CRCLEME
Cooperative Research Centre for
Landscape Environments
and Mineral Exploration

Department of Water
Government of Western Australia

Department of Agriculture and Food
Government of Western Australia

action
Salinity & Water
AUSTRALIA

OPEN FILE
REPORT
SERIES

AVON CATCHMENT ACIDIC GROUNDWATER – GEOCHEMICAL RISK ASSESSMENT

P. Shand and B. Degens
(Editors)

CRC LEME OPEN FILE REPORT 191

June 2008

CRC LEME is an unincorporated joint venture between CSIRO-Exploration & Mining, and Land & Water, The Australian National University, Curtin University of Technology, University of Adelaide, Geoscience Australia, Primary Industries and Resources SA, NSW Department of Primary Industries and Minerals Council of Australia, established and supported under the Australian Government's Cooperative Research Centres Program.

Department of Water
Government of Western Australia

Department of Agriculture and Food
Government of Western Australia

action
Salinity & Water
AUSTRALIA

CRCLEME
Cooperative Research Centre for
Landscape Environments
and Mineral Exploration

AVON CATCHMENT
ACIDIC GROUNDWATER – GEOCHEMICAL RISK ASSESSMENT

P. Shand and B. Degens
(Editors)

CRC LEME OPEN FILE REPORT 191

June 2008

CRC LEME is an unincorporated joint venture between CSIRO-Exploration & Mining, and Land & Water, The Australian National University, Curtin University of Technology, University of Adelaide, Geoscience Australia, Primary Industries and Resources SA, NSW Department of Primary Industries and Minerals Council of Australia.

Headquarters: CRC LEME c/o CSIRO Exploration and Mining, PO Box 1130, Bentley WA 6102, Australia

Hard copies will be retained in the Australian National Library, the Western Australian State Reference Library, Libraries at The Australian National University and Geoscience Australia, Canberra, The University of Adelaide and Australian Resources Research Centre, Kensington, Western Australia.

Reference:
Shand P. & Degens B (Eds.). 2008. **Avon Catchment acidic groundwater – geochemical risk assessment.** *CRC LEME Open File Report 191.* 82pp

Keywords:
1. Regolith – Western Australia, 2. Geochemistry – Acidic groundwater, 3. Landforms – New South Wales,

ISSN 1329 4768
ISBN 0 643 09152 1

Addresses and affiliations of authors

Dr Paul Shand
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Land and Water
Private Bag 2
Glen Osmond SA 5064

Dr Brad Degens
Water Resource Management Division
Department of Water WA
P.O. Box K822
Perth WA 6842

Dr Andrew Baker
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Land and Water
Private Bag 2
Glen Osmond SA 5064

Dr Grant Douglas
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Land and Water
Private Bag No. 5
Wembley WA 6913

Dr Rob W Fitzpatrick
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Land and Water
Private Bag 2
Glen Osmond SA 5064

Dr Richard George
Natural Resource Management
Department of Agriculture and Food -WA
PO Box 1287
Bunbury WA 6231

Dr David Gray
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Exploration and Mining
26 Dick Perry Avenue
Kensington WA 6151

Dr Warren Hicks
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Land and Water
GPO Box 1666
Canberra ACT 2601

Adam Lillicrap
Natural Resource Management
Department of Agriculture and Food -WA
444 Albany Highway
Albany WA 6330

Mark Raven
CSIRO Land and Water
Private Bag 2
Glen Osmond SA 5064

Dr Steve Rogers
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Exploration and Mining
26 Dick Perry Avenue
Kensington WA 6151

Margaret Smith
Cooperative Research Centre for Landscape
Environments and Mineral Exploration
CSIRO Exploration and Mining
26 Dick Perry Avenue
Kensington WA 6151

Publisher:
CRC LEME, c/o CSIRO Exploration and Mining
PO Box 1130, Bentley, Western Australia 6102

EXECUTIVE SUMMARY

Saline groundwaters are extensive in the Western Australian (WA) Wheatbelt and the area affected by shallow saline water tables is expected to increase in future decades. Deep (2-3m) open drains are increasingly being used by farmers to manage shallow groundwaters in valley floors and protect low-lying land from salinisation or rehabilitate marginally saline lands. Although they discharge saline waters, some drains also contain acidic waters. There is increasing interest in expanding areas managed using artificial drains and increasing the regionalisation of existing drainage systems. This requires assessment of the risks, and development of appropriate management strategies, particularly geochemical risks and potential impacts on receiving environments.

In considering the feasibility of deep drainage options, landholders, community, local government authorities and land management agencies have raised concerns about the possibility of increased downstream inundation and flooding and water quality impacts. These concerns are being addressed in WA by the Department of Water Engineering Evaluation Initiative (EEI) and the Wheatbelt Drainage Evaluation Project, both commissioned as part of the National Action Plan for Salinity and Water Quality (NAPSWQ). This report presents the findings of a regional hydrochemical survey of groundwaters, drainage waters and lakes in the Wheatbelt region of the Avon basin, Western Australia.

This report presents results from a multi-agency EEI research project involving the Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC-LEME), CSIRO Land and Water, the Department of Water (WA) and the Department of Agriculture and Food (WA) to quantify the geochemical risks associated with deep drainage options at regional scales designed to manage rising saline groundwaters in the Avon Basin. Outcomes of the first regional assessment of geochemical risks of acidic groundwaters in the agricultural zone of WA are presented with respect to the implications for management of drainage and those environments receiving drainage.

Acidic groundwaters can be found in all agricultural regions of the Avon catchment. Occurrences increase from the higher rainfall, steeper areas to the drier, flatter areas. Although geology, regolith and depth play some role in explaining the spatial patterns of acidic groundwater, it is not possible to use these to reliably map the spatial distribution of the waters.

More than 45% of baseflows in drains in the central eastern Wheatbelt (east of a line from Dumbleyung to Dalwallinu) were found to contain acidic ($pH < 4.5$), saline waters (at least 40 000 mg l^{-1} TDS), with over half containing high concentrations of soluble iron (>5 mg l^{-1} and up to >200 mg l^{-1}), aluminium (>80 mg l^{-1} and up to >200 mg l^{-1}) and manganese (>5 mg l^{-1} and up to >40 mg l^{-1}).

Some acidic waters also contained high concentrations (>0.5 mg l^{-1}) of trace metals such as lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), uranium (U) and rare earth elements (REE). Similar salinity, acidity, and concentrations of elements were also found to be present in the regional groundwater (not directly impacted by drainage). The trace element chemistry of the acidic drain waters is dominated by dissolved iron and aluminium, with iron considered to play a major role in the formation of low pH in groundwaters, drains and lakes.

Complex geochemical processes also occur within drains that play a role in influencing the acid and trace metal transport within drains. Several key processes identified by soil studies include: formation of sulfidic sediments that can store acidity (but may subsequently release this); precipitation of iron and/or aluminium oxyhydroxide and oxyhydroxysulfate minerals (e.g. akaganéite, schwertmannite, jarosite) that can store acidity and influence trace metal concentrations in drain waters; and precipitation of a range of sodium (Na), calcium (Ca) and magnesium (Mg) salts, some of which contain high concentrations of trace metals. These processes play a major role in influencing transport of acidity and trace metals from the drains and vary with season and drain ageing processes. For example, during summer-autumn, drain pH can decrease due to a combination of evaporation of drainage waters (confirmed by modelling) and minerals forming or dissolving.

Geochemical modelling showed that there may be limited neutralisation of acidic drainage waters (and acidic waters stored in lakes) by high pH floodwaters, typically the volume of floodwater needs to be up to 99 times that of drainage waters to achieve a neutral pH.

Over 50% of the reference lakes and lakes receiving acidic drainage in the Avon contained acidic waters frequently less than pH 4. Some acidic reference lakes may have been acidic since before land-clearing began, however there is evidence in the sediments that some lakes may have only acidified in recent times, most likely because of increased regional acidic groundwater discharge. This increase may be continuing in some parts of the Avon catchment. Those Lakes which receive acidic drainage waters were all acidic, however these appear to be geochemically similar to acidic reference lakes (not receiving acidic drainage). A characteristic of all acidic lakes was that a lot of acidity is stored in bed sediments and soils of the beach zones.

