

Lower Murray Reclaimed Irrigation Area (LMRIA) Acidification Project

Modelling of acid drainage discharges to the Lower River Murray

This project is a joint project between the Murray–Darling Basin Authority and the State Government of South Australia.

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Abbreviations

ANZECC	Australian and New Zealand Environment Conservation Council
ARMS	Aquatic Realtime Management System
ASS	acid sulfate soils
CAEDYM	Computational Aquatic Ecosystem Dynamics Model
DEWNR	Department for Environment, Water and Natural Resources
DHA	Department of Health and Ageing
ELCOM	Estuary Lake and Coastal Ocean Model
EPA	South Australian Environment Protection Authority
LMRIA	Lower Murray Reclaimed Irrigation Area
MDBA	Murray–Darling Basin Authority
PIRSA	Primary Industries and Regions South Australia
PHREEQC	pH–Redox–Equilibrium
SAMDB NRM	South Australian Murray–Darling Basin Natural Resources Management Board

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Executive summary

Exposure of acid sulfate soils occurred in the Lower Murray Reclaimed Irrigation Area (LMRIA) from 2007–10 due to extremely low River Murray and adjacent floodplain groundwater levels. The soils dried and cracked and the sulfidic soil material (pH>4) oxidised to form sulfuric material (pH<4). When river and groundwater levels returned to normal levels, low pH water with high soluble metal levels entered the LMRIA drainage channels and was pumped into the River Murray, a practice necessary to maintain agricultural activity in the region.

There were concerns about potential impacts of the acid discharges on river water quality, particularly under lower flow conditions. To assess the magnitude and nature of potential water quality risks a 3-dimensional (3D) hydrodynamic and geochemical model (ELCOM-CAEDYM1) was constructed.

Initial testing of the ELCOM-CAEDYM model was undertaken against another geochemical code, PHREEQC². ELCOM-CAEDYM generally performed well (<3% difference for key parameters such as pH and dissolved inorganic carbon), particularly given the fundamental differences between the two codes.

An ELCOM-CAEDYM model grid was constructed for the 84-km length of the River Murray between Mannum and Wellington. The model grid was straightened to improve model efficiency and achieve suitable runtimes (\approx 25:1) for full 3D geochemical simulation. The key inputs for the model were the upstream flow and water quality, LMRIA drainage pump flow and water quality, and meteorological data.

The model was initially used in conservative ELCOM tracer mode to explore the likelihood of major water quality impacts occurring. The model results suggested that except under worst case pumping scenarios (all pumps continuously running), water quality should remain within guidelines.

ELCOM-CAEDYM geochemical model performance checking was undertaken during a five-month period from November 2011 to April 2012. The model gave satisfactory results against measured parameters at the SA Tailem Bend water offtake and was able to represent widely varying concentrations. The model also performed adequately when representing the localised plume behaviour.

Lower flow conditions (1,000–10,000 ML/day) were simulated in the model. Results indicated that water quality risks to the main channel could increase if the flow over Lock 1 reduced below 5,000 ML/day. The main issue of concern identified in the modelling results to date is the potential for soluble manganese to more regularly exceed SA Water treatment guidelines (non-health guideline) at Tailem Bend.

The health guidelines are not predicted to be exceeded and pH is predicted to be maintained within guidelines for protection of drinking water and aquatic ecosystems. Soluble nickel (which exceeded guidelines in the undiluted drain water) was not predicted to pose any risks to raw water offtakes under lower flow conditions. Hence, under the currently modelled conditions, the LMRIA water quality impacts are predicted to remain acceptable and manageable (for soluble manganese) in terms of water supplies and acute ecosystem impacts. Further model performance checking and assessment is recommended if lower flow (<2,500 ML/day over Lock 1) conditions occur while the LMRIA acid drainage problem is persisting.

1 ELCOM: Estuary and Lake Computer Model; CAEDYM: Computational Aquatic Ecosystem Dynamics Model

2 PHREEQC: Parkhurst DL and Appelo CAJ 2013, *Description of input and examples for PHREEQC version 3 – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, US Geological Survey Techniques and Methods, book 6, chapter A43, 497 pp, viewed 6 December 2013, <http://pubs.usgs.gov/tm/06/a43/>.

1 Introduction

Background

There is approximately 5,200 hectares of flood irrigated agriculture protected by a levee bank system on the former floodplain of the River Murray in South Australia, between the townships of Mannum and Wellington. This area comprises 24 individual irrigation areas and is known collectively as the Lower Murray Reclaimed Irrigation Area (LMRIA).

Historically, dairy farming is the predominant land use with a smaller area for beef cattle, fodder production and lifestyle farming. The irrigation bays are typically 1.0–1.5 m below the normal river pool level (+0.75 m AHD), enabling gravity fed flood irrigation. The drainage from irrigation and regional groundwater inputs to the LMRIA is returned to the river using large pumps. Pumping of drainage water to the river is necessary to prevent rising saline water impacting on the agricultural activities although it has been shown that these discharges can impact whole-of-river water quality (Mosley and Fleming 2010).

From 2006–09, drought conditions and long-term low inflows from the Murray–Darling led to unprecedented low water levels below Lock 1. During April 2009 the water level in the Lower Murray fell to below –1 m AHD, the lowest levels in over 90 years of records, and likely for much longer as before construction of the barrages near the river mouth sea water would have entered during times of drought and likely have maintained water levels at \approx 0 m AHD. The low water levels and restricted water allocations during the drought meant that most of the LMRIA was not able to be irrigated for substantial periods of time and the groundwater level dropped substantially (1–2 m) from pre-drought levels. The heavy clay soils subsequently salinised, dried and cracked, causing extensive damage to the irrigation bays and associated infrastructure, and major socio-economic impacts.

Since 2010, river and ground water levels have recovered in the Lower Murray and irrigation has recommenced in a limited manner in the LMRIA. In some cases water has flooded back onto pasture through cracks and fissures in the soil profile. Water quality monitoring by the South Australian Environment Protection Authority (EPA) in late February 2011 found acid drainage water being returned to the river from 13 irrigation areas (comprising 3,300 ha) in the LMRIA (Figure 1). The River Murray had been in a high flow period since that time which resulted in a large amount of dilution flow for the LMRIA acid drainage discharges. However it was considered necessary to assess the water quality risks under a likely return to lower flows in the future.

The low pH and high metal levels in acid drainage water are key aspects required to be modelled to assess aquatic ecosystem and other risks (eg to drinking water supplies). These parameters show non-conservative (non-linear) behaviour when acidic water mixes with pH neutral river water (Simpson *et al* 2010, Mosley *et al* 2010). To satisfactorily account for this behaviour it was considered important to use a model that could adequately simulate geochemistry.

Zero-dimensional (0D) geochemical equilibrium models have been applied to assessing surface water impacts from acid discharges (Balistrieri *et al* 2007, Nystrand and Österholm 2013). The major limitations of these models for our specific needs are that (1) they consider the water body as completely mixed and homogeneous in all spatial directions. In our context of a river system receiving multiple acid drainage discharges along tens of kilometres it is difficult to use these models to assess regional water quality risks, and (2) the individual LMRIA acid drainage pumps discharge into localised areas and the resultant plumes are much more saline and dense than the river water, so that saline stratification is observed during mixing. A 0D model cannot represent these processes adequately.

Three-dimensional (3D) hydrodynamic and geochemical modelling was desirable to account for these processes. Since Hipsey *et al* (2010) used the 3D ELCOM-CAEDYM modelling platform to successfully predict acidification impacts for the Lower Lakes system, there was enough impetus to also use these models to assess water quality risks to rivers from acid drainage water. To our knowledge, this was the first time such an approach was used to assess surface water quality risks from the impacts of acid drainage water.

Aims of study

The aims of the study were to:

- 1 Construct a 3D hydrodynamic and geochemical model (ELCOM-CAEDYM platform) to simulate the impact of acid drainage discharges from the LMRIA on the water quality of the River Murray.

- 2 Assess the model's performance in comparison to another geochemical code (PHREEQC) and observed water quality data.
- 3 Undertake simulations of lower flow conditions to assess risk to the aquatic ecosystem and beneficial uses of the river, in particular drinking water supplies.

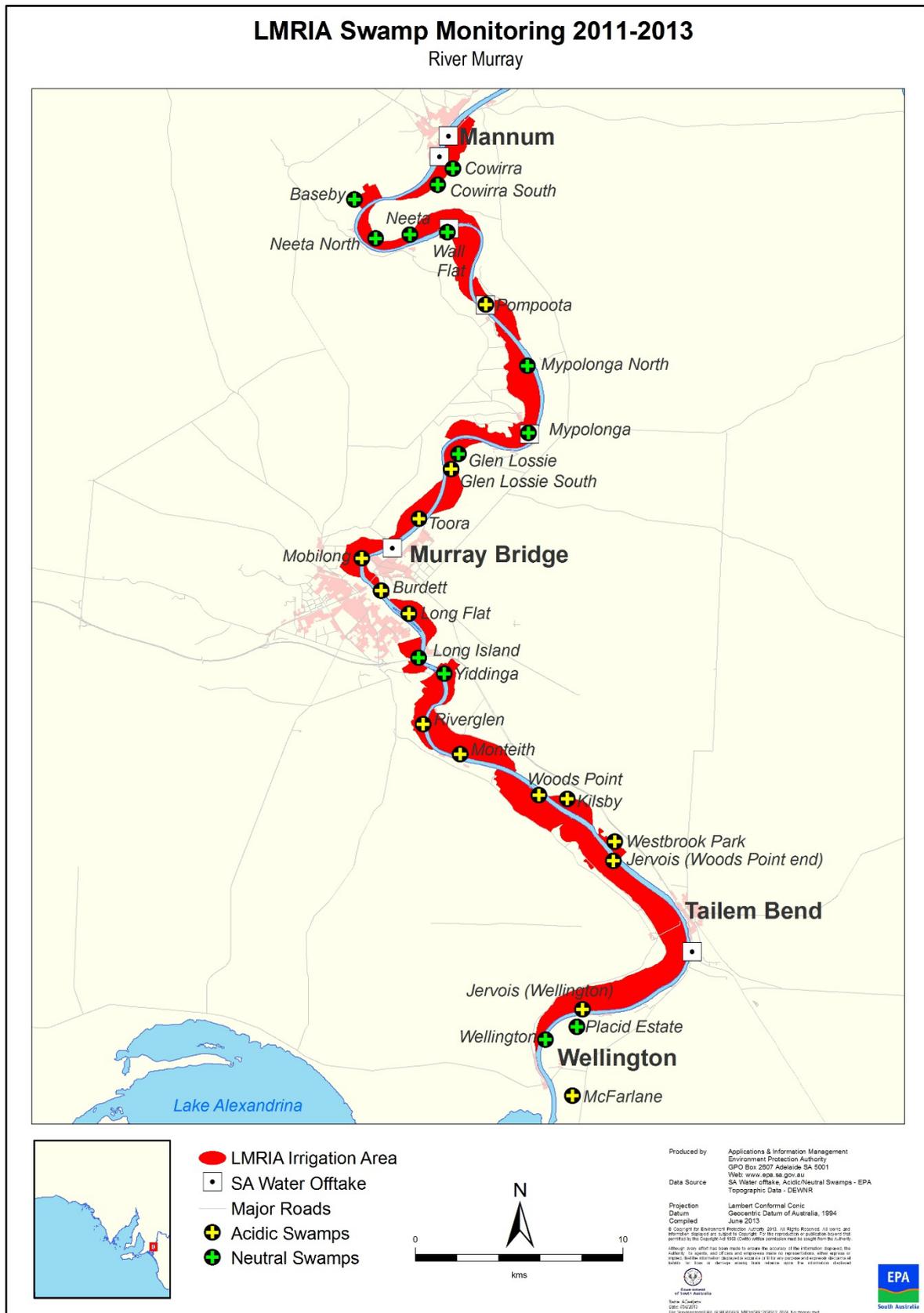


Figure 1 Map of the acidic and neutral irrigation areas (swamps) and pump discharges in the LMRIA. The locations of major drinking water offtakes are also shown.

