and how transitions occur from one buffer system to the next, is limited. Yet most of the key contaminant cycles are highly pH sensitive, and thus it is critical that we quantify the controls on pH, and the subsequent impact on alkalinity generating processes, such as Fe and SO₄ diagenesis in the lake sediments.

Over the last three years, a consortium including the Australian Coal Association, Wesfarmers Premier Coal Ltd, Griffin Coal Mining Company Pty Ltd and the Western Australian Department of Premier and Cabinet, has funded us to develop a coupled lake stratification - biogeochemical model for long-term prediction of water quality in legacy pit lakes. In 2006, we have completed the inclusion of an aqueous and mineral geochemical module and a dynamic diagenesis module into the previously existing stratification-ecological model (DYRESM-CAEDYM). All of these components are required to allow investigation of the interaction between mineral dissolution processes under low pH conditions (geochemical module), buffering capabilities (geochemical module), nitrate, iron, manganese and sulfate reduction processes (diagenesis module), the cycling of allocthonous and autocthonous carbon sources (CAEDYM) and how all of these processes are affected by seasonal stratification cycles (DYRESM). In this paper we present the initial results of this modelling effort, with a focus on water column processes, and finally with some validation against collected field data.

2 BACKGROUND

2.1 Site Description

Lake Kepwari, formerly known as Mine Lake WO5B, is a pit lake located in the Cardiff Sub-basin of the Collie Coal Basin, 160 km south-southeast of Perth, Western Australia (Figure 1). The void started to fill with groundwater after the cessation of coal mining in 1999, and has been progressively filled via a winter diversion from the nearby Collie River South Branch, until 2005 when it reached capacity of 24 GL. During the field investigations described in this paper, the maximum depth of the lake was 65 m, with a surface area of 10^4 m^2 . The pH of the newly created lake is considered problematic for potential recreational users and it was hoped that the river diversion would ameliorate the pH to more neutral conditions. The diversion water was close to pH 7; the lake pH (around 4) increased during the diversion periods (Figure 2) however after each diversion slowly decreased again.

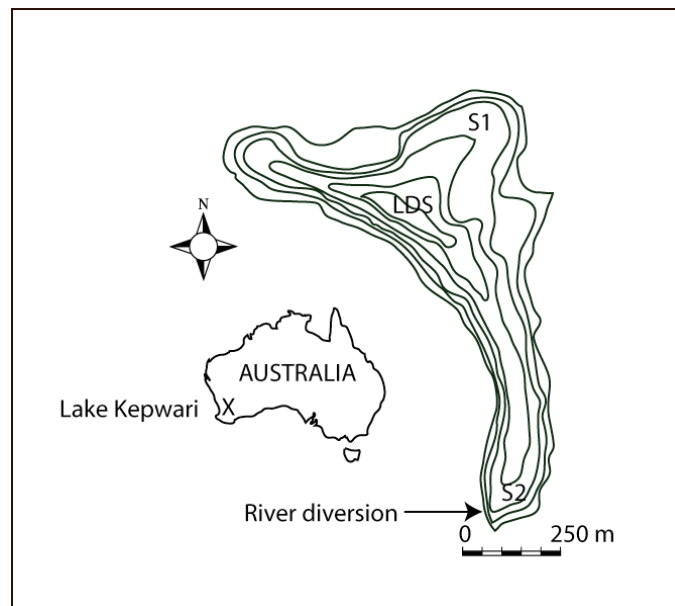


Figure 1 Lake Kepwari, in the south west of Western Australia, showing bathymetry using 10 m depth contours. The Lake Diagnostic System (LDS) was located at the centre of the lake; water samples were typically collected close to the LDS and from station S1