The risks outlined in this project contain a number of implications for the management of drains intercepting acidic groundwaters. The broad distribution of acidic groundwaters highlights that any activity involving drainage or pumping of saline groundwater from the palaeodrainage systems of the Avon catchment should consider the likelihood of acidification or the interception of acidic groundwaters and the risks that these may carry. It is recommended that on-site characterisation of acidic groundwater risk be carried out as part of preliminary investigations. The design of drains in areas with acidic groundwaters should focus on maintaining minimal flow velocities and avoid flushing of acidity and trace metals. It will also be necessary to consider management of sediments removed during maintenance of drains to minimise transport back into the drain or surface waterways during rainfall run-off events. Selection of disposal sites for acidic drainage waters will need to consider the storage of acidity that will occur in sites and the risks to down-stream environments should acidity and trace metals be flushed downstream. Floodwaters may provide some capacity to neutralise acidic drainage waters, though only if present in substantial volumes and if the flooding occurs frequently to minimise accumulation of acidity in the soils of storage sites. Treatment of waters may be necessary in the context of managing risks of acidity and trace metals to downstream environments.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

1. INTRODUCTION

Brad Degens

Salinised land in the Wheatbelt of Western Australia (WA) contained within the Avon River Basin (Figure 1.1) is expected to increase to over 3 million hectares (McFarlane *et al.*, 2004), although if the recent declining trend in rainfall continues to occur this may constrain the future area affected by groundwater rise (Heath and George, 2007). Mixed success with vegetation based options to manage salinity in many parts of the WA Wheatbelt has resulted in increased emphasis on the use of engineering options to counter rising saline groundwaters (Clarke *et al.*, 2002). The conclusion that much (of the order of at least 50%) of the area in eastern Wheatbelt catchments may need to be revegetated to control recharge (George *et al.*, 1999) has contributed to increased landholder interest in using drainage engineering to manage discharge.

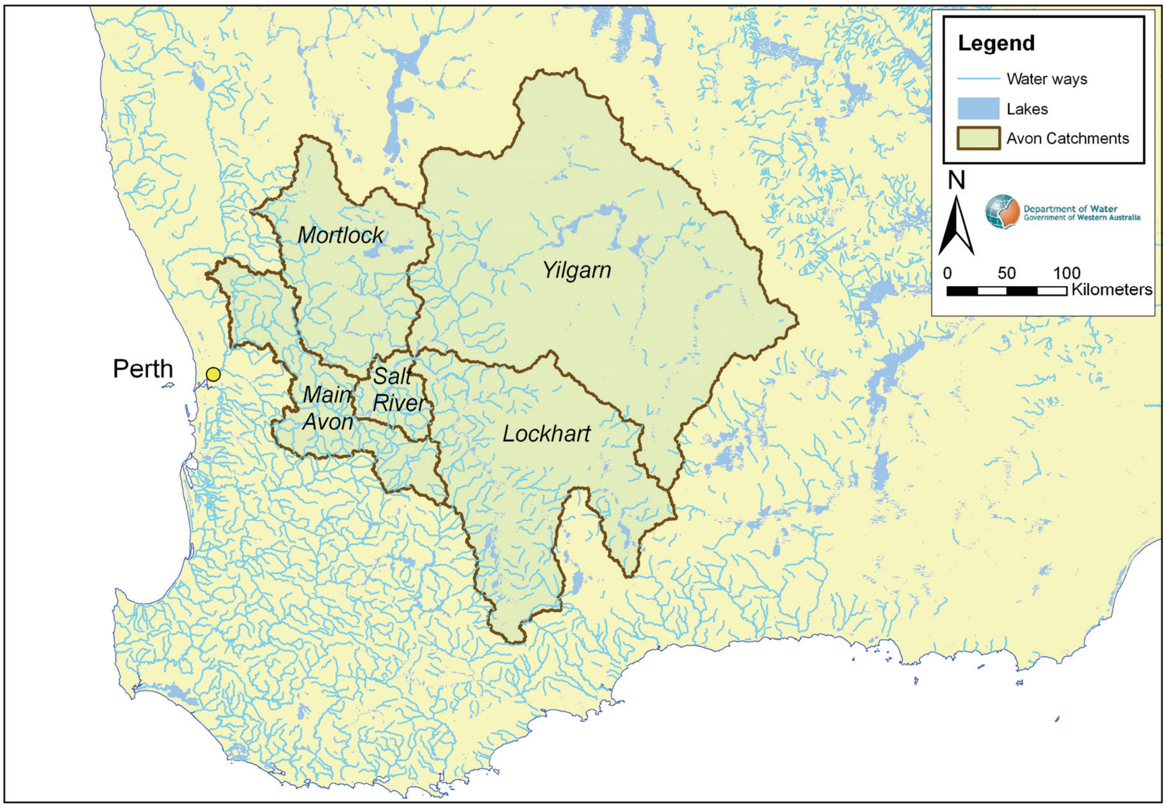

Figure 1.1 Avon river basin (WA) and sub-catchments.

The main engineering option of choice for many Wheatbelt valleys has been the use of deep (2-3m) open drains, which are increasingly being used to protect low-lying land areas from salinisation and to rehabilitate marginally saline lands (Dogramaci and Degens 2003; Kingwell and Cook, 2007). More than 10,000 kilometres of salinity earthworks have already been constructed in parts of the WA Wheatbelt (ABS, 2003) and it is likely that at least 4,000 kilometres of these are deep open drains that intercept groundwater. Few deep drains have regional linkages (Ali *et al.*, 2004a) although many discharge to saline sites, principally playas in the floodways of the main palaeodrainage systems and the tributaries to these (Dogramaci and Degens 2003; de Broekert and Coles, 2004; Ali *et al.*, 2004b).

There is increasing interest amongst some farmers in valley floors of the WA Wheatbelt to increase the area and scale of the deep drainage systems (Kingwell and Cook, 2007) and link smaller farm scale systems into larger regional drainage schemes (100's km in length covering 1000's km^2; Ruprecht *et al.*, 2004; Paterson, 2005). In considering the feasibility of this scale of drainage, landholders, community and local government authorities have raised concerns about the possibility of increased inundation and water quality impacts occurring at catchment to landscape scales arising from such drainage schemes (Dogramaci and Degens 2003; Ruprecht *et al*., 2004). These concerns are being addressed in WA by the Engineering Evaluation Initiative (EEI) and the Wheatbelt Drainage Evaluation Project, both commissioned as part of the National Action Plan for Salinity and Water Quality (NAPSWQ).

The prospect of increasing volumes of drainage water has increased concerns about the impacts of these on receiving environments (Dogramaci and Degens 2003). Initial investigations of some major drainage schemes have found that these can discharge waters of pH 2-3 with a salinity of 30000 to 50000 mg l^{-1} at 5-10 ML per day (Ali *et al*., 2004b). There are no reports of investigations to characterise the geochemical risks associated with these drainage waters, though limited studies indicate that the waters can contain elevated Al, Mn, Co, Ni and Pb (Ali *et al.,* 2004b; Tapley *et al.,* 2004). Shallow acidic groundwaters likely to be intercepted by the deep drains can contain significant concentrations of Al, Cu, Fe Mn, Pb and Si (Mann, 1983; Lee and Gilkes, 2005).

The spatial extent and geochemical characteristics of acidic groundwater risk in the WA Wheatbelt is poorly understood. Acidic groundwater has long been recognised to occur in the eastern Wheatbelt, particularly in deeper strata (Bettenay *et al*., 1964; Mann, 1983). Surface water monitoring in the eastern Avon identified acidic baseflow in waterways across the inland Avon basin, indicating that shallow acidic groundwaters may be more widespread that originally thought (Degens and Muirden, 2006). The significance of increasing discharge of acidic waters for trace metal mobilisation, and the risk that this poses to aquatic ecosystems, should increasing drainage occur, has not been investigated and is the main focus of this report.