2 Methods

Lower Murray River study area description

The Lower Murray region study area comprised the lower reaches of the River Murray, below Lock 1 between the townships of Mannum and Wellington (Figure 1). There are no major tributaries to the River Murray downstream of Lock 1, which is the last river regulating structure along its reach. Below Lock 1, the Lower Murray flows for approximately 250 km and varies from 5–20 m deep. The water quality in this region is typically characterised by circum-neutral pH, high turbidity, nutrient and algal levels (Mackay *et al* 1988, Mosley and Fleming 2010), with periodic temperature stratification and toxic cyanobacterial blooms (Maier *et al* 2001). The river channel discharges into the Lower Lakes which are the end of the freshwater region of the Murray– Darling Basin.

As well as the agricultural values associated with the LMRIA, the Lower Murray region contains major drinking water supply offtakes for the city of Adelaide (population 1.2 million) and several regional townships. It also is a very important area for recreational activities such as swimming, boating and fishing. The presence of acid drainage discharges in this region poses a threat to these values and the magnitude of these threats are assessed in this report.

ELCOM-CAEDYM Model background

The 3D Estuary, Lake and Coastal Ocean Model (ELCOM) can be used to predict the hydrodynamics, temperature and salinity distribution of a water body in response to environmental forcing (wind, solar radiation, temperature, inflows and outflows). The Computational Aquatic Ecosystem Dynamics Model (CAEDYM) is coupled to ELCOM to simulate numerous biogeochemical processes and parameters including inorganic particles, oxygen, organic and inorganic nutrients (C, N, P and Si), and phytoplankton groups.

CAEDYM also includes a geochemistry module able to solve the equilibrium speciation of geochemical components [Al, Ca, Mg, Na, K, Fe(II), Fe(III), Mn(II), SiO₂, Cl, DIC, SO₄, PO₄, NO₃, and NH₄], including precipitation/dissolution of mineral phases [Fe(OH)₃, Al(OH)₃, MnO₂ and CaCO₃] and kinetic processes (eg microbially mediated redox transformations). The geochemical model has previously been used in mine lakes impacted by acid mine drainage (Oldham *et al* 2009) and in acid sulfate soil impacts on natural lake water (Hipsey *et al* 2010).

The ability of a natural water body to cope with acid additions is determined by its alkalinity, with the higher the alkalinity the more acid input it requires to cause acidification (Stumm and Morgan 1996). In the River Murray, as in most natural waters, the bicarbonate (HCO₃⁻), and to a lesser extent carbonate (CO₃⁻²), ions provide the ability to neutralise acid inputs by buffering increases in H⁺ ion concentrations. The dissolved inorganic carbon (DIC) provides a measure of HCO₃⁻ and CO₃⁻², along with dissolved CO₂. Metal hydrolysis reactions are also important as the acidity in drainage water from acid sulfate soils can be very high in dissolved metals, typically Fe^{+2/+3}, Mn⁺² and Al⁺³ ions (Cook *et al* 2000). Dissolved metals can subsequently cause H⁺ acidity to be created via hydrolysis reactions (eg Fe⁺³ + 3 H₂O = Fe(OH)_{3(aq)} + 3 H⁺, see Kirby and Cravotta 2005). Both pH and metals are very important parameters to measure and model as biological damages to ecosystems start below pH ≈ 6.5 and increase with further lowering of pH and metal concentrations (ANZECC 2000, Vinebrook *et al* 2003).

In similarity with other geochemical codes, CAEDYM solves the equations for pH, solution speciation, and mineral and/or gas phases (Hipsey *et al* 2013). Kinetic transformations between geochemical components can also be simulated. This is potentially important as discussed for Fe⁺² and Mn⁺² oxidation in the diluted LMRIA drainage water. The geochemical components link with the other biogeochemical processes within CAEDYM, such that any biological activity (eg algal nutrient uptake and photosynthesis, microbial respiration, and nitrification) will dynamically affect the aqueous speciation and pH.

CAEDYM also contains a charge balance input parameter that can be used to correct for any charge imbalance present in the solution. If this parameter is not provided then CAEDYM will correct any charge imbalance using pH. Unlike other geochemical codes such as PHREEQC there is no functionality to charge balance on major ions such as Cl and SO₄. It should be noted there is a risk in CAEDYM that pH predictions may be in error if any significant charge imbalance is not corrected for. This would be highly likely where there are analytical errors and/or unanalysed species (eg any missing major ions).

Set up of ELCOM-CAEDYM Model for the Lower Murray

The river bathymetry was initially used to create a 25 x 25 m grid of the Lower Murray between Mannum and Wellington (Figure 2, left). This grid ran quite efficiently (30 day of simulation time = 1 day of real time) when just ELCOM (salinity and hydrodynamics only) was used. However testing of this model grid with CAEDYM turned on (for geochemistry) showed it led to unacceptably long runtimes (1 day of simulation time = 1 day of real time). This is due to the very large number of grid cells/computational units in the model that complex geochemical equations must be solved on. To achieve faster runtime for geochemistry simulations the model grid was straightened (Figure 2, right) and merged to create a 25 m wide by 200 m long by 0.5 m deep model grid cell. Testing of this grid gave acceptable results for hydrodynamic parameters and resulted in runtimes of the order of 25:1. Results from this grid are presented in this report.

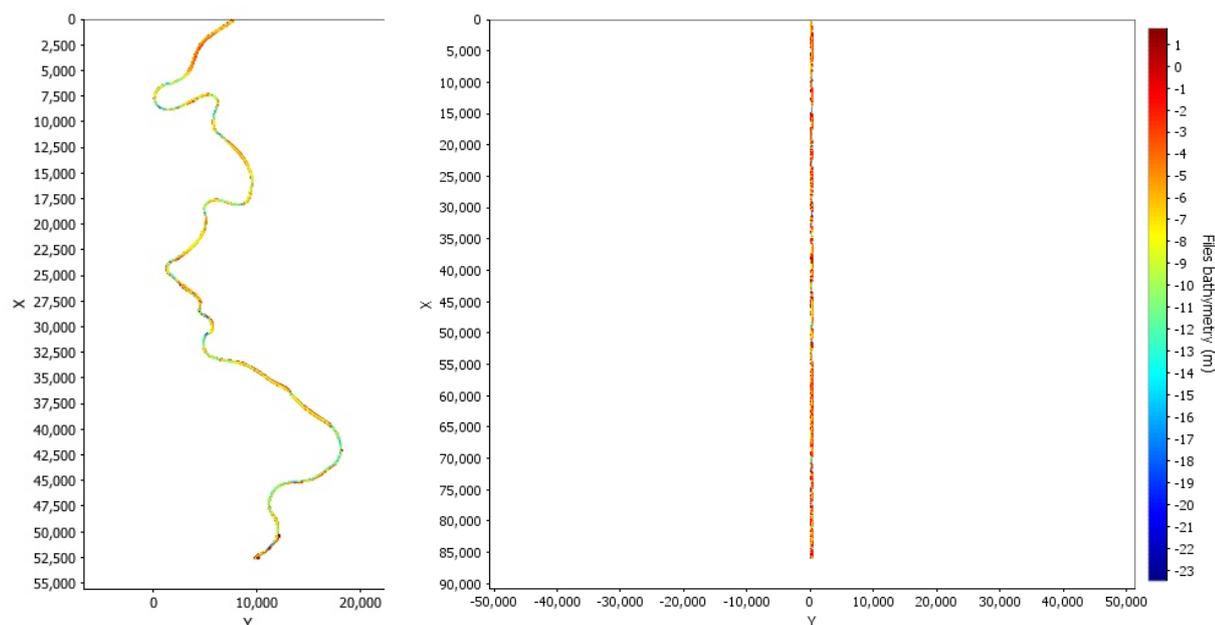


Figure 2 Lower Murray unstraightened (left) and straightened grid (right)

Parameterisation of ELCOM-CAEDYM Model

Data was obtained from various sources to parameterise the model as shown in Table 1. Data for the ELCOM (hydrodynamics) component of the model was available hourly–daily via automated telemetry systems. Data for the CAEDYM geochemical component of the model was available weekly–fortnightly which represented the sampling frequency for these parameters.

For the CAEDYM parameters in the river, water quality data were obtained from SA Water offtake locations at Mannum, Murray Bridge and Taillem Bend (Figure 1). For the CAEDYM parameters in the drainage inputs to the river, water quality data were obtained via grab sampling at the point of discharge to the river. All sampling was undertaken in accordance with standard methods (APHA 2005). New polyethylene bottles, washed and rinsed with de-ionised water, were used to collect samples for laboratory analysis of acidity, alkalinity, major ions and nutrients. Acid-cleaned bottles were used to collect samples for metal analysis.

Laboratory analyses were undertaken by the Australian Water Quality Centre's National Association of Testing Authorities (NATA) accredited laboratory using Standard Methods (APHA 2005 and EPA 200.8). NATA accreditation requires maintenance and documentation of strict quality control procedures. pH, specific electrical conductivity ($\mu\text{S}/\text{cm}$ at 25°C), dissolved oxygen and oxidation-reduction potential were measured in the field at the time of sample collection using a calibrated instrument (YSI Pro Plus). Total alkalinity in the field and laboratory was measured by titration to a pH 4.5 end-point. The field titrations were performed using a commercially available test kit (HACH model AL-DT).

Soluble ($<0.4 \mu\text{m}$ filtered) and total (following EPA 200.8 reflux digestion with nitric and hydrochloric acids) metals (Al, Fe, Mn, Ni) were measured by ICP-MS (Agilent 7500 series). Major ions (SO_4 , Ca, Mg, Na, K) were also measured by ICP-MS and chloride (Cl) by a Ferricyanide method (APHA 4500-Cl- E), turbidity was measured by a nephelometer, and

nutrients (ammonia NH_4 , total phosphorus TP, total nitrogen TN) by standard colorimetric methods. Specific electrical conductivity (EC, $\mu\text{S}/\text{cm}$ at 25°C) and pH were also measured in the laboratory using calibrated electrodes.

Quality assurance and control checks were carried out in both the field and laboratory, and acceptable results were achieved for replicates (within 10%), blanks, and spikes (85–115 % recovery). Some parameters required additional calculations (listed in Table 1) to be suitable for input into the ELCOM-CAEDYM Model. Some of these calculations also required assumptions to be made on the form or speciation of a particular parameter as described in Table 1.

The key acid neutralising reaction, metal hydrolysis reactions, and solid phases used in the LMRIA CAEDYM Model are shown in Table S1 of the [Appendix](#). The reactions and equilibrium constants (log K values) are the default parameters in the widely used WATEQ4F database (Ball and Nordstrom 1990) and no modification was undertaken of these equilibrium constants in this project.

An additional accompanying model platform, the Aquatic Realtime Management System (ARMS) was used to obtain (via connection to other databases and telemetry systems), process and deliver inputs to the ELCOM-CAEDYM Model and to run different scenarios.