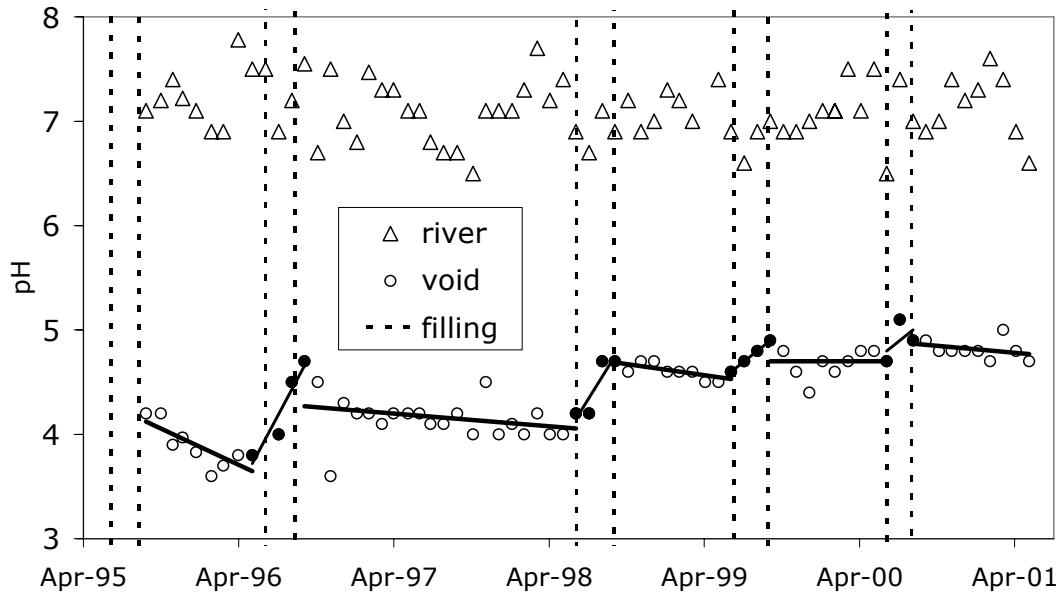


Figure 2 The Lake Kepwari void was filled with a diversion of the Collie River South Branch. The riverine diversion was ~ pH 7, and the lake pH increased during diversion periods. However after diversion was completed each year, the lake pH gradually dropped until the following winter diversion (Data supplied by Wesfarmers Premier Coal Ltd)

The region has a Mediterranean climate with hot, dry summers (12 to 29°C) and cool, wet winters (4 to 15°C). The 100-year average annual rainfall for the Collie Basin is between 730 and 950 mm, although this has decreased to an average of 690-840 mm over the past 20 years. The majority of the rainfall occurs between May and September and the average annual potential evaporation is estimated to be between 1450 and 1650 mm. The annual average wind speed at the centre of the lake is around 3 m s⁻¹, with peaks of up to 9 m s⁻¹.

Prior to mining of the Lake Kepwari pit, the largely unsaturated Cretaceous Nakina Formation, made up of claystone, sandstone and conglomerate, formed the surficial soils. This formation was extensively excavated to access the underlying Permean Muja Coal Measure (Varma 2002) however the remnant surficial sediments are lower in iron and alumina (bauxite) than adjacent basement areas (Le Blanc Smith 1993). The Collie Basin has a complex hydrogeology due to the prevalence of faults throughout the many geological formations and the large volumes of groundwater abstraction, both historically and ongoing today; the hydraulic properties of the surrounding aquifer are irregular and anisotropic, leading to the formation of preferential groundwater flow paths (URS 2001).

2.2 Pit Lake Characteristics

A Lake Diagnostic System (LDS, Precision Measurement Engineering), installed in the deepest point of the lake (Figure 1), measured wind speed, wind direction, air temperature, relative humidity and short wave and net radiation, and sampled water column temperature, via 20 thermistors over a depth of 60 m. Thermal stratification in the lake typically begins in late September, peaks in February (maximum surface temperatures of 25°C) and begins breaking down in May. By June the lake is usually fully mixed and remains isothermal over winter months; the minimum water temperature is typically 13°C. Note that river diversion occurred when the lake was isothermal. There is little horizontal variability across the lake in temperature, conductivity, pH, dissolved oxygen or ORP. Salinity usually increases in the epilimnion over the summer, likely due to evapo-concentration of the surface waters. The pH in the lake is between 4.5 and

5, with no obvious temporal trends. The lake water column remains oxic throughout the year; though in February 2005 a deep supersaturation layer was observed which coincided with a chlorophyll a peak ($0.2 \mu\text{g L}^{-1}$).