A multi-agency research project involving CRC LEME, CSIRO Land and Water, the Department of Water (DoW) and the Department of Agriculture and Food-WA (DAFWA) was launched in 2004 to quantify the geochemical risks associated with conducting deep drainage at regional scales to control rising saline watertables in the Avon Basin. The project was jointly funded and developed by CRC LEME and the WA Engineering Evaluation Initiative (EEI) as a recommendation of the CRC LEME Land Use and Advisory Council to the EEI. The objectives of the project were to:

- Understand the processes leading to acidic groundwater in the natural or pre-disturbance landscape and beneath the present day largely cleared landscape
- Forecast the impacts of engineering drainage on the transport and transformation of trace elements in drained and undrained environments
- Identify feasible management options (opportunities and constraints) for dealing with the geochemical risks.

This report outlines the main outcomes of this investigation including a conceptual model for the sources of acidity in the regolith, outcomes of geochemical surveys of existing deep drains, evaluation of geochemical risks in receiving environments into which deep drains discharge and geochemical models for the mixing of acidic drainage with alkaline floodwaters including subsequent evaporation. Feasible options to treat acidic discharge are reported in Douglas and Degens (2006).

2. HYDROGEOCHEMICAL CHARACTERISTICS OF GROUNDWATERS AND SURFACE WATERS IN THE WA WHEATBELT

Paul Shand

2.1 Introduction and general characteristics

This chapter provides a summary of the hydrochemical characteristics of surface waters (mostly drainage and lake waters) and groundwaters of the Avon catchment collected during the study, providing a background to later chapters dealing with the origin of acidity and geochemical risks (a more spatially extensive review of groundwater data, though limited to pH is presented in chapter 3).

The sites sampled in this study included flowing drains and lakes (sampled from 2004 to 2006) and groundwaters (Figure 2.1). Details of the sites sampled are shown in Appendix 1. All samples were filtered in the field through 0.45 µm mixed-cellulose ester membrane filters and either acidified with ultrapure HNO_3 or retained unacidified and stored at 5 degrees C, depending on the analysis performed. In-situ measurements of pH, EC, temperature and Eh were taken at many sites (when possible). Drain/creek flow was also estimated whenever possible. The concentrations of Cu, Zn, Co, Ni, Cr, Mn, P, V, Fe, Al, Ca, Mg, Ti, Na, K, and S were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The elements Ag, Ba, Cd, Mo, Pb, Sb, Sn, Y, Hf, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U and Se were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Arsenic was also determined using hydride generation coupled to ICP (see Appendix 2 for analyte suite).

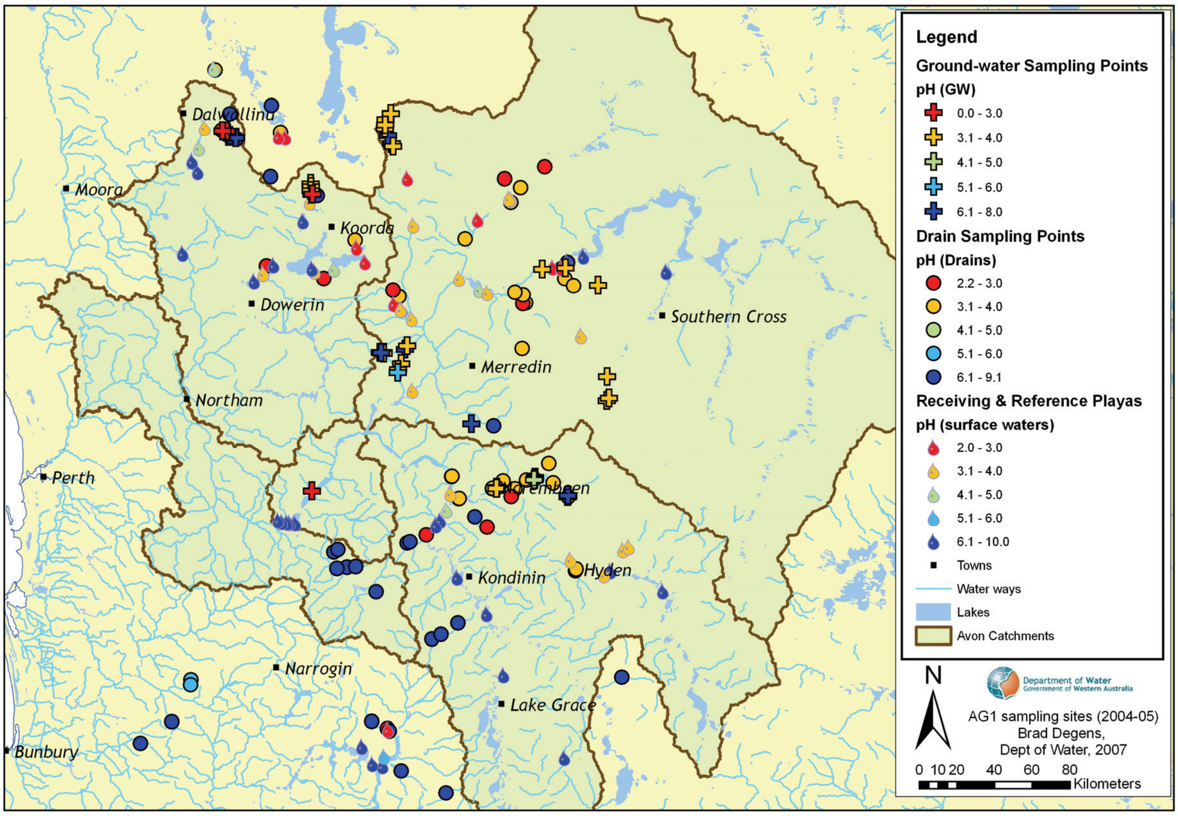

Figure 2.1 Locations of drain, lake and groundwater sampling sites (classified by sample pH) in the Avon catchment.

Surface waters and groundwaters in the catchment show a wide range in TDS (total dissolved solids) from relatively fresh up to brines, and display similar distributions and ranges on histograms (Figure 2.2). The pH shows a bimodal distribution, both in surface waters and groundwater. However, median concentrations and the interquartile ranges for TDS are higher in the surface waters and for pH, the median is lower (Figure 2.2).