Table 1 Hydrodynamic and water quality parameters used in ELCOM-CAEDYM model and how they were derived from measured data

ELCOM parameter	Units	Obtained	Calculation where applicable
Upstream boundary flow	m^3/s	Via telemetry and website ¹ for Lock 1	Flow in ML/day at Lock 1 converted to m^3/s
Upstream boundary salinity	g/L	Via telemetry for site AA4261161 (Mannum Town Wharf)	Conductivity (in $\mu\text{S}/\text{cm}$)* 0.59/1000 (local conversion factor)
Upstream boundary temperature	$^\circ\text{C}$	Via telemetry for site AA4261161 (Mannum Town Wharf)	N/a
Downstream boundary level	m AHD	Via telemetry for site A4261159 (2 km downstream Wellington Ferry)	N/a
Downstream boundary salinity	g/L	Via telemetry for site A4261159 (2 km downstream Wellington Ferry)	Conductivity (in $\mu\text{S}/\text{cm}$)* 0.59/1000 (local conversion factor)
Downstream boundary temperature	$^\circ\text{C}$	Via telemetry for site A4261159 (2km downstream Wellington Ferry)	N/a
Drainage ² flow	m^3/s	Via telemetry	N/a
Drainage ² salinity	g/L	Via telemetry	Conductivity (in $\mu\text{S}/\text{cm}$)* 0.59/1000 (local conversion factor)
Drainage ² temperature	$^\circ\text{C}$	Via telemetry	N/a
Temperature	$^\circ\text{C}$	Field probe	N/a
Salinity	g/L	Field probe	Conductivity (in $\mu\text{S}/\text{cm}$)* 0.59/1000 (local conversion factor)
pH		Field probe	N/a

ELCOM parameter	Units	Obtained	Calculation where applicable
pE		Field probe	$=((5040.1)/(\text{TempC} + 273.15)) * (\text{ORPmV} + 200) / 1000$, Set to 4 if ORP not available
DO	mg/L	Field probe	N/a
DIC	mg/L	Laboratory derived	Sum of bicarbonate and carbonate ions (derived parameters in laboratory data) converted to mg/L C
Ca	mg/L	Laboratory	Use Ca soluble value in mg/L from laboratory data
Mg	mg/L	Laboratory	Use Mg soluble value in mg/L from laboratory data
Na	mg/L	Laboratory	Use Na soluble value in mg/L from laboratory data
K	mg/L	Laboratory	Use K soluble value in mg/L from laboratory data
Cl	mg/L	Laboratory	Use Cl soluble value in mg/L from laboratory data
SO4	mg/L	Laboratory	Use SO ₄ soluble value in mg/L from laboratory data
F	mg/L	Laboratory	Use F soluble value in mg/L from laboratory data
Fe(3) Fe(2)	mg/L	Laboratory derived	Examined soluble Fe, Fe(2)/Fe(3) speciation from PHREEQC Set drain soluble Fe = Fe(2) in CAEDYM (Fe(3) = 0) Set river soluble Fe = Fe(3) in CAEDYM (Fe(2) = 0)
Al		Laboratory	Use Al soluble value in mg/L from laboratory data
MnII	mg/L	Laboratory derived	Use Mn soluble value in mg/L from laboratory data
Ni and other metals (Zn, Co, etc)	mg/L	Laboratory data	Use metal soluble value in mg/L from laboratory data
Goethite (FeOOH)	mol/L	Laboratory derived	$=((\text{Total Fe} - \text{Soluble Fe}) / (\text{MW Fe} / \text{MW Goethite})) / \text{MW Goethite} / 1000$ Where MW Goethite = 88.9, MW Fe = 55.9
Gibbsite (Al(OH) ₃)	mol/L	Laboratory derived	$=((\text{Total Al} - \text{Soluble Al}) / (\text{MW Al} / \text{MW Gibbsite})) / \text{MW Gibbsite} / 1000$ Where MW Gibbsite = 78, MW Al = 27

ELCOM parameter	Units	Obtained	Calculation where applicable
Birnessite (MnO ₂)	mol/L	Laboratory derived	= (((Total Mn – Soluble Mn)/(MW Mn/MW Birnessite))/MW Birnessite)/1000 Where MW Birnessite = 86.9, MW Mn = 54.9
DOCL	mg/L	Laboratory derived	Dissolved organic carbon in laboratory data. Assumed it was labile.
POCL	mg/L	Laboratory derived	Set to zero
PONL		Laboratory derived	= Total kjeldahl nitrogen – NH ₄ as N from laboratory data
DONL		Laboratory derived	Set to zero
POPL		Laboratory derived	= Total phosphorus – Filterable reactive P from laboratory data
DOPL		Laboratory derived	Set to zero
NH ₄		Laboratory	Use Ammonia as N in laboratory data
NO ₃		Laboratory	Use Nitrate as N in laboratory data
PO ₄		Laboratory	Used Filterable Reactive P as P in laboratory data
SiO ₂	mg/L	Laboratory	Silica – reactive in laboratory data
SSOL1		Laboratory derived	SSOL1 = (1.4406 * turbidity (NTU from river lab data) + 4.6884) * 0.75 From EPA LMRIA data, Mosley and Fleming 2010 $r^2 = 0.7142$ and SA Water particle size analysis (1 μm size fraction in river)
SSOL2		Laboratory derived	SSOL2 = (1.4406 * turbidity (NTU from river lab data) + 4.6884) * 0.25 From EPA LMRIA data, Mosley and Fleming 2010 $r^2 = 0.7142$ and SA Water particle size analysis (10 μm size fraction in river)
SSOL3		Laboratory derived	SSOL3 = (1.4406 * turbidity (NTU from drain lab data) + 4.6884) From EPA LMRIA data, Mosley and Fleming 2010 $r^2 = 0.7142$ (particles in drain water)
PIP		Laboratory derived	Set to zero
PIN		Laboratory derived	Set to zero

ELCOM parameter	Units	Obtained	Calculation where applicable
CYANO			Blue-green algae total from laboratory data converted to mg/L Chl. a
CHLOR			Set to zero
FDIAT			Set to zero
MDIAT			Set to zero
IN for above phyto groups			Set to 1 (from Hipsey <i>et al</i> 2010)
IP for above phyto groups			Set to 0.1 (from Hipsey <i>et al</i> 2010)

¹ Available at www.sawater.com.au/SAWater/Environment/TheRiverMurray/RMOU/Dailyflow.htm

² Sites with monitoring were Burdett, Jervois (Woods Point), Jervois (Wellington end), Long Flat, Monteith, Pompoota, River Glen, Toora, Woods Point. Other minor drainage contributions from Westbrook Park, Kilsby, Mobilong, McFarlanes, and Glen Lossie irrigation areas were not included in the model.

Conservative tracer modelling

Preliminary hydrodynamic modelling using just ELCOM (no CAEDYM geochemistry) was undertaken using the unstraightened grid to assess dilution rates for the acid drainage discharges. This was undertaken by assigning a conservative tracer in ELCOM for each acidic drainage discharge and assessing their combined dilution over time under different river flow scenarios and pump rate scenarios. As discussed earlier using these tracers in ELCOM is much more computationally efficient compared to full geochemical simulation. This allowed the combined effect of flow and pump rates to be more easily assessed without the need to run multiple time consuming scenarios. The disadvantage is that these assume conservative dilution when many parameters (eg pH, metals) are known to behave non-conservatively. Nevertheless, tracer modelling provides a useful starting point for sensitivity testing of the likelihood of significant water quality changes occurring.

The following scenarios were modelled.

Scenario 1 – worst case

In this scenario all of the pumps are running continuously at their maximum rated capacity. This is intended to demonstrate that there is potential to exceed guideline values under worst case conditions.

River conditions: constant flow at Lock 1 of 4,000, 3,000 and 2,000 ML/day. Mean river level set at 0.75 m. Historical salinity and temperature for the river were used as model input as well as short-term fluctuations in river level, ie from wind.

Weather conditions: the model requires input data for meteorological conditions during the simulation. Historical weather conditions from Tailem Bend were used to generate weather conditions consistent with the time of year to be simulated by the model. Weather information includes wind (speed and direction), temperature, precipitation, humidity and solar radiation.

Irrigation drainage return: Pumping of drainage water into the river was simulated for the following areas of concern; Jervois, Woods Point, Monteith, River Glen, Pompoota, Long Flat, Baseby, Toora, Kilsby and Burdett. Pumps were assumed to be running continuously at maximum efficiency. The temperature of drainage water was based on previous data (EPA), salinity was based on data collected at similar time to metal samples, and assumed to be constant over the modelled time period. Conservative, dimensionless tracers for each site were modelled to represent the pollutants in each drain and assumed to be constant over the simulation time period. Modelled downstream tracer concentrations were used with drain-water analysis data to estimate river water quality using a mass balance approach.

Simulation parameters: flow, temperature, salinity, conservative tracers.

Scenario 2 – typical summer pumping

In this scenario pumps are running to a more realistic schedule. This is intended to demonstrate the likely outcome under normal conditions.

River conditions: same as scenario 1.

Weather conditions: similar to scenario 1, November–February.

Irrigation drainage return: similar to scenario 1, except pumps were running in a stop-start fashion similar to actual recorded pumping for the season. Pump rates were assumed to be the last known ratings (measured). Flows from Baseby and Kilsby were not simulated on advice from the EPA that these sites were neutral or not pumping.

Simulation parameters: Flow, temperature, salinity, conservative tracers.

Scenario 3 – typical winter pumping

In this scenario pumps are running to a more realistic schedule. This is intended to demonstrate the likely outcome under normal conditions.

River conditions: Same as scenario 1.

Weather conditions: Similar to scenario 1, June–September.

Irrigation drainage return: Similar to scenario 1, except pumps were running in a stop-start fashion similar to actual recorded pumping for the season. Pump rates were assumed to be the last known ratings (measured). Flows from Baseby and Kilsby were not simulated on advice from the EPA that these sites were neutral or not pumping.

Simulation parameters: Flow, temperature, salinity, conservative tracers.

Comparison scenarios

A series of dilution curves were generated to put the hydrodynamic modelling into context and help to illustrate the expected trend in dilution with decreasing flow. These curves are based on a simple 0D approach where the mass of pollutant added by pumping is fully diluted into the flow in the river. The curves represent four scenarios:

- 1 all pumps operating continuously at maximum rated pump capacity (same as worst case above)
- 2 all pumps operating continuously at their last measured pump capacity
- 3 one pump per site operating continuously at their last measured pump capacity
- 4 typical pumping for each site such that the annual total is equal to previously measured values (Tonkin Consulting, 2007). Similar to scenarios 2 and 3.

Testing ELCOM-CAEDYM code against PHREEQC

Although ELCOM-CAEDYM is a well-established model for hydrodynamics and nutrient-algal interactions there has been limited application to examining surface water acidification and metal geochemistry (Hipsey *et al* 2010). It was considered necessary to undertake fundamental testing of the ELCOM-CAEDYM code against another more established geochemical code, PHREEQC (Parkhurst and Appelo 2013).

A simplified grid was established for testing CAEDYM in an efficient and controlled manner. The grid comprised 10-m grid cells and had total dimensions 100 m wide x 100 m high x 2 m deep (Figure 2). A free slip bottom boundary condition (BC code 2 in ELCOM) was applied and scalar concentrations were forced at the inflow boundary (IFORCEBCSCALARS keyword in ELCOM). The initial water level was initialised at 1 m giving a water volume of 10,000 m³. There was an additional 1m height in bathymetry to add an inflow of acidity to the domain as described further below. Air temperature was matched to the initial water temperature (25°C).

The initial inorganic conditions in the model domain were based on a typical River Murray water composition (temp = 25°C, pH= 8.48, pE = 4, Na =33.4 mg/L, Ca = 20.4 mg/L, Mg = 9.5 mg/L, K = 7.3 mg/L, Cl = 55.23 mg/L, DIC = 21.3 mg/L as C, SO₄ = 2.8 mg/L). In the acid drainage water input in some of the simulations, typical values were used for pH (pH 3)

and soluble metals (Fe = 100 mg/L, Al = 10 mg/L and Mn = 10 mg/L) but for model comparison purposes only SO₄ was adjusted (to 396.7 mg/L) to maintain charge balance with the other major ions (apart from DIC which was zero at that pH) the same concentration as in the river water.