The major dissolved ions were Cl and Na, followed by SO_4 , Mg, and Ca; other elements were low or below the detection limit (Table 1). Acidity was measured to be 12-20 $\text{mg CaCO}_3 \text{ L}^{-1}$, which agreed fairly well with the calculated $\sim 10 \text{ mg CaCO}_3 \text{ L}^{-1}$, of which approximately 80% was due to Al, 10% to free protons, and the remainder to Fe and Mn. Total concentrations of most inorganic elements were the same as dissolved concentrations, with the exception of slightly higher total Fe and Al concentrations on some sampling occasions (Table 1). Saturation index (SI) calculations using the geochemical equilibrium program PHREEQC (Parkhurst and Appelo, 1999) in conjunction with the WATEQ4F database (Ball and Nordstrom, 1991) and additional thermodynamic data for schwertmannite (Yu et al., 2002) indicated that precipitation/dissolution of an iron hydroxide likely controlled Fe(III) concentrations at all depths. Aluminium concentrations were possibly controlled by solubility equilibrium between solution and a hydroxysulfate or hydroxide phase.

Table 1 Depth averaged solute concentrations in Lake Kepwari, measured in July 2004

Parameter	Concentration	Units	Parameter	Concentration	Units
pH	4.8		Fe	0.15	mg/L
Cl	769	mg/L	Total Fe	0.3	mg/L
Na	329	mg/L	Silicate	3867	$\mu\text{g Si/L}$
Mg	77	mg/L	NPOC-TOC	2.1	mg C/L
SO_4	108	mg/L	NPOC-DOC	1.9	mg C/L
Ca	28	mg/L	Total-N	1378	$\mu\text{g N/L}$
K	5	mg/L	$\text{NO}_3 + \text{NO}_2$	972	$\mu\text{g N/L}$
Al	1.1	mg/L	Ammonium	239	$\mu\text{g N/L}$
Total Al	1.3	mg/L	Total-P	7	$\mu\text{g P/L}$
Zn	0.47	mg/L	FRP	2	$\mu\text{g P/L}$
Mn	0.21	mg/L			

2.3 Model Description

2.3.1 DYRESM

To describe the physical processes occurring in Lake Kepwari, we used the one-dimensional DYNAMIC REServoir Simulation Model (DYRESM). This model predicts the vertical distribution of temperature, salinity and density in lakes and reservoirs based upon the vertically integrated turbulent kinetic energy equation (Imberger and Patterson 1981). At each time step, the model uses field measurements of meteorological fluxes as well as surface and subsurface inflow measurements to determine whether sufficient kinetic energy has been introduced to mix adjacent layers within the water column. DYRESM may be considered a pseudo two-dimensional model capable of predicting the response of the water column to physical processes that occur over relatively short timescales. DYRESM has been used successfully to predict seasonal and inter-annual variability within numerous lakes and reservoirs. (e.g. Yeates and Imberger 2003).

2.3.2 CAEDYM

The Computational Aquatic Ecology Dynamic Model (CAEDYM) was designed to be readily linked to hydrodynamic models such as DYRESM. CAEDYM allows flexible ecological configurations that can be tailored for specific applications, however major elemental cycling and at least one algal group is compulsory. The model includes comprehensive process representation of the C, N, P, Si and DO cycles, several size classes of inorganic suspended solids, and phytoplankton dynamics. CAEDYM is more advanced than traditional N-P-Z models, as it is a general biogeochemical model that can resolve species- or group-specific ecological interactions. Also, as well as a detailed description of biological processes, CAEDYM allows implementation of heterogenous and homogeneous abiotic kinetic processes, such as Fe(II) oxidation.

