Exploring a New Water Economy Post Mining in a Coal Mining Region

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Abstract

Pit lakes are shaped by interactions between water sources. Understanding these interactions is essential for managing water quality and ecological risks post-mining. We studied Lake Kepwari, a rehabilitated coal mine void in Collie, Western Australia. To quantify relative contributions of source waters and evaluate hydrologic controls on lake chemistry, we used diagnostic tools of mixing models (DTMM) and end-member mixing analysis (EMMA). Water samples collected were analysed for isotopic and geochemical compositions. EMMA solutions determined the dominant source waters highlighting potential in determining the sources of salinity or acidity, evaluating lake-groundwater interactions, and impacts on downstream waters.

Keywords: mining lakes, endmember mixing analysis, conservative tracers, groundwater, hydro-geochemistry

Introduction

The successful closure of mine voids as stable, non-polluting water bodies remains a major economic and environmental challenge. In the Collie Coal Basin, Western Australia, Lake Kepwari, a former coal pit, stands as a pioneering example pit lake rehabilitation that lead to the lake being formally relinquished back to the state. After mining ceased in 1997, the void was filled largely with diverted flows from the seasonal Collie River South Branch (CRSB). Since an accidental river breach in 2011, a permanent connection to the CRSB as part of the closure strategy has maintained lake water levels and transformed the system into a flow-through lake, providing intermittent but effective neutralisation of acidity, reduction of dissolved metals, and nutrient inputs (Lund *et al.* 2020; Lund *et al.* 2018). Like many post-mining pit lakes, Kepwari's long-term hydrogeochemical behaviour is governed by intricate interactions between groundwater, surface runoff, spoil geochemistry, submerged sediments, and pit-wall erosion. Hydrogeology is complex due to faulting, mining disturbances, and groundwater abstraction. The pit void intersects the Permian Muja coal measures aquifer hydraulically connecting to the larger regional groundwater system (Varma, 2002).

Geochemical modelling (PHREEQC) and mass balance framework by Salmon *et al.* (2008) suggested that acidity in Lake Kepwari was potentially controlled by iron-rich regional groundwater inflows or internal sources like pyrite oxidation, while river water supplied alkalinity. Later, Salmon *et al.* (2017) using a coupled hydrodynamic-bio-geochemical model (DYRESM–CAEDYM) further demonstrated that water quality evolution was governed by externally driven acidity loading and Fe–Al solubility-controlled processes. The model inferred that the external acidity loading delivered by groundwater throughflow exerted primary geochemical control over the long-term evolution of water quality. PITLAKQ modelling by Müller *et al.* (2010) predicted that besides groundwater exchange, high acidity surface runoff and bank erosion may explain the lake's re-acidification following the neutral river inflow. Both models were completed prior to river flow through, only including river contributions used to fill the lake. Recent work by Lund *et al.* (2018) suggests that groundwater inflow (based on estimates from Varma, 2002) has declined markedly from ≈2.1 GL per year in 1999 to <0.3 GL per year by 2016, yet internal acidity generation persists and is currently neutralised primarily by river inflows. None of the previous investigations into Lake Kepwari have empirically quantified the proportional contribution of dominant source waters to the lake. Water budget analysis for 2010–2016 indicate that inputs are dominated by highly variable river inflow (28–10,793 ML yr^{-1}), followed by rainfall (397–1,011 ML yr^{-1}), groundwater (≈220–293 ML yr^{-1}), and surface runoff (58–133 ML yr^{-1}). However, large residual errors (–2,244 to +941 ML yr^{-1}) indicate substantial uncertainty in flux estimates and data gaps (Lund *et al.*, 2018).

Environmental tracer techniques have been acknowledged as a powerful tool in understanding the interactions between surface waters and groundwaters including mixing dynamics within the lakes. Specifically, naturally occurring isotopes of water and conservative geochemical tracers are routinely used to quantify source water contributions and track flow path. The literature points to a limited application of these tracer approach within pit lake systems and where it is used, the mixing model and tracers selected can heavily influence the interpretation of the data. This study directly addresses that gap and provides a preliminary first order understanding of mixing processes in the lake, offering new insight into the hydrological controls on acidity generation, solute dynamics, and seasonal transitions.