The standard WATEQ4F database in PHREEQC (Ball and Nordstrom 1991) was used for the PHREEQC calculations with the same equilibrium constants and reactions as implemented in the CAEDYM model. For the purposes of the geochemical code testing all biological functions were turned off and all organic carbon concentrations set to zero. Code comparison tests included simulating the carbonate system chemistry with and without acid inputs, and simulations that also included soluble metal (Al, Fe, Mn) acidity and respective potential solid phases (Gibbsite, Goethite, Birnessite).

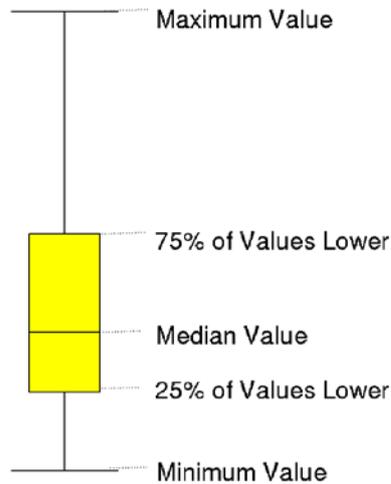
The PHREEQC model was equilibrated both with and without a constant near atmospheric partial pressure of oxygen (-0.7) and carbon dioxide (-3.5). CAEDYM calculates partial pressure of these gases dynamically although equilibrium with the atmosphere will be established over time. CAEDYM simulations were run for four weeks which was generally sufficient to achieve equilibrium as indicated by stability of parameters such as pH and DIC.

Simulations of acid inputs (H⁺ and soluble Fe, Mn and Al) were undertaken by configuring an inflow (1,000 m³ over day 1) in CAEDYM and using the MIX function in PHREEQC (1:10 ratio of drainage water to river water). Results from CAEDYM and PHREEQC were compared at the end of the simulation (28 days) with the results presented for PHREEQC being the atmosphere equilibrated results.

3 Results

Conservative tracer modelling

The amount of pumping that occurs from the LMRIA potentially has a huge impact on the downstream water quality. Other than river flow, this is the major source of uncertainty for future scenarios as the pump usage of landholders cannot be predicted. Figures 3–9 show results of a basic (fully mixed) conservative tracer modelling approach applied to a number of different pumping scenarios. The results of hydrodynamic modelling are overlaid on these curves and represented as box and whisker to indicate the range of values that occur (refer to diagram).



The worst case scenario represents ‘what if all landholders pumped continuously’ and corresponds with for ‘all pumps maximum rated pump rate’ (black line). The hydrodynamic modelling results (Figures 3 and 4) are lower because of incomplete mixing causing salty drain water to pass by the offtake along the bottom of the river.

The worst case scenario represents conditions that are far from what would be expected to occur under normal circumstances. Most irrigation areas typically pump drain water overnight during the off-peak electricity tariff and also using only one pump at a time (if they have more than one). Under these circumstances the risk to water quality is substantially reduced as illustrated by the lowest curve (green) which represents landholders pumping to reach an annual total in line with historical data ie ‘what if landholders pump like normal’.

For the ‘typical summer pumping’ (Figures 5 and 6) discharges occurred in a start-stop manner based on previous pumping. This type of pumping behaviour results in peaks and troughs in the downstream water quality depending on how the discharges from each site overlap with each other. In comparison to a basic modelling approach, some of the peaks are higher because pump rates are faster than the annual average but pumps are only on for some of the time, peaks occur when discharges from multiple sites overlap. However for >75% of the time water quality is better than expected. Based on this type of scenario, health guidelines would not be exceeded for anticipated river flows (>2,000 ML/day). ‘Typical winter pumping’ scenarios (not shown) gave similar results to the summer scenarios.

For the Murray Bridge off-take, modelling showed that guideline values would not be exceeded for any of the scenarios that were simulated (including the worst case). This is because discharge from the only two acidic drains upstream of the offtake does not show any significant effect, even during lower summer flows.

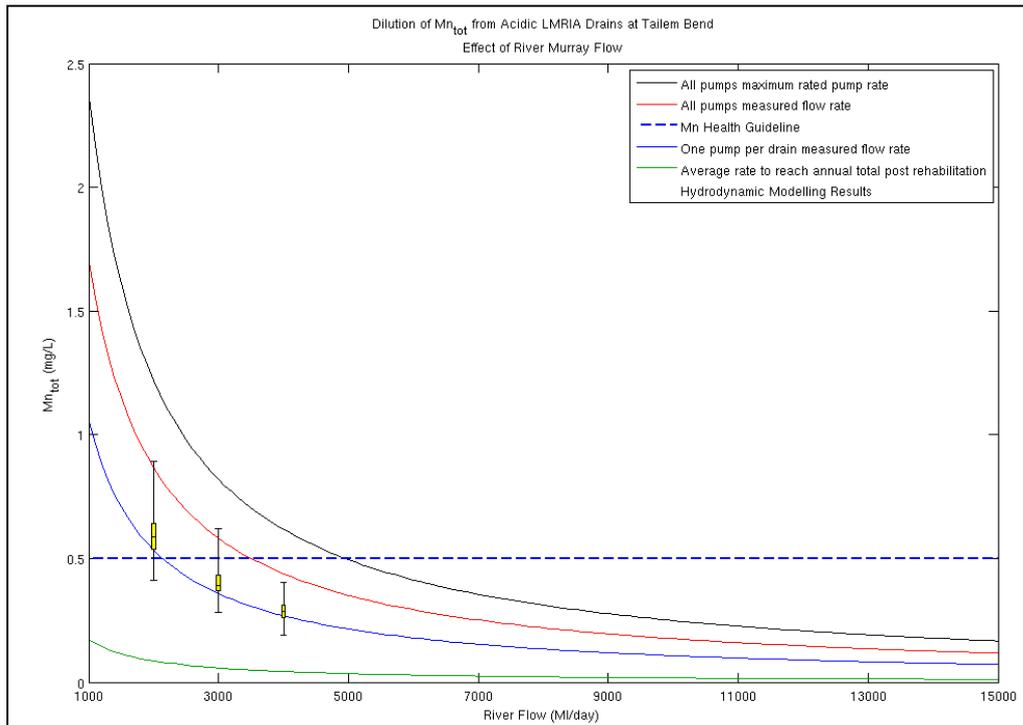


Figure 3 Comparison of ELCOM total Mn modelling results for the worst case scenario (box and whisker) against basic mass balance model (curves, assumes complete mixing). Manganese health guideline value exceeded for >75% of time at a flow of ~2,000 ML/day with all pumps operating 24/7 for each drain.

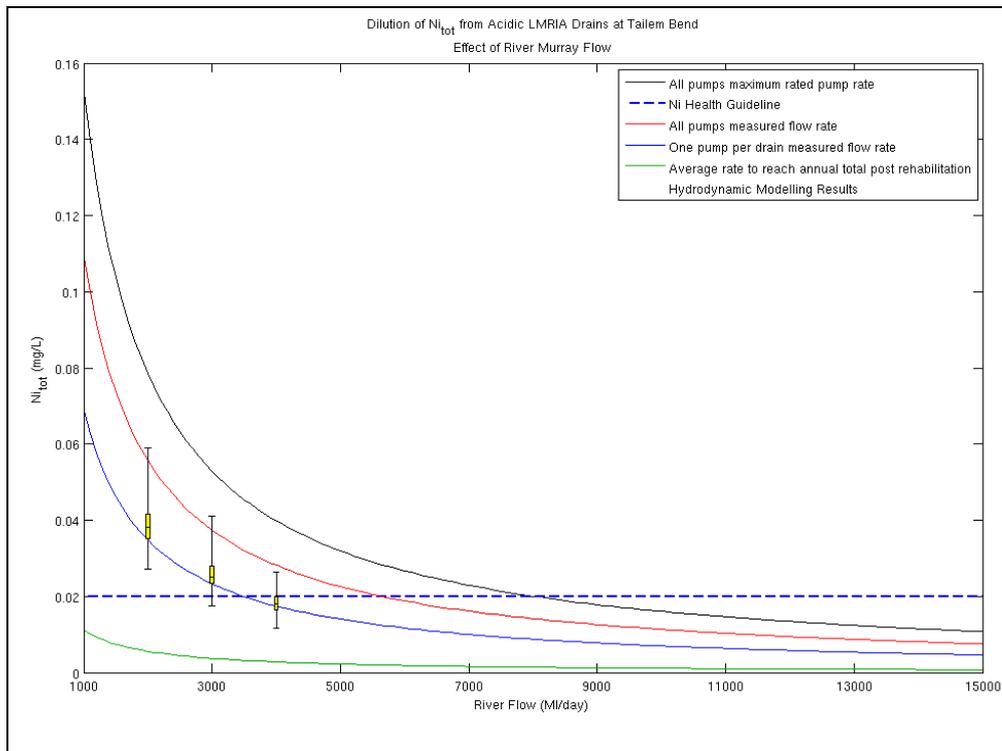


Figure 4 Comparison of ELCOM total Ni modelling results for the worst case scenario (box and whisker) against basic mass balance model (curves, assumes complete mixing). Nickel health guideline value exceeded for >75% of time at a flow of ~3,000 ML/day with all pumps operating 24/7 for each drain.

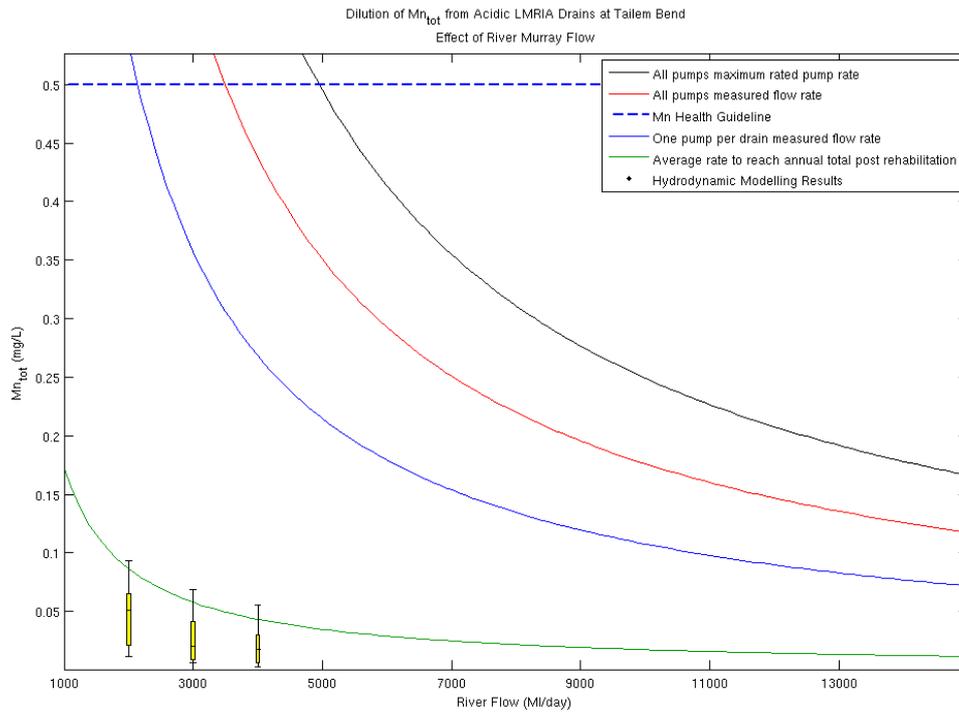


Figure 5 Comparison of ELCOM total manganese modelling results for a typical summer scenario (box and whisker) against basic mass balance model. Manganese health guideline value never exceeded under conditions tested. Aesthetic guideline (0.1 mg/L) may be reached when flow <2,000 ML/day