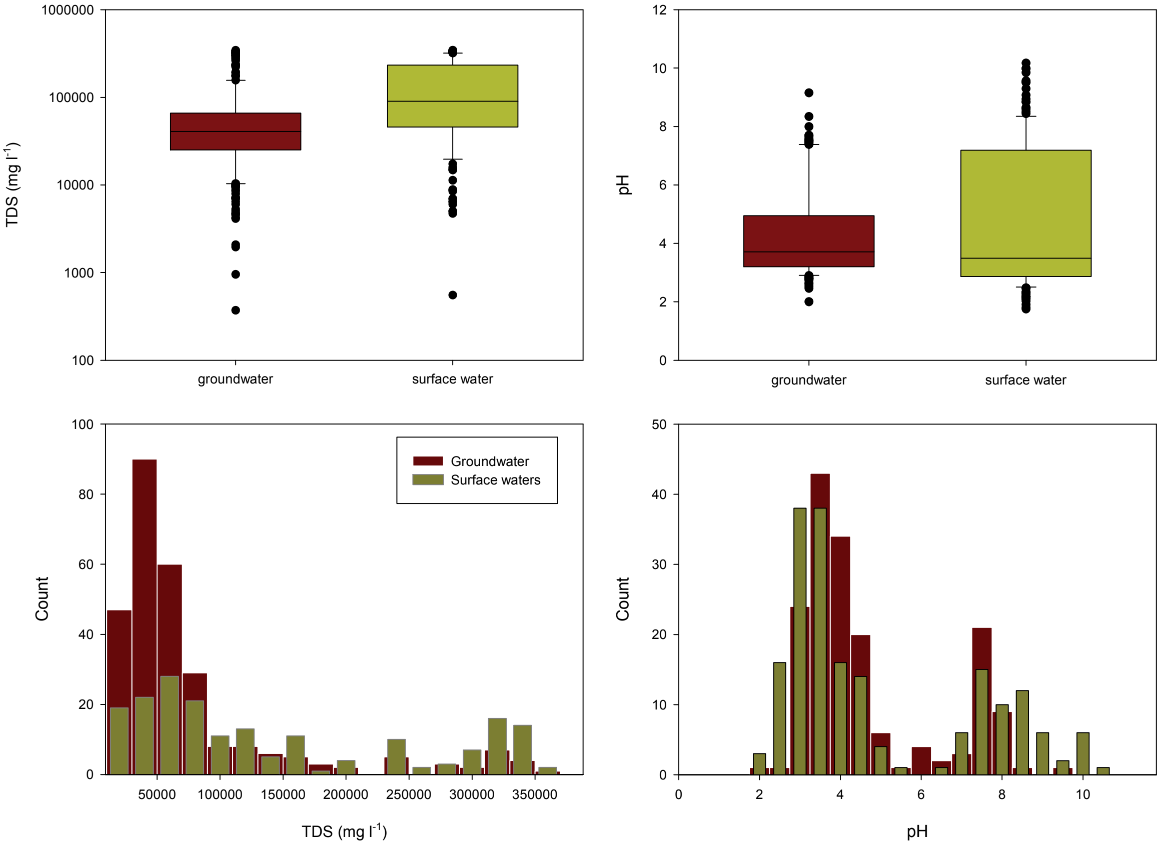

Figure 2.2 Boxplots (displaying median, interquartile ranges and outliers) and histograms for TDS (left) and pH (right) in surface waters and groundwaters of the Avon catchment.

The water types are mainly of Na-Cl type but show significant variation from the relative proportions of seawater (Figure 2.3). There is a trend in some of the fresh groundwaters towards Na-HCO_3 composition, possibly due to ion-exchange processes in the aquifer.

The redox potential (Eh) was measured in just a few groundwaters and varied from moderately reducing to oxidising. Although similar variations were found in surface waters, the Eh measurements may not reflect the true Eh particularly if the waters contain oxygen.

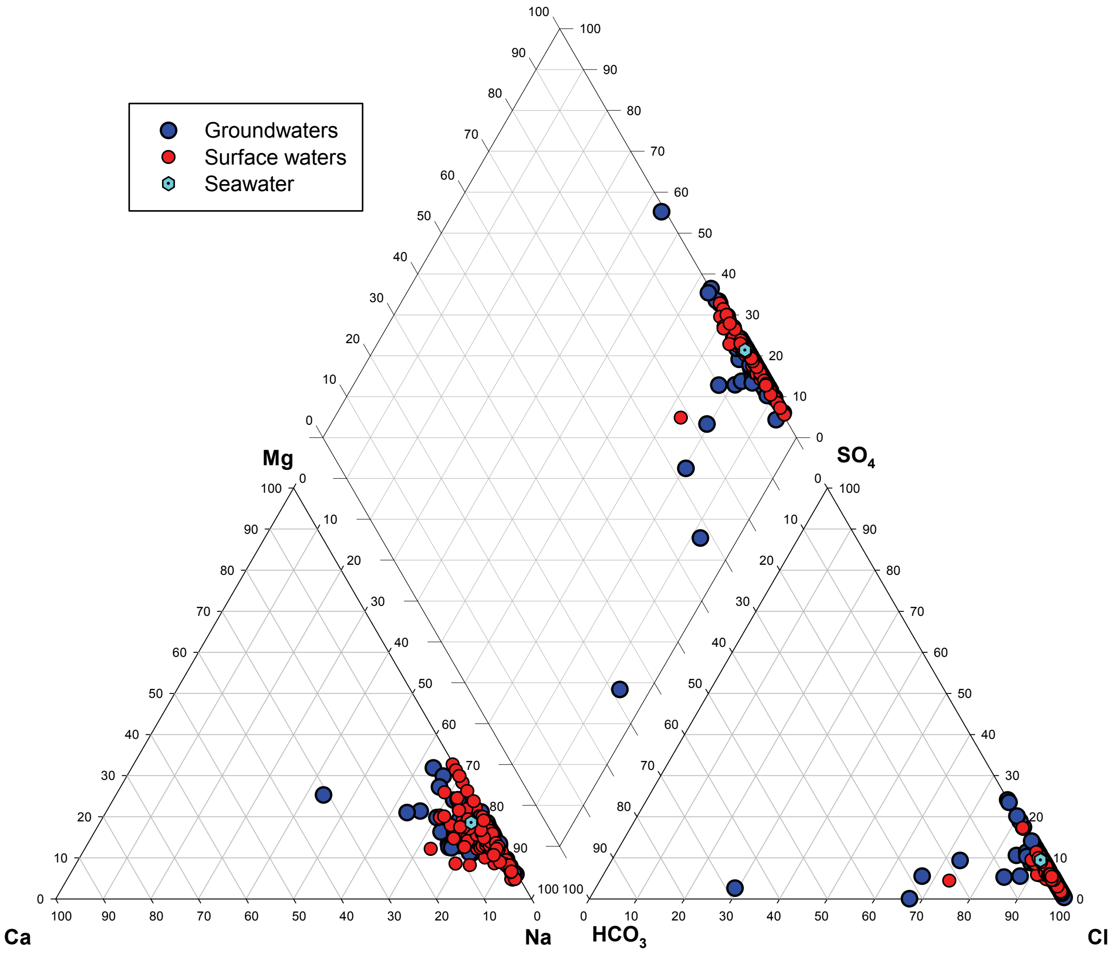

Figure 2.3 PIPER plot for surface waters and groundwaters of the Avon catchment.

2.2 Major element variations

The major elements and total dissolved solids (TDS) displayed large variations in chemistry, typically over several orders of magnitude. The ranges and averages are shown on Figure 2.4 as boxplots for groundwaters and surface waters. Median Na concentrations lie close to the normalised seawater line indicating a dominance of Na from a similar (marine) source, consistent with previous studies in the region (Mazor and George, 1992), however median concentrations for the other major elements are generally below the line indicating a loss from these waters.

Major element data are plotted against pH and Cl concentration on Figures 2.5 and 2.6. High TDS is present in both acidic and alkaline surface waters and groundwaters (Figure 2.5), although the former have much higher TDS, largely due to evaporation. Sodium displays a good correlation with Cl (r^2=0.99) but the other major elements correlate poorly indicating gains or losses relative to seawater (Figure 2.6). The surface waters in particular show low ratios of Ca, Mg and SO_4 to Cl relative to seawater consistent with removal processes such as mineral precipitation and/or removal through redox processes.

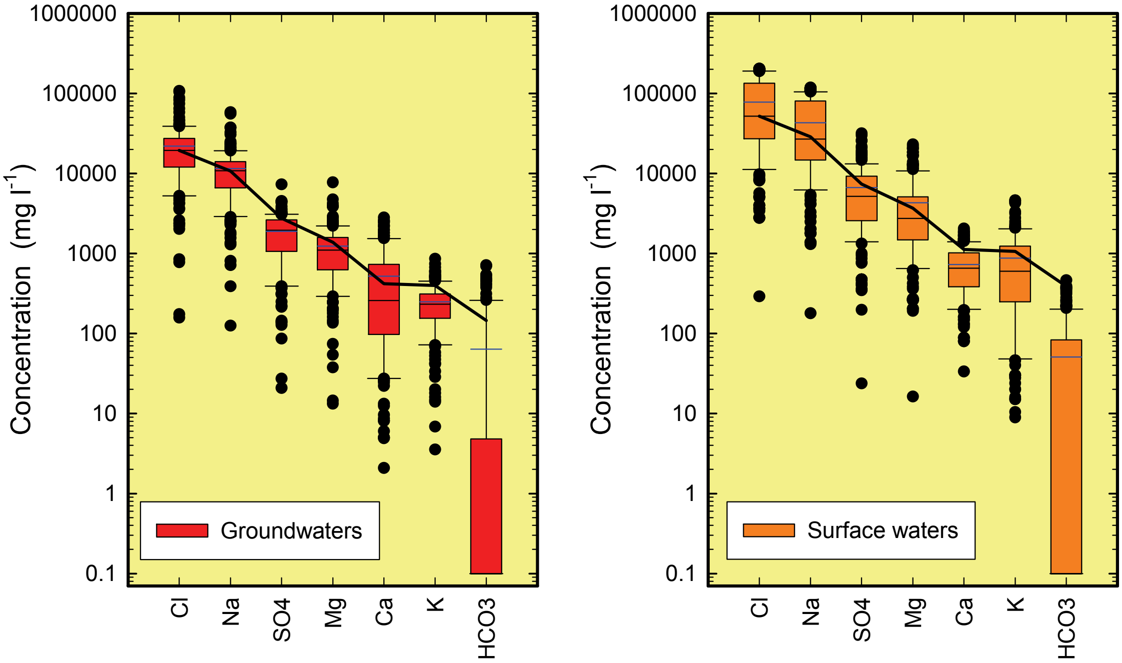

Figure 2.4 Boxplots showing percentile ranges and averages (blue: median; black: mean). Solid black line represents seawater curve normalised to the median concentration of the dataset on each boxplot to indicate enrichments or depletions relative to Cl.