Methods

Grab water samples were collected in September and October 2025 from all the potential source waters contributing to Lake Kepwari: CRSB inflow and CRSB outflow or lake outflow (n = 4); Groundwater samples (n = 10) from 5 monitoring bore wells (depth ranging from 13 to >100 m below top of casing); Shallow subsurface matrix flow was characterised using drainage lysimeters (n = 3) installed around the lake to intercept near-surface runoff generated during storm events. Additionally, piezometers (n = 3) were installed around the lake perimeter to intercept bank seepage before it entered the lake, enabling characterisation of water derived from wall erosion, subsurface leaching, and near-shore spoil material. A rain sample (n = 2) was obtained from a monthly bulk precipitation collector within the lake catchment. Lake-water samples (n = 12) were collected from surface and bottom waters at three sites located near the inflow, outflow, and mid-lake sections. At each site, full-depth physicochemical profiling was conducted throughout the water column to characterise thermal structure, stratification, and vertical chemical gradients.

Water samples were collected in new 1 L high-density polyethylene (HDPE) bottles and divided into three aliquots for geochemical analysis and one for isotopic analysis. Nutrients and metals/metalloids samples were filtered through disposable 0.45 µm polypropylene syringe filter with glass microfiber (GMF) membrane (Thermo Scientific, USA) within 24 h of collection and stored in 60 mL clean HDPE bottles. Metal samples were acidified to pH <2 using 70% nitric acid and stored at 4 °C. Nutrient and major anion samples were frozen at -20 °C before analysis. Isotope samples were stored in 30 mL glass bottles and sealed with screw caps with no headspace to avoid fractionation and stored at 4 °C until analysis.

Filtered water samples were analysed at Edith Cowan University (ECU) Analytical Facility for dissolved trace metals and metalloids (Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, Pb, Mn, Hg, In, Li, Ni, Rb, Sb, Se, Si, Sr, Ti, U, V, and Zn) and common metals (Na^+, K^+, Ca^{2+}, and Mg^{2+}) using inductively coupled plasma-mass spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES). Common ions (Cl^- and SO_4^{2-}) were analysed by Ion Chromatography. Nutrients (NO_X and NH/NH_4) were measured on a Lachat autoanalyser (Hach, USA) and carbon (non-purgeable organic carbon (NPOC) and dissolved inorganic carbon (DIC)) were measured using a total carbon analyser (Shimadzu, Japan). Total alkalinity was determined by titration using a mini-titrator (Hanna Instruments, USA) on an unfiltered aliquot of the sample to a pH endpoint of 4.5. Samples were also analysed for water isotopes including oxygen-18 (^{18}O) and deuterium (^{2}H) by a L2130-*i* Picarro Cavity Ringdown Spectrometer, at Australian Biogeochemistry Centre, University of Western Australia.

Following the EMMA procedure of Liu *et al.* (2008), end-members (or source waters) and their relative contributions to the lake and river outflow were determined. The conservative tracers and number of end-members were determined without any information from end-members based on the DTMM developed by Hooper (2003). To achieve that, principal component analysis (PCA) was applied on the correlation matrix of standardised lake and river outflow chemistry. Eigenvectors extracted were then used to project lake and river outflow chemistry into mixing U-space following Christophersen and Hooper (1992). This analysis helps identify tracers that exhibit linear mixing behaviour (conservative mixing of end-members with unique chemistry is a linear process), and to determine the dimensionality of the mixing subspace, where the number of U-space dimensions is one less than the number of end-members required (Liu *et al.* 2008; Liu *et al.* 2013). The residuals between the reprojected pit lake chemistry and original values were then examined to evaluate tracer suitability: no structure or trend, randomly distributed residuals ($p>0.05$) indicate conservative behaviour, while systemic trends indicate non-conservative processes. The relative root-mean-square error (RRMSE) was also used to assess the appropriate number of dimensions and to screen out non-conservative tracers; in a well-posed model, RRMSE typically decreases from a one-dimensional (1-D, two–end member) subspace to higher-dimensional subspaces (Frisbee *et al.* 2011; Liu *et al.* 2008).