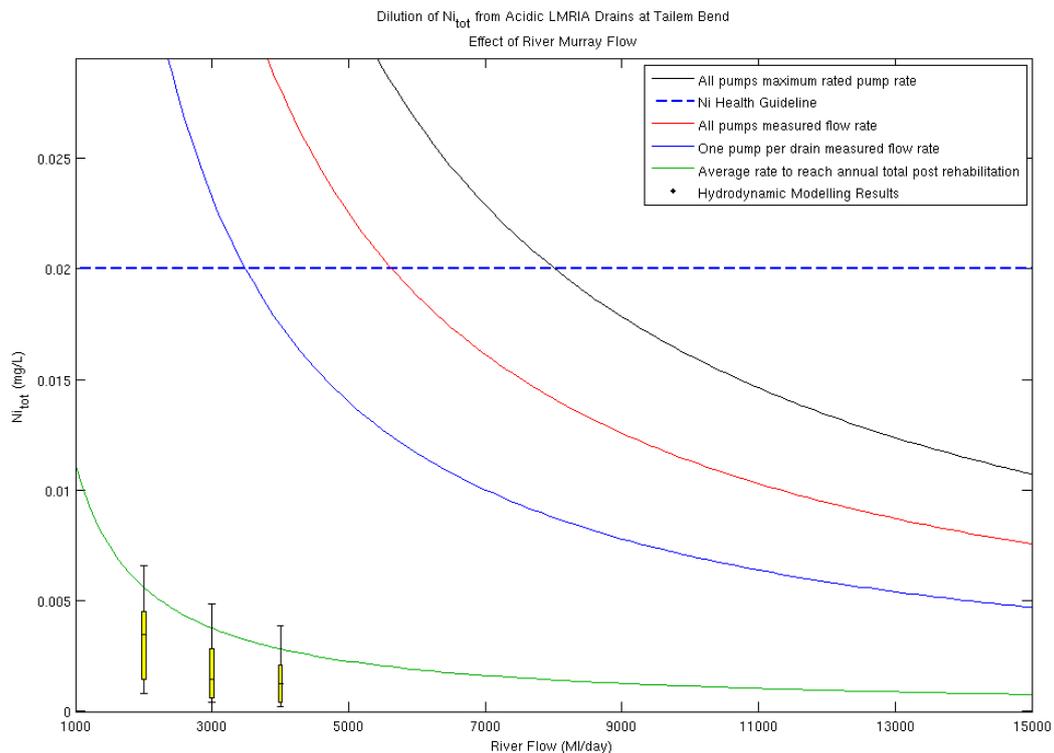


Figure 6 Comparison of ELCOM total nickel modelling results for a typical summer scenario (box and whisker) against basic mass balance model (curves, assumes complete mixing). Nickel health guideline value never exceeded under conditions tested.

Code testing of CAEDYM and PHREEQC

Simulation 1 assessed if, in the absence of acid inputs, CAEDYM could accurately represent the CO₂ system in comparison with PHREEQC, and whether CAEDYM could maintain stability of the CO₂ system in the absence of external inputs. Excellent agreement (0% difference) was obtained between PHREEQC and CAEDYM for pH and DIC and the CAEDYM simulation was stable over the 28-day test period (Table 2).

Table 2 Simulation 1: comparison of PHREEQC and CAEDYM results for simulating the CO₂ system with no acid inputs

Parameter	PHREEQC	CAEDYM	Difference	% Difference
pH	8.48	8.48	0.000	0.0
DIC (mg C/L)	21.3	21.3	0.000	0.0

Simulation 2 added a known amount of acid in the form of H⁺ via a pH 3 inflow. The CAEDYM results were in good agreement (<2% difference) with the PHREEQC results (Table 3) for pH and DIC.

Table 3 Simulation 2: comparison of PHREEQC and CAEDYM results for simulating the CO₂ system with acid inputs in form of H⁺ only

PHREEQC & CAEDYM	PHREEQC	CAEDYM	Difference (Day 28)	% Difference
pH	8.409	8.32	0.089	1.2
DIC (mg C/L)	18.216	18.3	-0.084	-0.4

Simulation 3 added a known amount of acid in the form of H⁺ (pH 3) and soluble metals (Fe, Al, Mn). The pH results were in good agreement with the PHREEQC results for pH (Table 4) but the DIC showed slightly worse agreement (10% different) compared to simulations 1 and 2. This could be due to biological influences as DIC also includes dissolved CO₂.

Table 4 Simulation 3: comparison of PHREEQC and CAEDYM results for simulating the CO₂ system with acid inputs in form of H⁺ and soluble Al, Fe and Mn

Parameter	PHREEQC	CAEDYM	Difference	% Difference
pH	8.20	8.25	-0.05	-0.6
DIC (mg C/L)	11.28	12.5	-1.24	-9.4
Fe (mg/L)	9.089	9.08	0.01	0.1
Al (mg/L)	0.907	0.91	0.00	-0.4
Mn (mg/L)	0.909	0.91	0.00	-0.1

Given the inherent differences between PHREEQC (static equilibrium model with no biological functionality) and CAEDYM (dynamic equilibrium geochemical model with linked biological processes), some differences in results would be expected. The generally close agreement between the two models suggests that CAEDYM is generally performing satisfactorily for modelling acid drainage discharges to a neutral water body.

Model performance in the far-field (whole river reach)

Comparison of measured to modelled water quality at Taillem Bend is shown in Figures 7a–c. The model gave satisfactory results for most parameters.

Key hydrodynamic parameters of water level and salinity were well represented in the model (Figure 7a). Temperature was slightly overestimated in the model and the reason for this is unclear and requires further investigation.

The alkalinity was also well represented by the model although pH showed some over-prediction for one part of the time period (Figure 7a). The model performed well against the measured values for dissolved oxygen (Figure 7a), chloride and sulfate (Figure 7b).

The model could generally predict the trends in metal (Al, Fe and Mn) satisfactorily (Figures 7b–c). The large spike observed in soluble Mn in December 2011 was also well predicted in the model.

Model results where the LMRIA inputs were set to zero are also shown in Figures 7b and c for some parameters that are very high in the acidic drainage water (sulfate, soluble Fe and Mn). As expected a lowering in concentration of these parameters is observed.

Model performance statistics (r^2 and root mean square error, RMSE) for the tested period are shown in Table 5. (See Arhonditsis and Brett (2004) for further details on model performance checking for geochemical simulations.) The model performed well ($r^2 = 0.7$ – 0.9) against measured data for water level, salinity, alkalinity, total and soluble aluminium and, iron, and soluble manganese. Poor results were obtained for total manganese which may relate to the rate of oxidation of soluble manganese in the model being different than observed in the river. Poorer results were also obtained for pH and dissolved oxygen ($r^2 = 0.2$, although relative error only 5.6%). This may relate to the biological processes within the CAEDYM model having an influence on the results. We did not have sufficient time to work on refining the biological aspects of the model.

The model results under simulated lower flow conditions are discussed further below.

Table 5 Model performance checking statistics (linear correlation coefficient, r^2 and root mean square error, RMSE) between modelled and measured values of water level, salinity, temperature, dissolved oxygen (DO), pH, alkalinity (Alk.), total (tot.) and soluble (sol.) Mn, Fe and Al, sulfate (SO₄), chloride (Cl), and nickel (Ni).

Statistic	Level	Salinity	Temp	DO	pH	Alk.	Mn(sol)	Mn(tot)
r^2	0.967	0.832	0.801	-0.290	0.214	0.776	0.776	0.077
RMSE	0.022	0.012	3.479	0.931	0.580	5.758	0.007	0.000

Statistic	Fe(sol)	Fe(tot)	Al(sol)	Al(tot)	SO ₄	Cl	Ni
r^2	0.829	0.807	0.852	0.812	0.517	0.522	0.451
RMSE	0.049	0.000	0.066	0.000	2.047	5.735	0.000

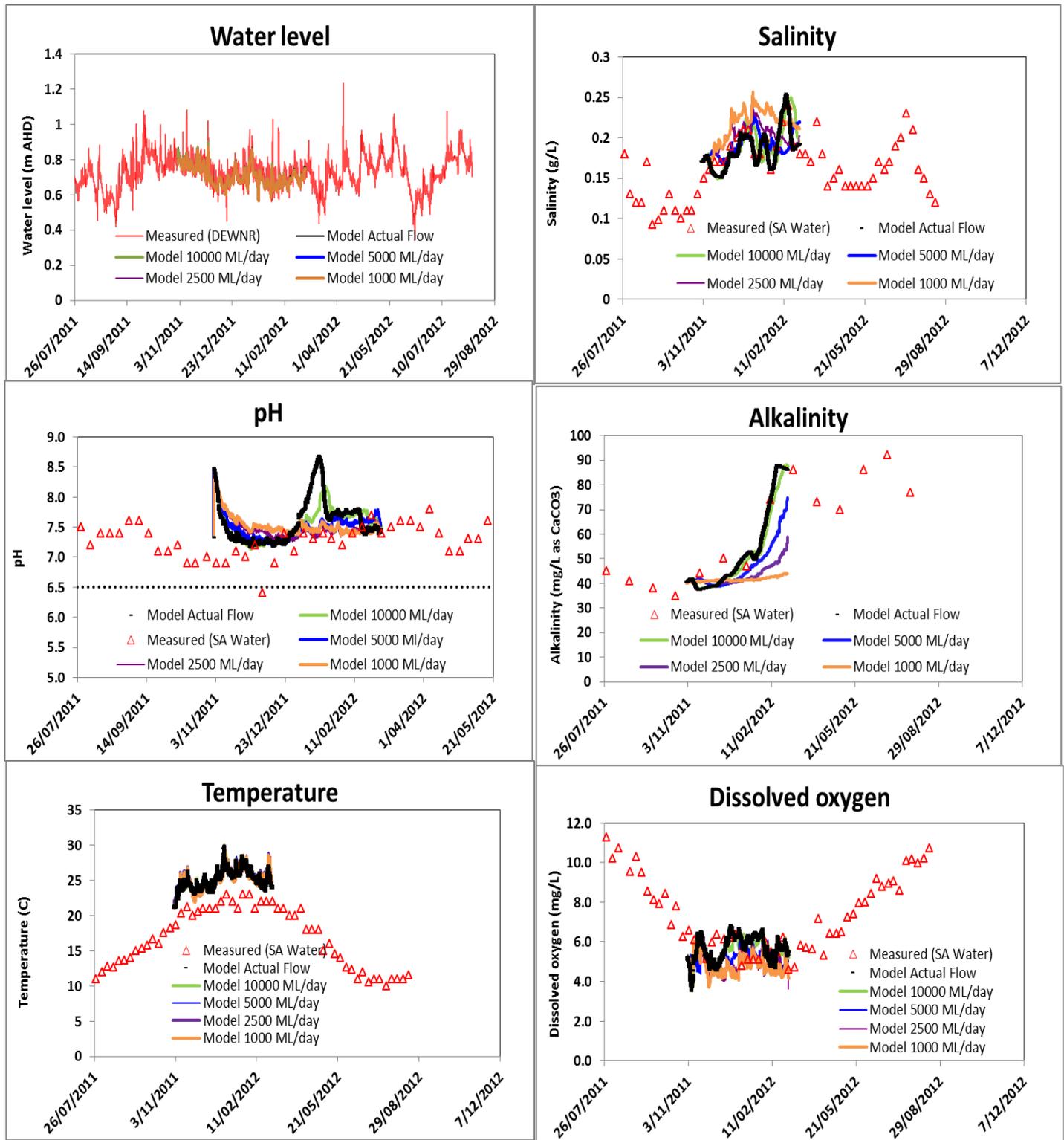


Figure 7a Measured (triangles) versus modelled (thick, black line) water level and water quality (salinity, pH, temperature, alkalinity, dissolved oxygen) at the Tailm Bend SA Water offtake. Lower river flow scenarios are also shown along with a no drain input scenario for SO₄. The dashed line is the guideline where applicable from ADWG (2010).