The newly developed geochemistry module in CAEDYM implements aqueous speciation and solubility equilibrium, following the numerical approach used in the commonly used geochemical equilibrium model PHREEQC (Parkhurst and Appelo, 1999). Default values for equilibrium constants are sourced from Ball and Nordstrom (1991), however the choice of components, species, thermodynamic data, and mineral phase controls is totally user-defined. The mineral phases included in the CAEDYM geochemistry module used for the Lake Kepwari modelling study were specifically chosen based on the saturation index calculations on Lake Kepwari water column analyses. Mineral phases currently included are gibbsite and $\text{Fe}(\text{OH})_3(\text{a})$.

A schematic is given below of how the aqueous geochemistry and solid phase precipitation and dissolution interact with the biogeochemical cycling that was previously described in CAEDYM.

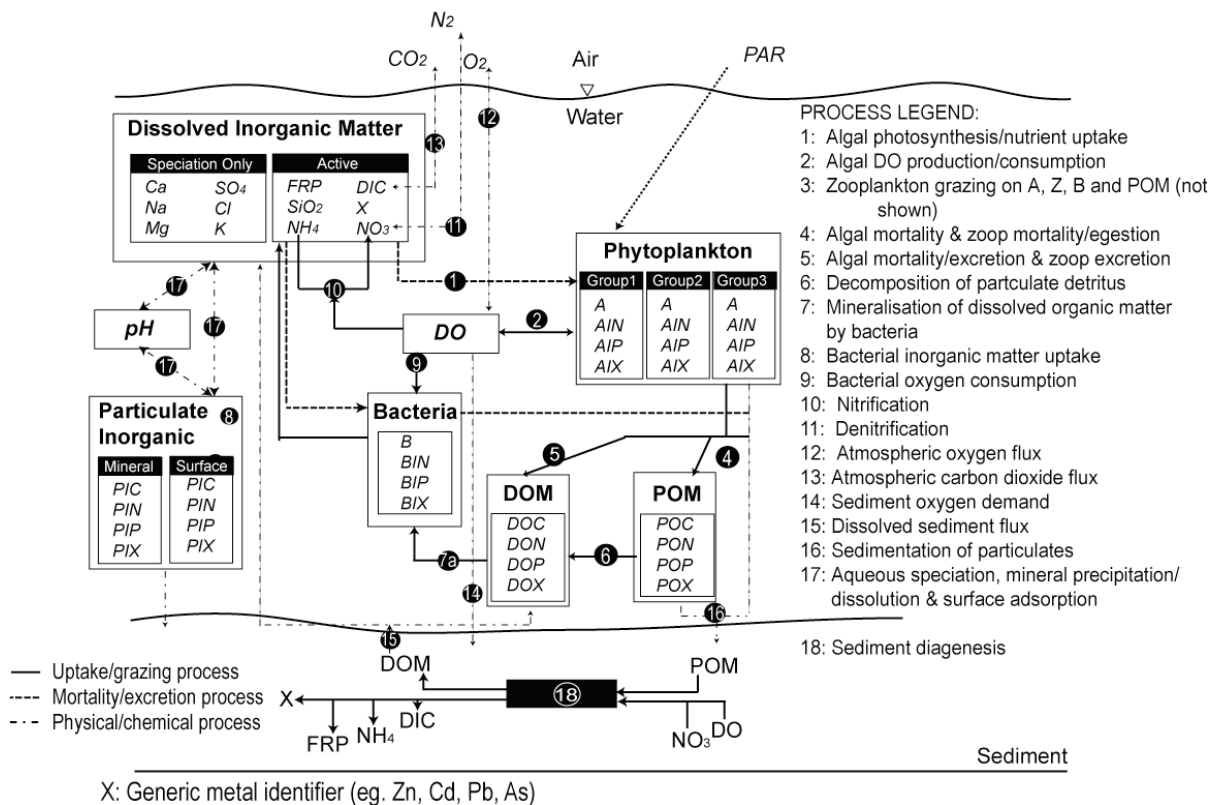


Figure 3 Schematic of the newly extended Computational Aquatic Ecological Dynamic Model, CAEDYM, indicating interactions between the geochemical, nutrient and biological cycles. Note that the sediment module shown is simplistic and is not the more sophisticated diagenesis module currently being developed