After defining the conservative tracers and mixing dimensionality, PCA was again performed to extract eigenvectors using a correlation matrix of the standardized conservative tracer set. The lake and river outflow chemistry data were then orthogonally projected using the eigenvectors along with all the end-members. The first two principal components of these tracers were used to construct mixing diagrams in U-space, and candidate end-members were evaluated based on (a) whether they form a polygon that encloses all pit-lake samples, and (b) how well their predicted fractions and concentrations reproduce observed lake chemistry. Final end-member fractions were then solved using the simultaneous-equation approach of Liu *et al.* (2020).

Results and Discussion

All the chemical data of lake and river outflow samples were included in DTMM to identify conservative tracers and the number of end-members. The residuals analysis showed a random distribution for Na^{+}, Mg^{2+}, Ca^{2+}, K^{+}, Cl^{-}, NO_x, Fe, Co, Ni, Sr and U under two dimensions (2-D) ($R^2 \approx 0$; $p > 0.05$) suggesting their conservative behaviour upon mixing of three end-members in lake waters. However, their RRMSE in 2-D mixing spaces exhibited conservative behaviour only for Na^{+}, Mg^{2+}, Ca^{2+}, K^{+}, Cl^{-}, Ni, Sr and U. U was excluded from the conservative tracer set considering its instability in the pit lake system (Gunten *et al.* 2018). The first two eigenvectors (PC1 and PC2) of selected conservative tracers explained 98% of variance confirming that the conservative mixing space is effectively two-dimensional and consistent with a three end-member mixing model. A mixing diagram (Fig. 1a) was constructed in U-space using PC1 and PC2 for the geometric evaluation of end-member mixing. Multiple combinations of three candidate end-members could form a geometrically viable mixing triangle in U-space. However, the mixing triangle that best circumscribed the lake and river outflow sample cloud defined by three vertices were: A groundwater (GW3), river inflow (CRSB-In), and hypolimnetic water (K2 Bottom). The K2 Bottom is not a source water *per se*; rather, it represented a distinct geochemically evolved water mass likely evolved due to evapo-concentration and stratification decoupling itself from a volumetric mixture of inflow waters.

Persistent stratification is evident from temperature contrasts between surface waters (14.2-16.9 °C in September; 17.5-17.8 °C in October) and bottom waters (12.6-12.7 °C), while electrical conductivity increases systematically with depth (2,280-2,390 µS cm^{-1} at the surface versus 2,930-2,980 µS cm^{-1} at depth), indicating solute accumulation and prolonged hypolimnetic residence times. Dissolved oxygen declines with depth (e.g. 11.36 mg L^{-1} at K1 Top versus 8.34 mg L^{-1} at K1 Bottom in September, and 95% versus 73-77% saturation in October).

EMMA demonstrates a pronounced vertical separation of water sources within Lake Kepwari during initial stratified conditions (Fig. 1b). Surface waters (K1-K3 Top) comprise mixed proportions of groundwater (41-45%) and river inflow (27-58%), with hypolimnetic fraction of 1-30%. The K2 Top consisted of 45% groundwater and 38% river inflow in September, shifting towards relatively higher river influence in October (56-58% river inflow at K1-K3 Top). In contrast, bottom waters (K1–K3 Bottom) are consistently dominated by the hypolimnetic fraction (41-83%), with moderate groundwater input (<33%) and negligible river influence in September but considerably higher river fraction in October (38-39%). The river outflow (CRSB-Out) had a mixed river–groundwater signature in both months (river 32-51%; groundwater 41-43%), while hypolimnetic fractions declined from 24% in September to 8% in October.