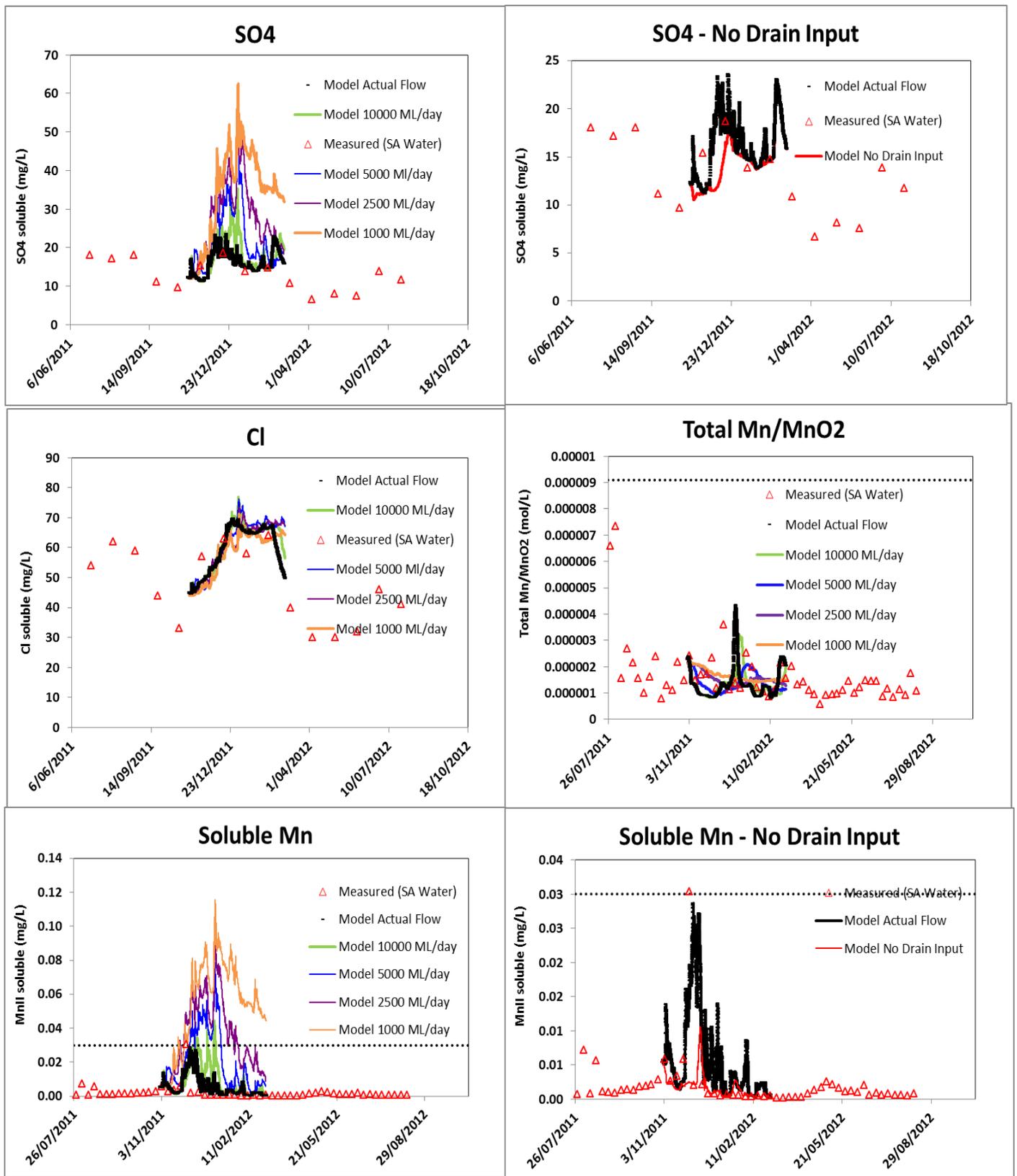


Figure 7b Measured (triangles) versus modelled (thick, black line) water quality (sulfate, chloride, pH, total and soluble manganese, Mn) at the Taillem Bend SA Water offtake. Lower river flow scenarios are also shown along with a no drain input scenario for sulfate and soluble Mn. The dashed line is the guideline where applicable from ADWG (2010).

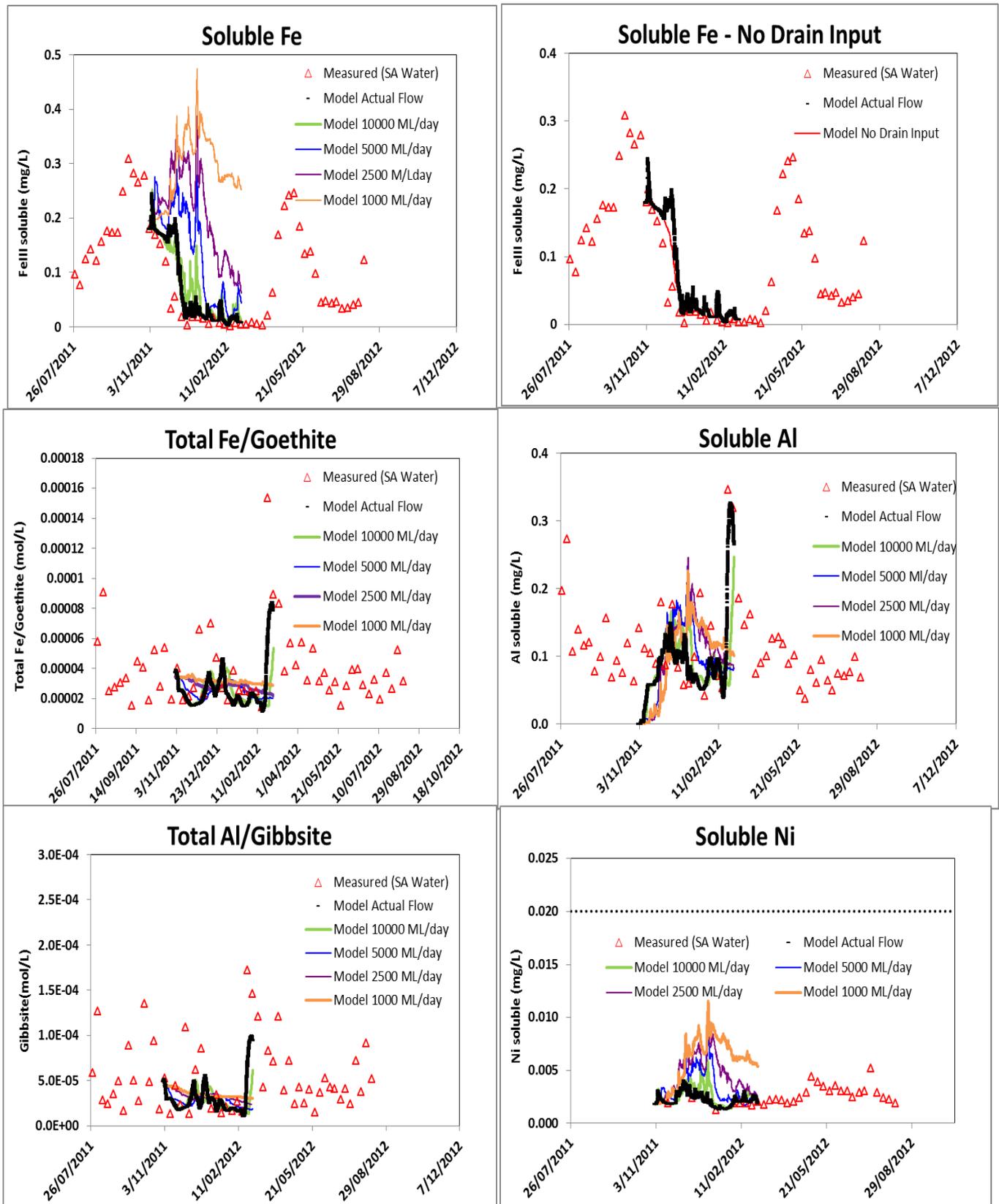


Figure 7c Measured (triangle) versus modelled (thick, black line) water quality (total and soluble iron Fe and aluminium Al, and soluble nickel Ni) at the Tailm Bend SA Water offtake. Lower river flow scenarios are also shown along with a no drain input scenario for soluble Fe. The dashed line is the guideline where applicable from ADWG (2010).

Model performance in the near-field (localised discharge zone)

It was also considered important to assess the localised risk of acid discharges, particularly for aquatic ecosystems in the immediate vicinity, and to assess the potential for the size of the impacted zones to increase under lower flows. Figure 8 shows the model results for an acid drainage discharge in comparison to the measured results. The general behaviour of the measured plume was satisfactorily represented in the model. The plume sinks to the bottom of the river near the discharge zone and travels downstream with observed effects still remaining after 1–2 km. Comparison of a measured and modelled salinity profile is shown in Figure 9.

The general features of the plume are adequately represented in the model but the plume tends to disperse more upwards in the model than in reality. This is likely due to “numerical diffusion”, an artefact of the computational processes used in ELCOM-CAEDYM and other similar models. Further model refinement to attempt to reduce these numerical diffusion issues would be beneficial but this issue is likely not critical in terms of management outcomes. The consequences are that the plume disperses more rapidly throughout the water column in the model, leading to a less conservative model prediction in the near-field.

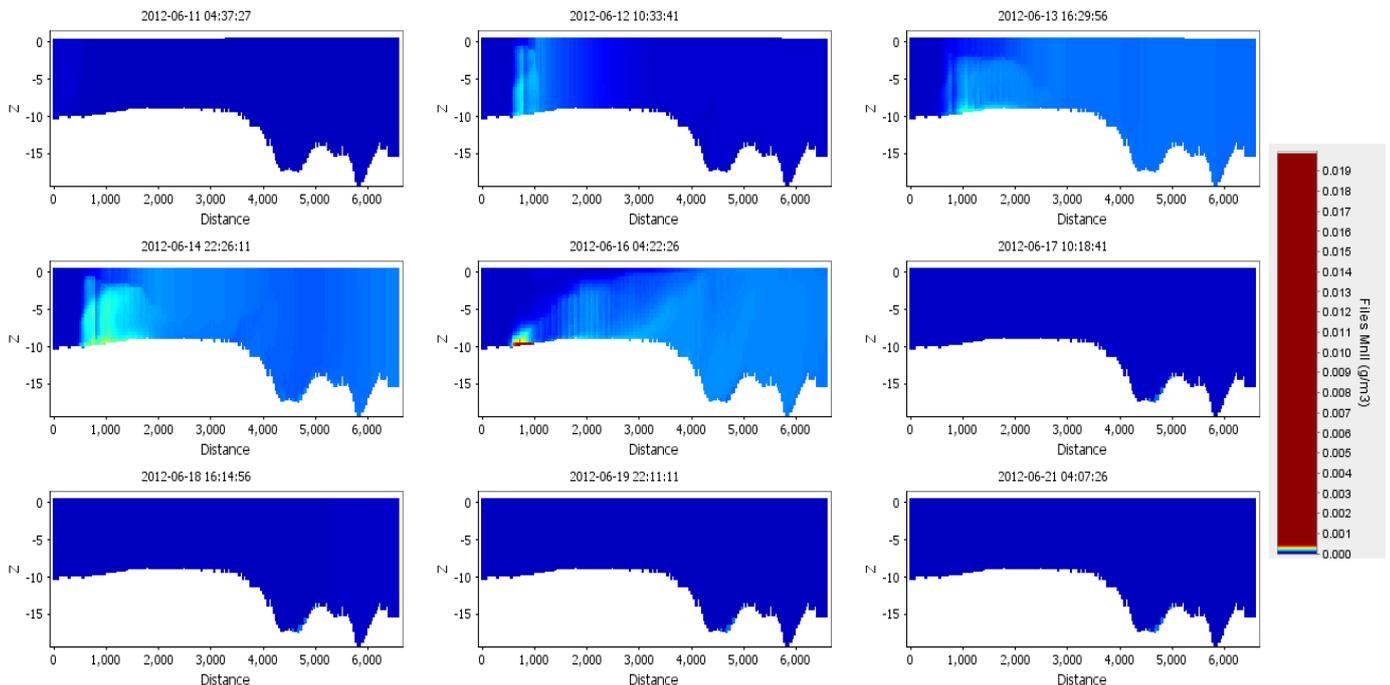


Figure 8 TOP—Measured (red symbols) versus modelled (black line) soluble manganese (Mn) at the Taillem Bend SA Water off take from the 3D geochemical model. Lower river flow scenarios are also shown. The dashed line is the SA Water aesthetic guideline for Mn. BOTTOM—Modelling of the soluble Mn in the acid drainage discharge from Jervois (Woods Pt end) with distance (m) downstream towards Taillem Bend (raw water off take at approximately 4,500 m). The discharge began on 13 June 2012 and ceased by 17 June 2012.