3 RESULTS AND DISCUSSION

As a first step in modelling water quality in Lake Kepwari, the ability of the hydrodynamic model, DYRESM, to describe Lake Kepwari stratification dynamics was tested. DYRESM output from October 2003 – October 2005, was compared to water column temperature data collected by the LDS across the same period (Figure 4). Confidence in DYRESM’s ability to match measured temperature data is essential prior to using DYRESM for long term forecasting of stratification conditions.

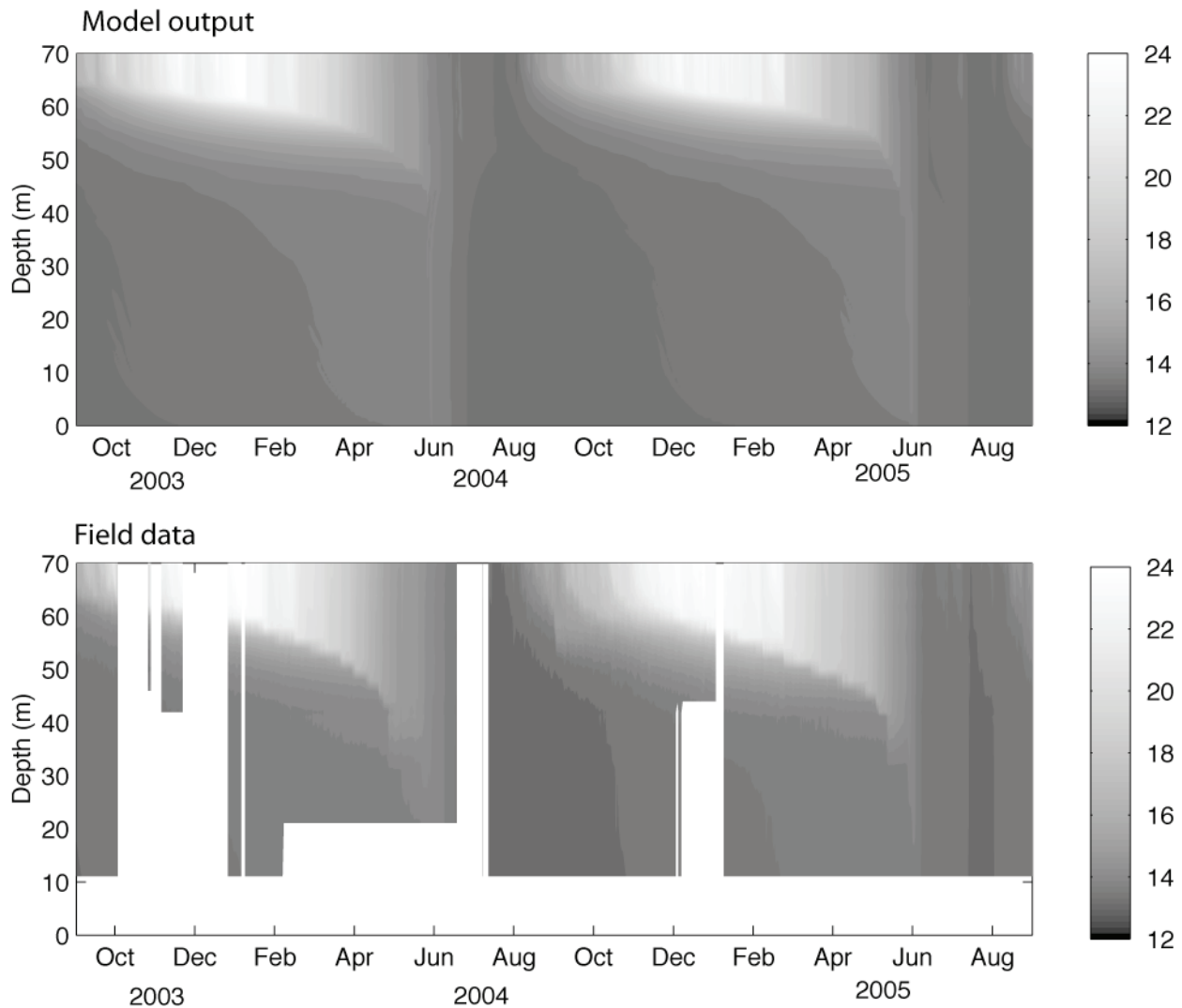


Figure 4 Temperature stratification cycles in Lake Kepwari from October 2003 – October 2005. The top panel shows DYRESM output, and the bottom panel shows LDS field data. Temperature stratification occurs from October to May each year. Note that the riverine diversion occurs when the lake is isothermal, and therefore its signature is rarely detectable

Initial comparisons of DYRESM output with LDS data showed reasonable agreement with respect to vertical stratification patterns and temporal dynamics. However there was an anomaly between the total heat budget of the lake, as calculated by DYRESM, and the heat budget estimated from measured temperature data. There was also an anomaly between water budgets, when estimated cumulative riverine diversions were compared to measured lake levels. Groundwater is known to contribute to the lake’s water budget and typically enters the lake at 17C. Groundwater inflows were estimated from local hydraulic gradients, and

inserted into the lake across the hypolimnion, as a constant inflow throughout the year. This significantly improved the match between modelled and measured heat budgets.

More detailed comparisons between DYRESM output and LDS data highlighted that during extreme storm events, DYRESM predicted the surface mixed layer to be shallower than measured. An intensive field experiment on Lake Kepwari in 2004 showed evidence of extensive wind sheltering by the lakes surrounding embankments. This effect is likely to be typical of pit lakes with their artificially constructed bathymetry. Further work has highlighted the impact of mining benches, which are subsequently under water in the lake, on the internal mixing processes, and ultimately the stratification dynamics (Huber et al., 2006). Finally, an improved parameterisation of the surface drag coefficient (see Wuest and Lorke, 2003), under the typically low wind conditions experienced by the lake, was incorporated into DYRESM.

All of the above modifications resulted in significant improvements in DYRESM's ability to describe measured hydrodynamic conditions in the lake. We then proceeded to test the modifications made to CAEDYM to allow prediction of water quality in mine lakes.