This finding quantitatively confirms earlier qualitative assessments that river reconnection improves surface-water quality without substantial export of hypolimnetic water during stratification (McCullough 2015; Salmon *et al.* 2017). Notably, EMMA resolves a key ambiguity in previous modelling by showing that groundwater can constitute nearly half of epilimnion volume even when surface-water quality remains favourable. The lake-water chemistry was well reproduced using the end-member fractions derived from EMMA and the ionic compositions of the identified end-members. Recreated versus measured concentrations had their R^2 values over 0.90 for all selected tracers giving confidence in the EMMA solution (Fig. 2).

The mean δ^2H and δ^{18}O of the water samples in September were -3.80±1.56‰ and -18.06±7.46‰, respectively. The δ^2H and δ^{18}O values were plotted with Global Meteoric Water Line (GMWL: $\delta^2H = 8\delta^{18}O + 10$) and Local Evaporation Line (LEL) was established using regression line of surface water samples as shown in Fig. 3. The Local Meteoric Water Line (LMWL) of Perth (WA) is shown as a reference (Griffiths *et al.* 2022). Precipitation and groundwater plot close to each other above the GMWL and along LMWL, confirming a meteoric origin with minimal evaporative modification prior to recharge (Priestley *et al.* 2020). Whereas lake waters plot below the GMWL along a LEL, indicating evaporation is also an important process controlling lake chemistry. The slope of 4.5 in LEL is indicative of

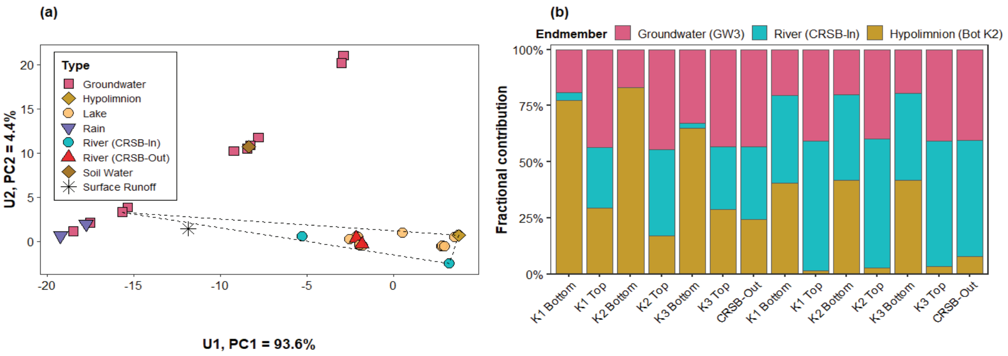

Figure 1 *(a) Mixing diagram using the first two principal components (PC1 and PC2) constructed from 7 tracers; (b) The fractional contributions of three end-members to the Lake Kepwari.*