2.3 Minor and trace element variations

Most minor and trace elements vary over several orders of magnitude (Figures 2.7 and 2.8). Silica concentrations are strongly elevated at low pH, and oversaturation with respect to amorphous silica exists for many of the more saline waters. Nearly 50% of the samples have F exceeding the World Health Organisation (WHO) drinking water guideline value of 1.5 mg l^{-1}. Nutrients and total organic carbon were measured only in surface waters but reach high concentrations: maxima of 1.4, 11, 45 and 255 mg l^{-1} for PO_4-P, NO_3-N, NH_4-N and TOC respectively.

The redox sensitive elements Fe and Mn are present at extremely high concentrations (Figure 2.7), in general being higher at lower pH. Aluminium concentrations also display a wide range, reaching maximum concentrations greater than 1000 mg l^{-1} at low pH. The acidic nature of both surface waters and groundwaters has allowed a number of trace elements to reach very high (some up to mg l^{-1}) concentrations including Co, Cr, Cu, La, Ni, Pb, U, Y and the rare earth elements (REE), many above water quality guideline values (ANZECC and ARMCANZ, 2000) for both fresh and saline (marine) waters (Figure 2.8) even at moderate species protection limits. Even those elements which are rarely present in waters at more typical pH such as Th, Pd and Tl are elevated above typical baseline. By contrast, alkaline drainage waters contained few trace elements, except for occasional instances of Se and As.

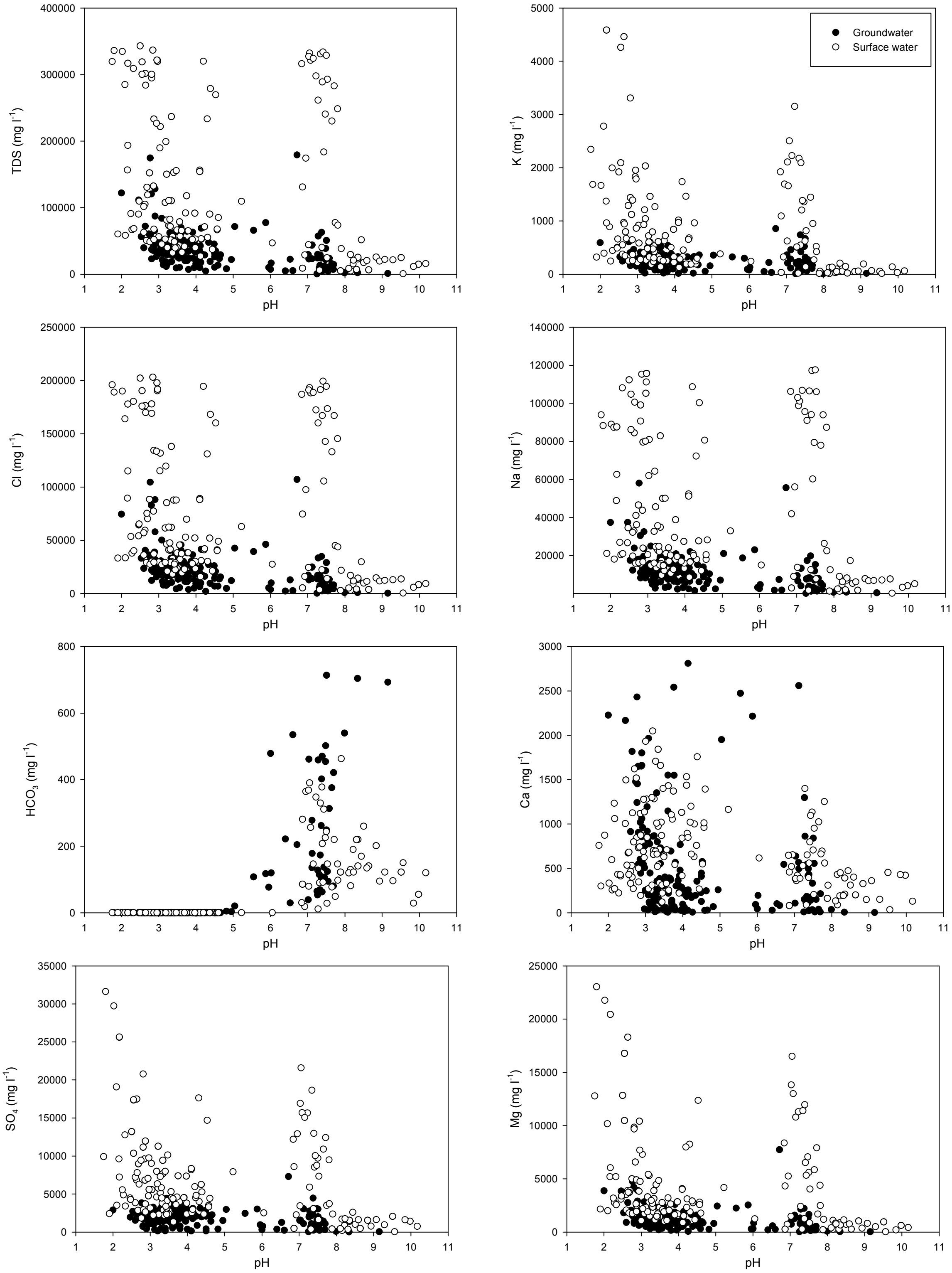

Figure 2.5 Relationship of TDS and major element concentrations to pH in surface waters and groundwaters of the Wheatbelt.