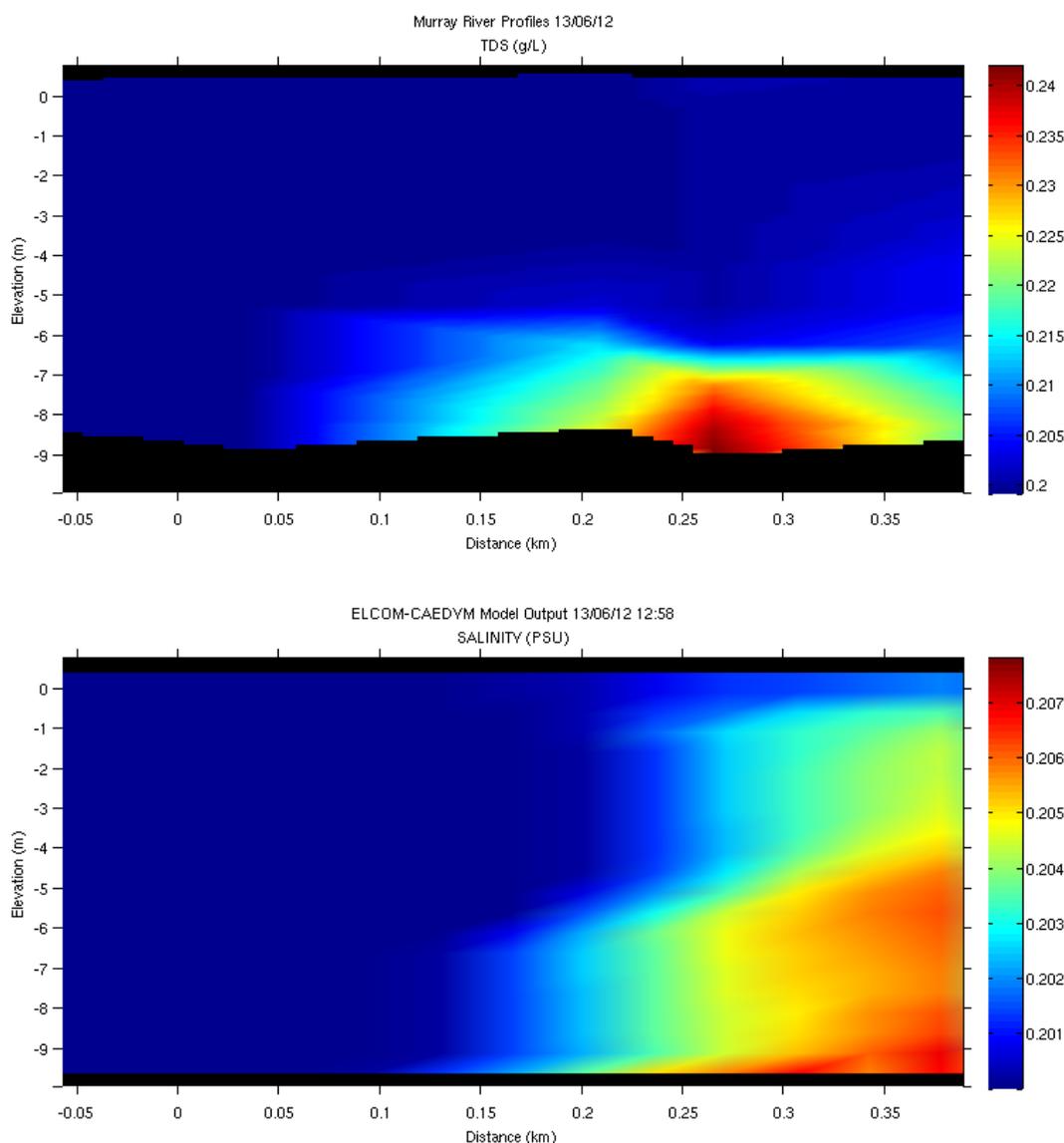


Figure 9 Measured vs modeled salinity in the LMRIA discharge from Jerois (Woods Point end) irrigation area on 13 June 2012

Simulated water quality risks under lower flow conditions

Model simulation results for lower river flows are also shown on Figure 7 for the Taillem Bend water offtake. pH and alkalinity are predicted to be maintained in the river at this location even at very low flows (1,000 ML/day). The results at 5,000 ML/day (approximately current river flows) are generally consistent with current water quality results showing minimal detectable effect on river alkalinity. The main issue of concern identified in the modelling results is the potential for soluble manganese (Mn) to more regularly exceed aesthetic raw drinking water guidelines (ADWG 2010) at Taillem Bend (Figure 7). This non-health based risk is likely manageable with potential for additional water treatment processes (pre-chlorination) to be employed if required.

The potential for water quality to be poorer at locations other than Taillem Bend was assessed using an exceedence (of water quality guidelines) plot for key parameters (Figure 10). There were very low (<5%) exceedences observed for pH < 6.5, and key metals of interest (Mn > 0.1 mg/L and Ni > 0.02 mg/L, relating to aesthetic guideline values in ADWG 2010) along the entire model domain. pH could fall below 7 (probability of exceedence 30–50 %) in some of the deeper reaches of the river but this is unlikely to be a major issue as long as it remains above 6.5 where alkalinity would be present. These results suggest regional water quality risks arising from the LMRIA should remain low throughout the model domain, even at lower flows.

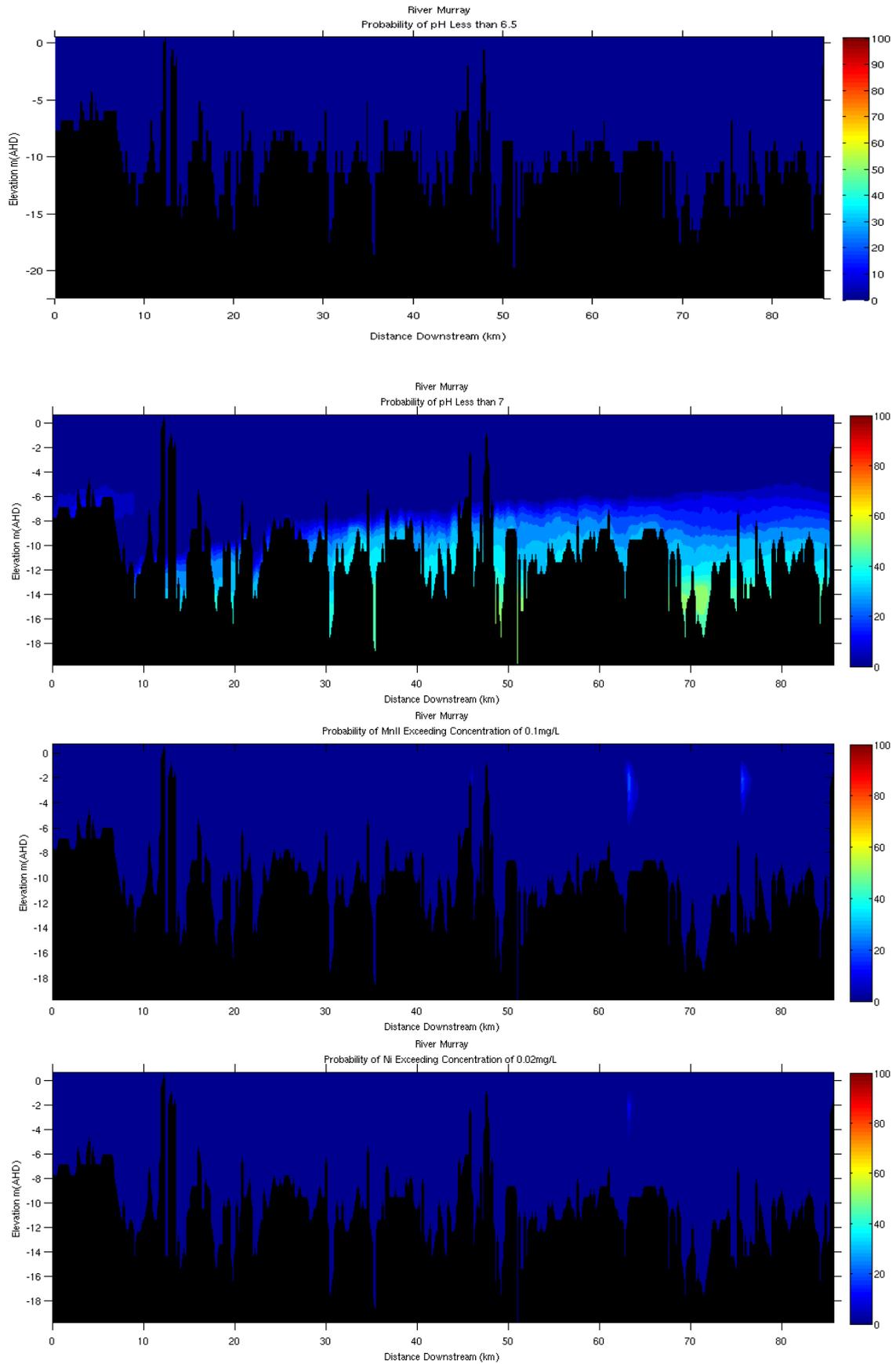


Figure 10 Probability of exceeding pH <6.5, pH <7, Mn >0.1 mg/L and Ni >0.02 mg/L for the entire model domain at a flow of 2,500 ML/day

Current CSIRO ecotoxicity experiments (Adams *et al* in prep) suggested that dilution of the acid drainage water to about 5–50% would be required to protect lethal toxicity to aquatic ecosystems. Sub-lethal impacts (eg growth, reproduction) could occur at lower dilutions. We used the conservative tracer function in ELCOM-CAEDYM to assess the extent of dilution at low flows (2,500 ML/day) of the LMRIA acid drainage discharges. The probability of exceeding 5, 0.5, 0.1 and 0.01 % dilutions of combined LMRIA acid drainages is shown in Figure 11. The results show that lethal toxicity is very unlikely as the 5% dilution is not exceeded except in two very localised points (large Jervois drain discharges). The possibility of sub-lethal impacts at lower dilutions requires further in situ ecotoxicity assessment and field sampling to determine the type of ecological community present in the vicinity of the acid discharges. No kills of fish or other aquatic species have been reported to our knowledge in the Lower Murray over the time period of the acid drainage discharges. This is consistent with the model findings.