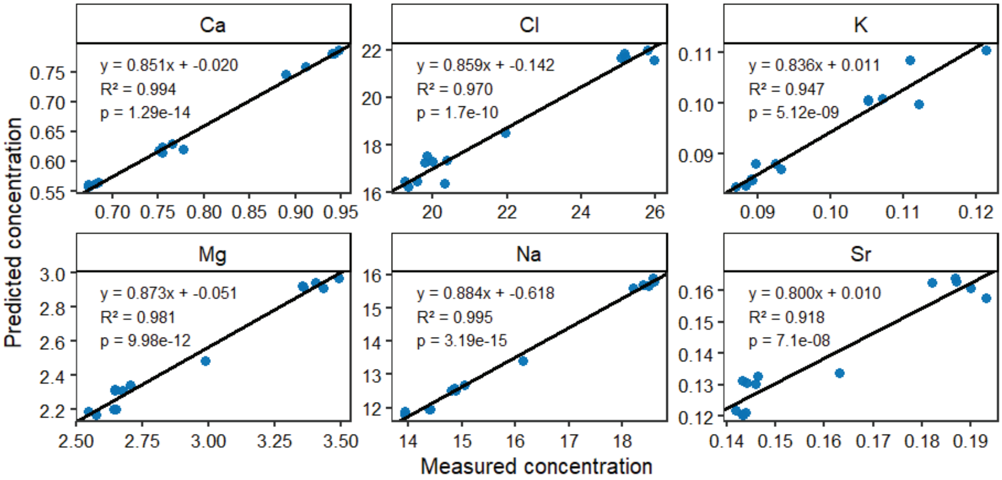

Figure 2 Recreation of ionic concentrations in lake waters based on relative contributions of endmembers determined by endmember mixing analysis (EMMA) and ionic concentrations in endmembers.

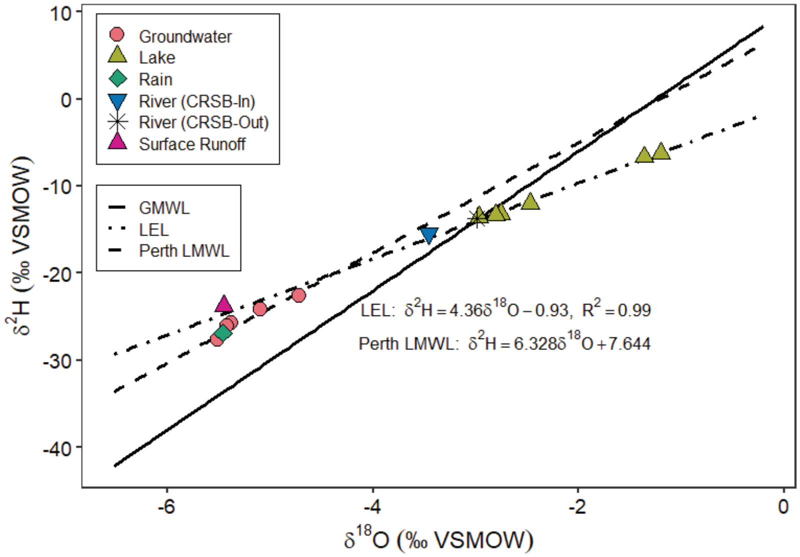

Figure 3 δ^2H–δ^{18}O stable-isotope cross-plot of lake waters and potential source waters in Lake Kepwari.

evaporation processes in free water bodies within arid or semi-arid regions with low relative humidity (Gibson *et al.* 2008). The K1–K3 Top samples are moderately enriched (δ^{18}O = −2.97 to −2.76‰; δ^2H = −13.60 to −13.18‰) and plot closer to river inflow (CRSB-In; δ^{18}O = −3.46‰, δ^2H = −15.44‰), consistent with EMMA results showing considerable river fraction and active renewal of the epilimnion during early stratification. Active surface-water renewal can promote oxygenation and buffering, favouring the oxidation and attenuation of dissolved metals like Fe(II). In contrast, K1–K3 Bottom are relatively more enriched (δ^{18}O = −2.47 to −1.20‰; δ^2H = −12.01 to −6.23‰), reflecting longer residence times and a stronger cumulative evaporative signal prior to isolation. Among bottom samples, K1 and K2 were the most highly evaporated plotting furthest from LMWL on a LEL. These isotopic characteristics align with EMMA results indicating hypolimnetic dominance, supporting the interpretation of chemically evolved bottom waters during stratified conditions. The river CRSB-Out plots along the LEL and overlaps surface-lake values, corroborating EMMA results showing mixed river and groundwater contributions and negligible hypolimnetic export.

Conclusions

These preliminary findings demonstrate the applicability of the conjunctive use of tracer-based DTMM and EMMA for determining source waters and their relative contributions in flow-through pit lakes, as supported by stable isotope results. Our results highlight the critical roles of hydrologic controls and evaporative enrichment in shaping the water quality of Lake Kepwari. Consequently, EMMA can provide a robust empirical tool for understanding hydrogeochemical processes that govern pit lake water quality and quantity, thereby guiding effective mine closure strategies.

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