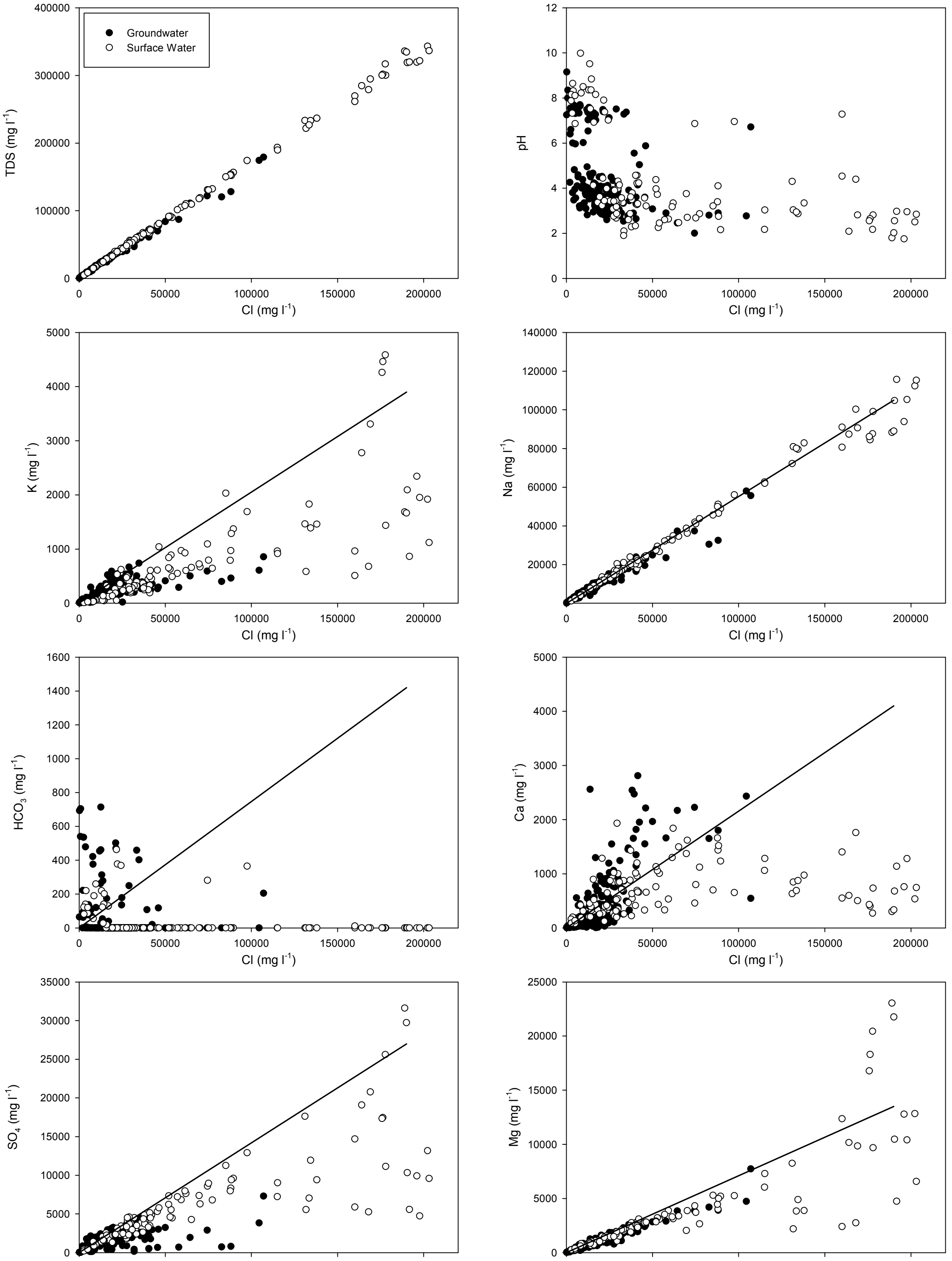

Figure 2.6 Relationship of TDS, pH and major element concentrations to Cl in surface waters and groundwaters of the Wheatbelt. Solid line is seawater dilution line.

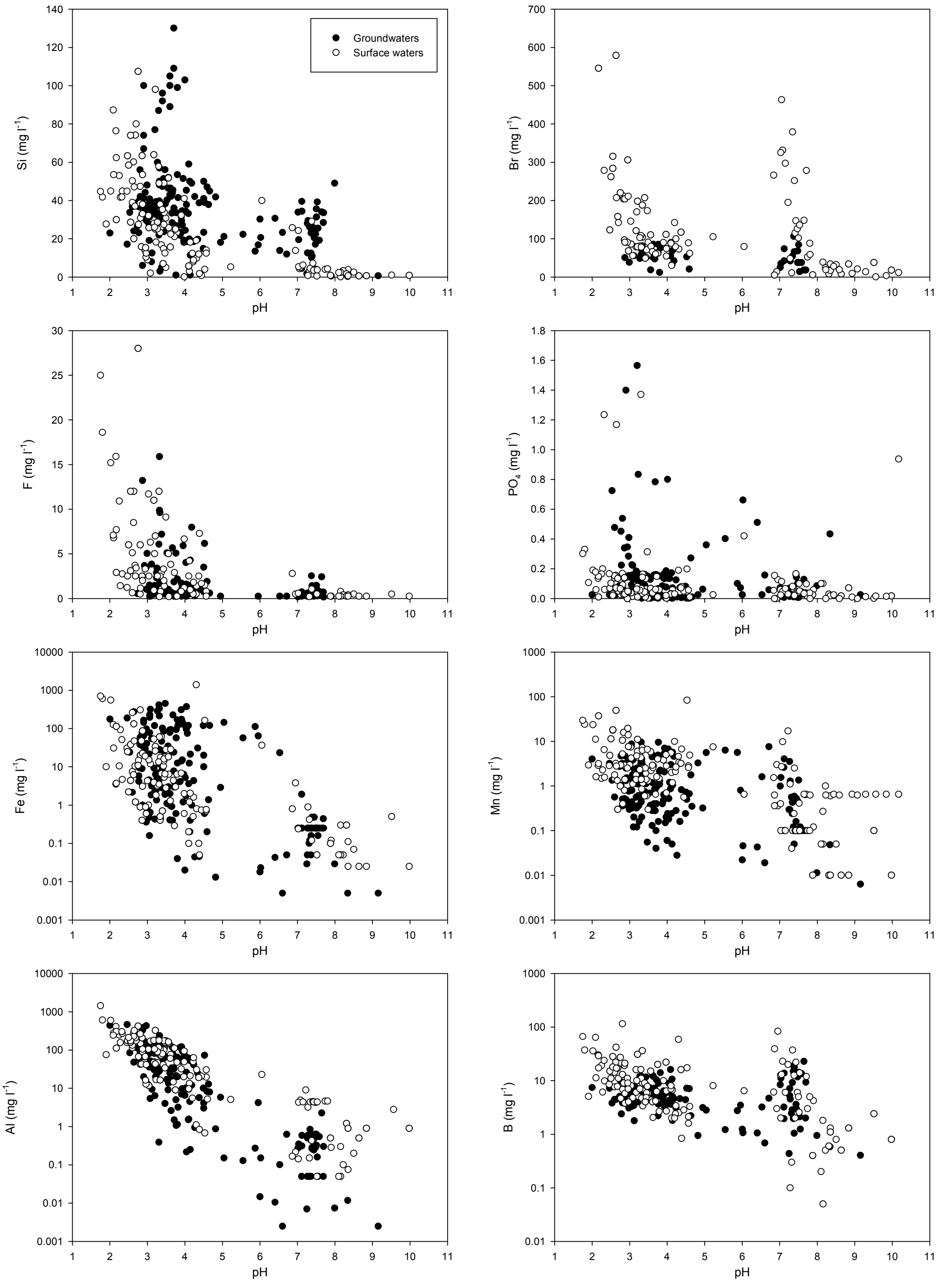

Figure 2.7 Concentrations of minor and trace elements plotted against pH. Note log scales for Fe and Mn .