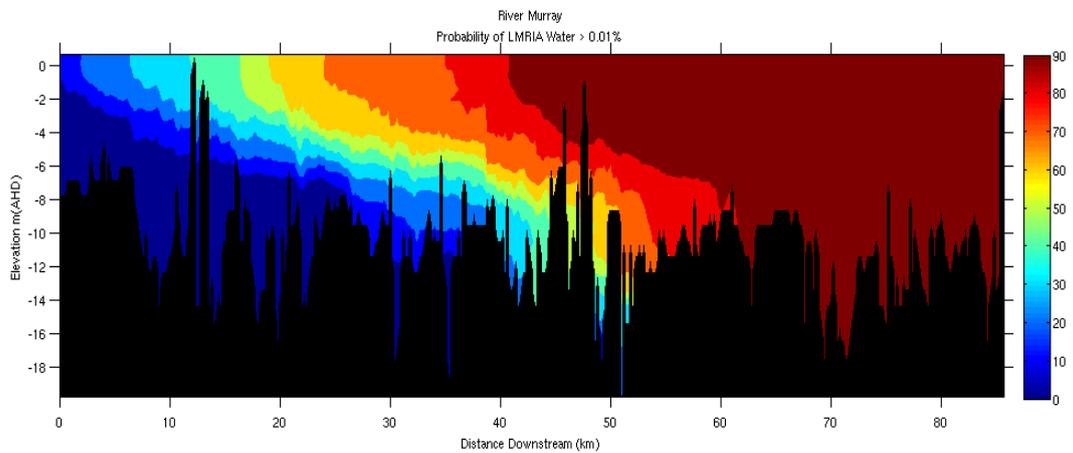
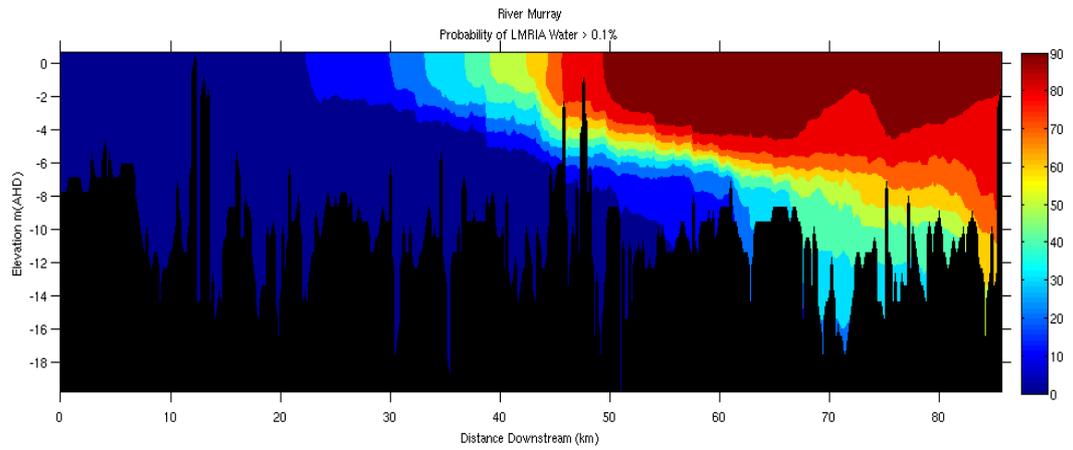
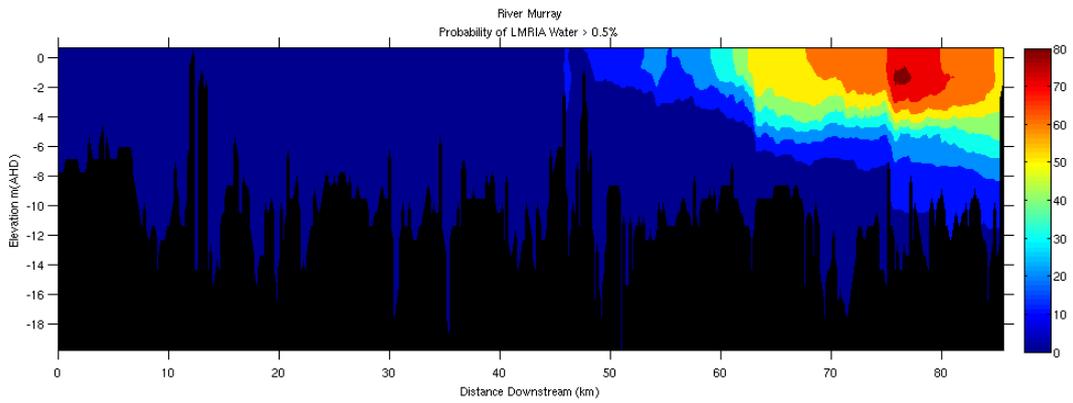
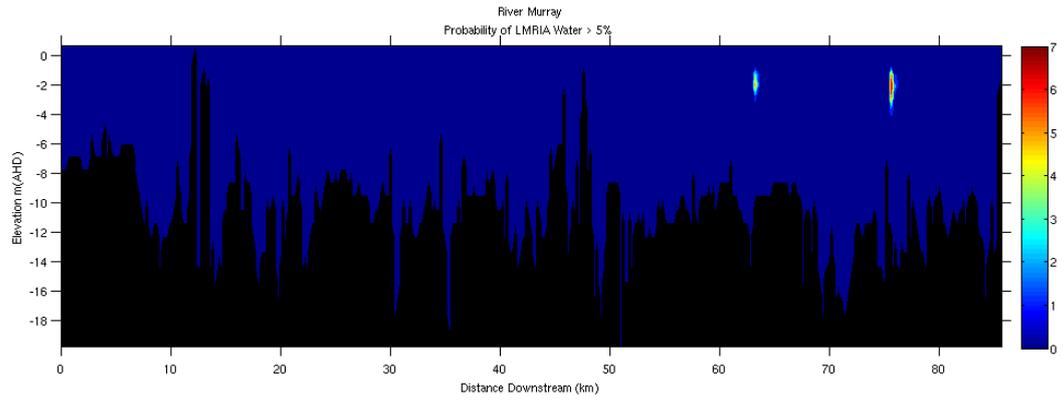


Figure 11 Water quality guideline exceedence probability for soluble Mn, and 5 and 0.5% dilutions in the entire Lower Murray river model domain

4 Conclusion

To our knowledge this is the first time a 3D model has been developed that successfully represents the complex hydrodynamic and geochemistry when acidic drainage water mixes with a pH neutral river system.

The model was applied to assess the potential water quality risks arising from acid drainage discharges from the LMRIA to the lower River Murray.

Initial testing of the model in conservative tracer (ELCOM) mode showed that major water quality risks were unlikely, except under unrealistic/worst case pumping scenarios.

The model grid was straightened to achieve acceptable runtimes for geochemical simulation using ELCOM-CAEDYM.

Testing of the ELCOM-CAEDYM model against PHREEQC gave generally satisfactory results for key parameters such as pH, DIC and soluble metals.

Model performance against observed water quality at Tailem Bend was good for pH, alkalinity, dissolved oxygen, soluble and total metals. Testing of the model performance in the localised mixing zone also gave satisfactory results.

The model was used to simulate lower flow conditions on the River Murray. The main risk that emerged was the potential for soluble Mn to exceed aesthetic (non-health based) guidelines at Tailem Bend raw water offtake. This risk is currently considered manageable considering what we currently know about the acid drain–river interaction and the overall River Murray system's behaviour. Soluble Ni (which exceeded guidelines in the undiluted drain water) was not predicted to pose any risks to raw water offtakes under lower flow conditions.

Further validation of the model under lower flow conditions is recommended. The risks to benthic ecosystems under lower flows, particularly in the reach of the river near Tailem Bend, also require further consideration.

5 Recommendations

While acid drainage is still being discharged to the River Murray the following is recommended:

- Ongoing targeted monitoring of soil, acid drainage water, ground water, and acid drainage plumes discharged to the River Murray for modelling and risk management purposes.
- Ongoing monitoring (via telemetry) to estimate drainage volumes discharged from the LMRIA pumps.
- Ongoing targeted monitoring of ambient river water quality parameters relevant to the acid sulfate issue and model performance checking.
- Further testing of model performance at low river flows.
- Ongoing implementation of the contingency plan.

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Appendix/supplementary material

Table S1 Species and reactions and equilibrium constants used in CAEDYM for the CO₂ system, acid neutralisation and metal hydrolysis

Species name	Reaction	Log K (25C)	Delta H (kJ/mol)
CO₂ system			
OH ⁻	OH ⁻ = H ₂ O - H ⁺	-14.000	55.907
CO ₂ *	CO ₂ = CO ₃ ⁻² + 2H ⁺ - H ₂ O	16.681	-24.008
HCO ₃ ⁻	HCO ₃ ⁻ = H ⁺ + CO ₃ ⁻²	10.329	-14.912
Iron			
FeOH ⁺	FeOH ⁺ = Fe ⁺² + H ₂ O - H ⁺	-9.500	55.229
Fe(OH) ₂	Fe(OH) ₂ = Fe ⁺² + 2H ₂ O - 2H ⁺	-20.570	119.516
Fe(OH) ₃ ⁻	Fe(OH) ₃ ⁻ = Fe ⁺² + 3H ₂ O - 3H ⁺	-31.000	126.775
FeOH ⁺²	FeOH ⁺² = Fe ⁺³ + H ₂ O - H ⁺	-2.190	43.514
Fe(OH) ₂ ⁺	Fe(OH) ₂ ⁺ = Fe ⁺³ + 2H ₂ O - 2H ⁺	-5.670	71.546
Fe(OH) ₃	Fe(OH) ₃ = Fe ⁺³ + 3H ₂ O - 3H ⁺	-12.560	103.763
Fe(OH) ₄ ⁻	Fe(OH) ₄ ⁻ = Fe ⁺³ + 4H ₂ O - 4H ⁺	-21.600	133.470
Aluminium			
AlOH ⁺²	AlOH ⁺² = Al ⁺³ + H ₂ O - H ⁺	-5.000	48.074
Al(OH) ₂ ⁺	Al(OH) ₂ ⁺ = Al ⁺³ + 2H ₂ O - 2H ⁺	-10.100	112.550
Al(OH) ₃	Al(OH) ₃ = Al ⁺³ + 3H ₂ O - 3H ⁺	-16.900	166.900
Al(OH) ₄ ⁻	Al(OH) ₄ ⁻ = Al ⁺³ + 4H ₂ O - 4H ⁺	-22.700	176.983
Manganese			
MnOH ⁺	MnOH ⁺ = Mn ⁺² + H ₂ O - H ⁺	-10.590	60.250
Mn(OH) ₃ ⁻	Mn(OH) ₃ ⁻ = Mn ⁺² + 3H ₂ O - 3H ⁺	-34.800	0.0
Sulfate			
HSO ₄ ⁻	HSO ₄ ⁻ = H ⁺ + SO ₄ ⁻	1.988	16.108
Solid phases			
Goethite	FeOOH = Fe ⁺³ + 2H ₂ O - 3H ⁺	-1.000	0.0
Gibbsite	Al(OH) ₃ = Al ⁺³ + 3H ₂ O - 3H ⁺	8.11	-95.42
Birnessite	MnO ₂ = Mn ⁺² + 2H ₂ O - 4H ⁺	43.601	0.0