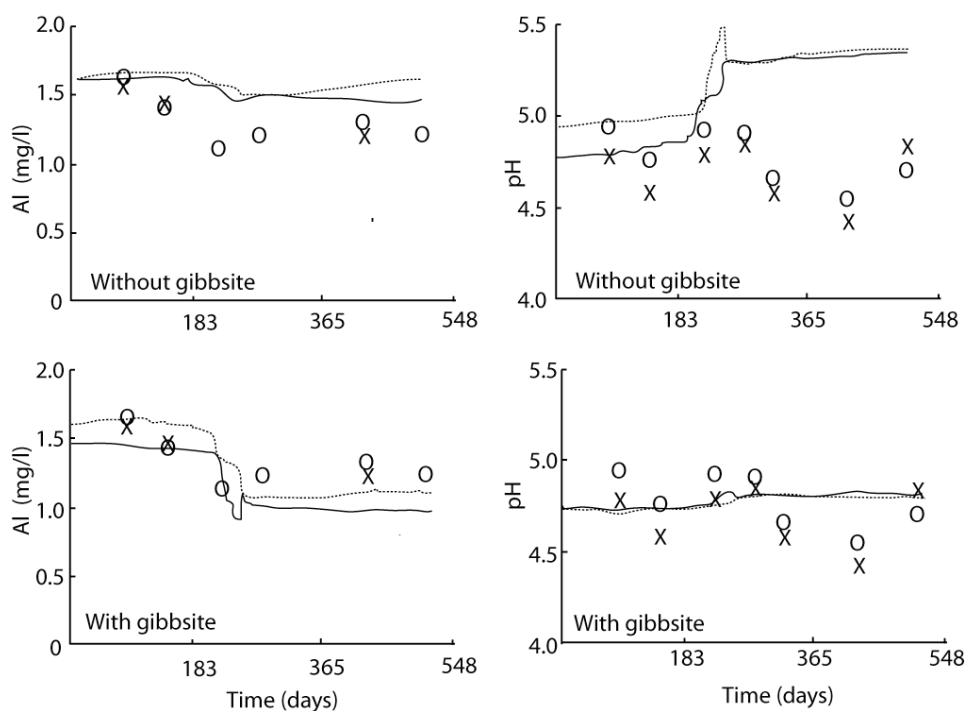


Figure 5 CAEDYM output (lines) compared to field data (symbols). Dashed lines indicate depth and volume averaged surface water concentrations, solid lines indicate depth and volume averaged bottom water concentrations. Crosses show measured bottom water concentrations, and circles show measured surface water concentrations. The addition of gibbsite solubility equilibrium control to CAEDYM improved its ability to simulate the response of Al concentrations and pH to riverine inflow

The newly modified DYRESM-CAEDYM was tested in Lake Kepwari, running a simulation from January 2004 to June 2005. CAEDYM output was compared with measured geochemical and nutrient data, collected in the lake on six occasions during this period. Modelling output and water column sampling results were depth and volume averaged to allow comparison of concentrations in the epilimnion and the hypolimnion. CAEDYM output showed good agreement with measured nutrients (NO_3 , NH_4 , TN, FRP and TP, DOC, DIC, TOC, TIC and DO) and geochemical species (Al, Zn, Si, Mg, Cl, Na, K and Ca).

The impact of the addition of the aqueous geochemistry module on CAEDYM output is highlighted in Figure 5. Preliminary modelling indicated that pH was likely controlled by the solubility of Al mineral phases such as gibbsite. Without gibbsite solubility equilibrium control, CAEDYM was not able to describe

the pH and Al dynamics of Lake Kepwari in response to riverine inflows in winter 2004, whereas once gibbsite solubility control was added to CAEDYM, there was improved prediction of pH and Al (Figure 5). Discrepancies still exist between predicted and some measured species concentrations (for example Fe) and pH, however it is expected that this agreement will improve further after final descriptions of geochemical and redox processes, and the detailed sediment diagenesis module, are implemented in CAEDYM. This work is scheduled for completion by the end of 2006.

4 CONCLUSIONS

The newly extended version of the coupled hydrodynamic-aquatic ecology model DYRESM-CAEDYM allows investigations into the controls on acidity and contaminants in mine waters. While here the model has been specifically applied to mine lakes, the ecological model CAEDYM, with the new module as described here, could be used for any water body with similar water quality issues.

The work presented here is only the first step of the development of a version of CAEDYM-DYRESM that is specifically applicable to mine lakes; development is currently underway to also include a detailed description of redox and geochemical processes in lake sediments. This new version of CAEDYM-DYRESM will allow thorough investigation into the interactions between geochemical and biological cycles in these lakes, under variable stratification conditions.

The information and understanding gained from such modelling exercises will facilitate improved assessment of possible passive and active remediation scenarios, prior to meso-scale or full-scale trials. This model will be particularly useful if questions arise about different end uses of surface and bottom waters; for example bottom waters could be used for industrial re-use and surface waters for recreation or aquaculture. No other model currently describes the impact of lake stratification on lake geochemical cycling nor simulates the interactions between the geochemical and nutrient cycles and lake biology, thus providing a multi-disciplinary systems approach to water quality modelling.

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