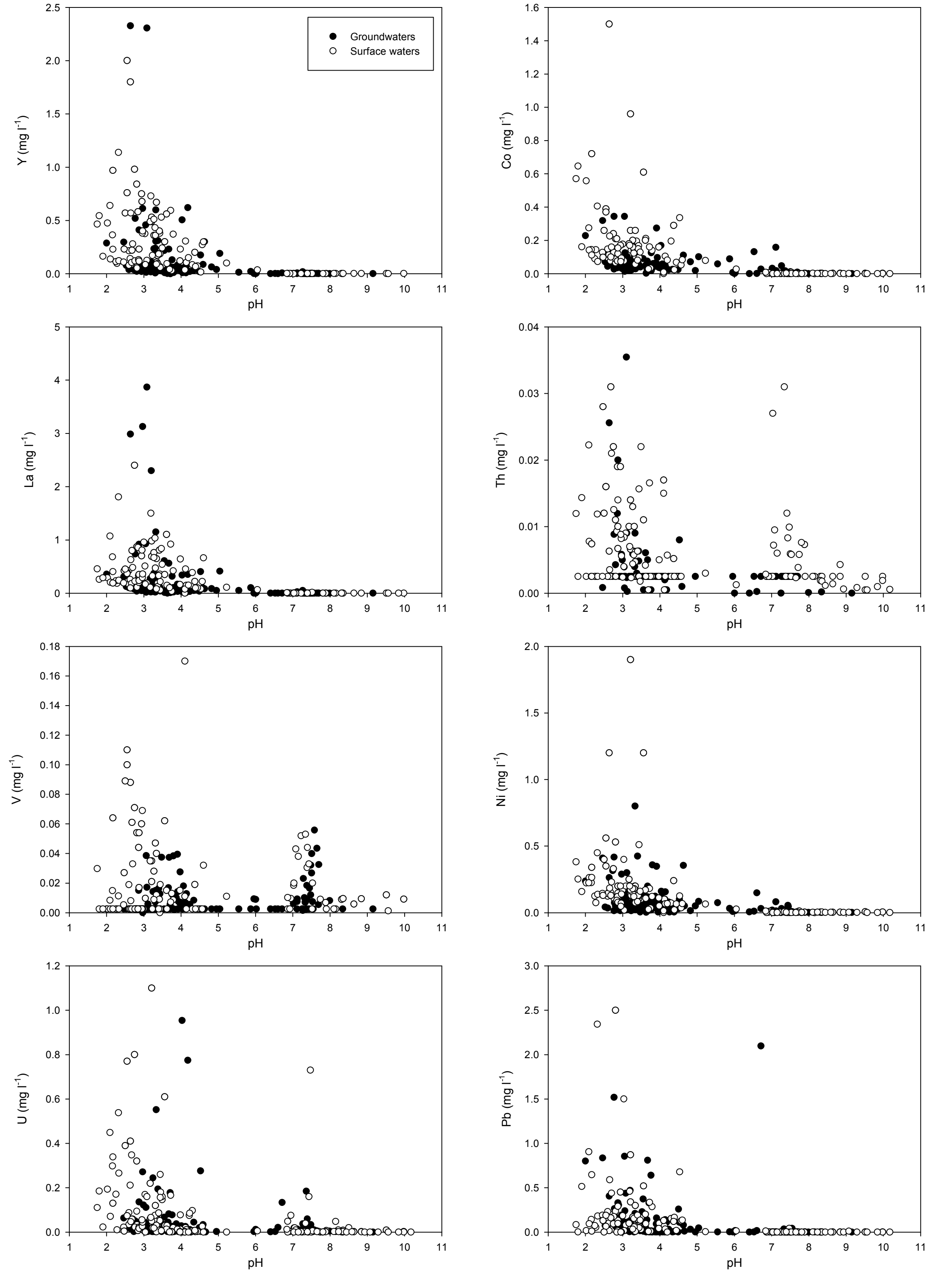

Figure 2.8 Concentrations of trace elements plotted against pH.

2.4 Water fluxes in the drains

There are very few data available quantifying the flow of water in the drains of the Wheatbelt. A summary of available information is shown on Figure 2.9. Flows during spring, when generally only groundwater discharge occurs, ranged from 30 l s^{-1} to less than 0.1 l s^{-1}. This approximates broadly to approximately 2592 kL d^{-1} to 8.6 kL d^{-1}. Flows of over 75% of drains were less than 2.5 l s^{-1}. The highest flows were encountered at the terminus of the Narembeen drainage network (over 150 km of drainage channels) and drains in tributaries of the Yilgarn River above the Baandee Lakes (e.g. 12 l s^{-1} near Trayning and 15 l s^{-1} near Boodarockin). Flows of some drains ceased in summer (particularly those less than 1 l s^{-1} in spring) or were greatly reduced.

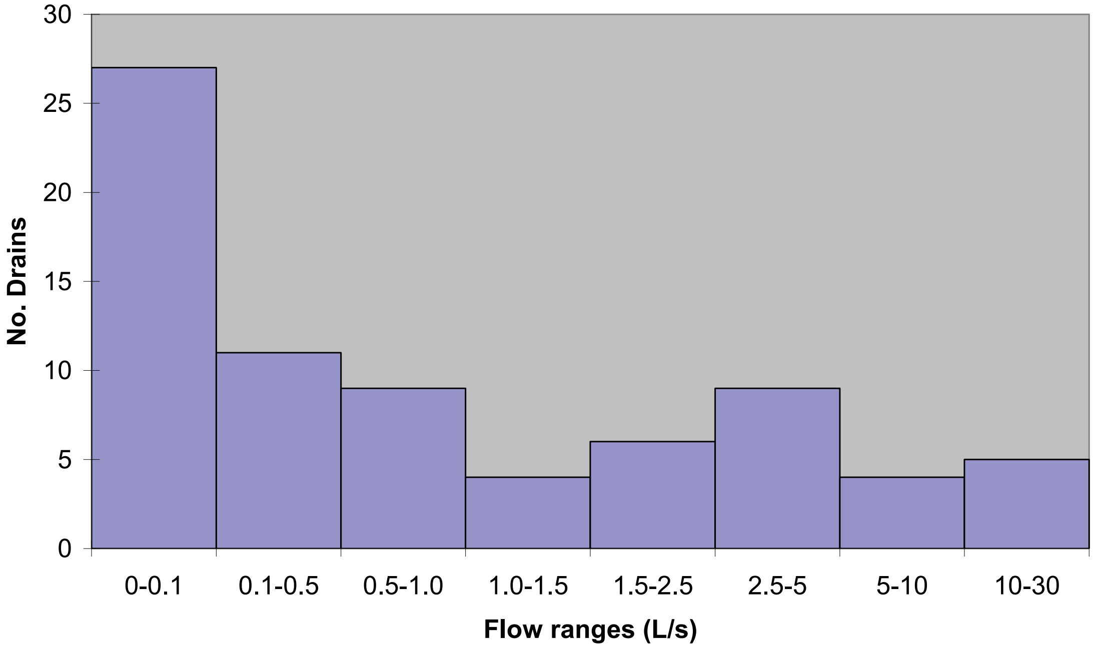

Figure 2.9 Histogram showing the range in flows of drains in the Wheatbelt.

3. ACIDIC GROUNDWATER IN THE SOUTH WEST OF WESTERN AUSTRALIA: DISTRIBUTION AND GEOSPATIAL RELATIONSHIPS

Adam Lillicrap and Richard George

3.1 Background

There is increased use of engineering options such as drainage or groundwater pumping to manage saline watertables and the presence of acidic groundwaters presents an additional environmental risk to these practices that needs to be considered. Therefore it is important to understand the distribution of acidic groundwaters in the landscape and the range over which it occurs. Additionally, it is necessary to understand the factors leading to formation of acidic groundwaters as this can lead to the development of acidic groundwater hazard maps.

The origins of the acidity found in some groundwaters of the WA Wheatbelt have not been clearly identified. Although work by Mann (1983) suggested that iron hydrolysis reactions in groundwater, referred to as 'ferrolysis' by Mann, were the mechanism for acidity, the source of the iron was not definitely identified. Mann attributed the iron in the groundwater to weathering reactions. McArthur *et al* (1991) further developed this hypothesis, and suggested that the source of iron in groundwater was due to microbial reduction of ferrous iron minerals such goethite. McArthur *et al* (1991) further suggested that the alkalinity common in many Wheatbelt soils was also a product of this process.

The aim of the study was to determine the extent of acidic groundwater in the agricultural regions of Western Australia and identify broad spatial factors that may explain its occurrence. Groundwater pH data were used from DAFWA, DoW)and CSIRO.

3.2 Methods

Each bore was assigned a rock type, regolith type and soil landscape based on spatial datasets from the Geological Survey of Western Australia (GSWA) (geology and regolith) and DAFWA (soil landscape). Each bore was assigned a depth class, where available (see details in Lillicrap and George, 2008).

The results showed that there was a distinct bi-modal distribution in groundwater pH (Figure 3.1; c.f. Figure 2.1). The main population (2338 bores) had a median pH of 6.6 and the other smaller distinctly acidic population (694 bores) had a median pH of 3.6. To simplify the statistical analysis and mapping the groundwaters were divided into two classes, acidic (pH<4.8) and non-acidic based on the frequency of pH distribution.

In order to determine the spatial extent and frequency of acidic groundwater occurrence, DAFWA soil landscape mapping, was used as the base spatial units as they represent distinct geological and geomorphological zones. The percentage of acidic bores in each zone was calculated.

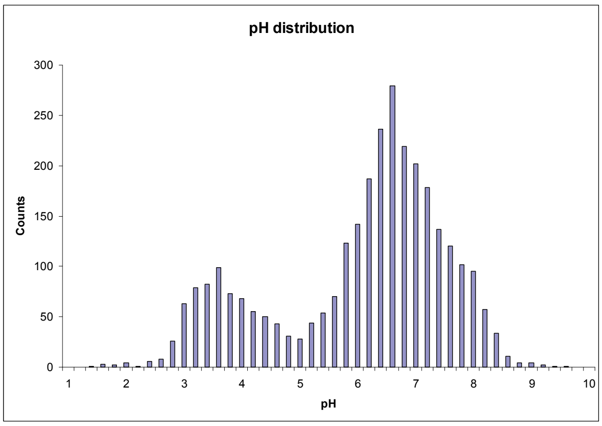

Figure 3.1 Bar chart showing the distribution of in-situ pH of groundwater in the SW of Western Australia.

Due to the nature of the dichotomous (acidic or non-acidic) dependent variable and categorical independent variables (geology, regolith and depth class), binomial (or binary) logistic regression was used to analyse the data. Logistic regression can be used to predict a dependent variable (acidity) on the basis of categorical independents (geology, depth and regolith) and to determine the percent of variance in the dependent variable explained by the independents; to rank the relative importance of independents and to assess interaction effects (Lillicrap and George, 2008).

3.3 Results and Discussion

The results showed acidic groundwater is widespread across all agricultural regions of Western Australia, however there is a regional trend in the occurrence of acidic groundwater (Figure 3.2). Acidic groundwater is least common in the steeper, higher rainfall areas and more common in the dryer, inland palaeodrainage. Within soil zones, the distribution is heterogeneous (Lillicrap and George, 2008).

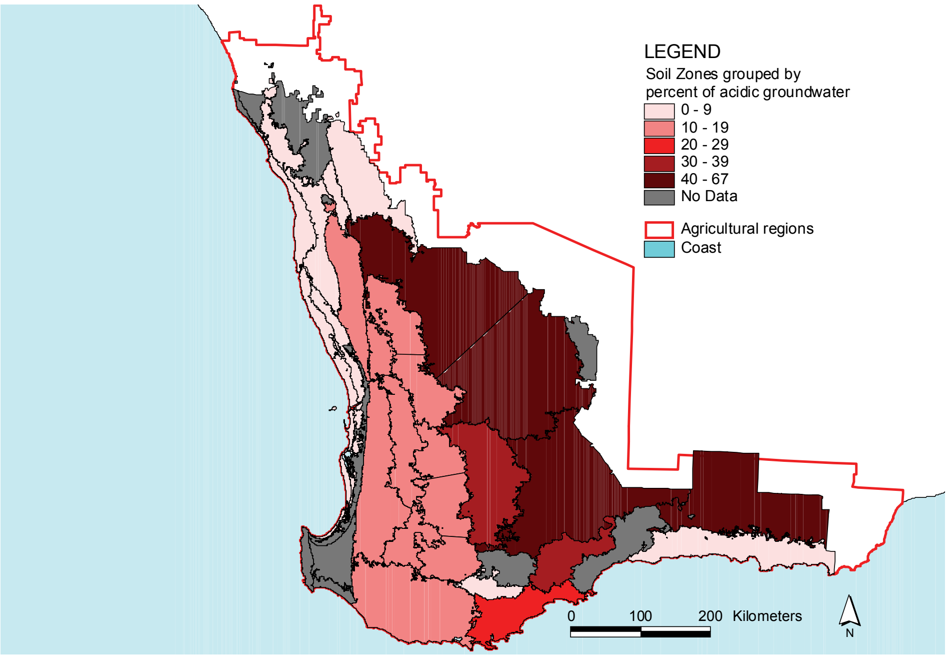

Figure 3.2 Distribution of acidic groundwaters in SW Western Australia, by frequency of acidic (pH<4.5) bores in each soil zone.

The linear regression models showed that all the independent variables: geology, depth and regolith to various extents explained the occurrence of acidic groundwater and were statistically significant ($p<0.05$) in (Table 1). There were also interaction effects between the variables.

Variable	Degrees of Freedom	deviance	Mean deviance	Deviance ratio	Approx Chi probability	Percent of deviance
Geology	7	47.868	6.838	6.84	<.001	22.7
Depth Class	2	9.303	4.652	4.65	0.01	4.4
Regolith	5	16.361	3.272	3.27	0.006	7.8
Geology. Regolith	26	47.703	1.835	1.83	0.006	19.4
Geology. Depth Class	13	21.773	1.675	1.67	0.059	8.9
Regolith. Depth Class	10	17.167	1.717	1.72	0.071	7.0
Residual	37	59.174	1.599			24.1
Geology. Regolith. Depth Class	38	59.174	1.557	1.56	0.015	24.1
Total	100	211.066	2.111			

Table 3.1 Results of linear regression models for individual variables and interaction effects.

Geology was the most important single variable to explain the occurrence of acidic groundwater. Acidic groundwaters were most commonly found in granitic or gneissic rocks and least frequently found in basic and sedimentary rocks (Lillicrap and George, 2008). Additionally, acidic groundwaters most frequently occurred in bores screened at intermediate depths (between 5 m and 10 m deep) (Lillicrap and George, 2008).

The interaction between geology, regolith and depth explained the greatest variance in acidic groundwater occurrence followed by the interaction between geology and regolith. However, the results show there is still a lot of unexplained variance (24.1%) which indicates there is another factor or factors responsible for the formation of acidic groundwater.

The analysis shows acidic groundwaters are widespread. Information on acidic groundwater risk will be required by landholders, local governments and state agencies to ensure that the risk is identified at an early stage in proposals to manage acidic groundwaters. Further work is necessary to identify factors other than those examined here that may be responsible for the occurrence of acidic groundwaters and to develop reliable acidic groundwater risk maps.

3.4 Main findings

- Groundwaters in the Wheatbelt show a distinct bi-modal distribution in pH with a clear acidic population (pH<4.8).
- Acidic groundwater is widespread across all agricultural regions and increases in occurrence from the higher rainfall, steeper areas to the drier, flatter areas.
- Geology, regolith and depth are important in explaining the spatial patterns of acidic groundwater. However, there are other not yet identified factors that may further explain acidic groundwater occurrence.

3.5 Management implications

- Acidic groundwater occurs throughout the agricultural zone and cannot be reliably predicted using existing regolith and geology map information.
- The broad distribution and extent highlights that consideration must be given to the potential occurrence of these waters for any activity involving pumping or drainage of groundwaters in the Avon catchment.
- Further work is required to further identify the factors responsible for acidic groundwater formation, before reliable acidic groundwater hazard maps can be produced, that would allow acidic groundwater risk to be identified at an early stage in plans to manage acidic groundwaters.

4. CONCEPTUAL MODELS FOR GEOCHEMICAL RISKS

David Gray

4.1 Sources of acidity in the regolith

The southern half of the Yilgarn Craton commonly contains acidic groundwaters (in some cases down to pH 3). This is clearly observed in the relatively undisturbed region east of the Wheatbelt. Because of major disturbance to hydraulic conditions in the Wheatbelt due to clearing, it is not clear whether the present high acidity pre-dates or has been exacerbated by land clearing. However, reports of acidic waters in certain regions go back decades (Mann, 1984) and relatively undisturbed areas south of the Wheatbelt also include some acidic groundwaters (M. Smith, Curtin University/CRC LEME, personal communication 2006).

Although the ultimate source of the acidity is unclear, Fe and S chemistry provide the currency though which acidity is transferred from deep to shallow groundwater and into surface drainage. The most common mechanism is Fe oxidation/hydrolysis, commonly referred to as "ferrolysis" (Mann, 1984):

Equation 4.1 $2Fe^{2+} + ½O_2 + 5H_2O \rightarrow 2Fe(OH)_{3(S)} + 4H^+$

Thus, when anoxic groundwaters containing dissolved Fe move into more oxidising conditions, such as into drainage channels or watertables rise into the unsaturated zone, this reaction can significantly lower pH. For example, in the absence of other buffers, oxidation of a neutral solution containing 280 mg l^{-1} Fe (c.f. Figure 4.1) would change the pH to approximately pH 2 by this mechanism. Note that this reaction can proceed in the other direction and provide a mechanism to store acidity in anoxic conditions (i.e. reductive iron dissolution). High dissolved Al is an additional store of acidity, as dissolved Al^{3+} can negate the effect of buffering or mixing with neutral/alkaline waters with 90 mg l^{-1} dissolved Al (c.f. Figure 4.2) equivalent to pH 2:

Equation 4.2 $Al^{3+} + 3HCO_3^- \rightarrow Al(OH)_{3(S)} + 3CO_2$

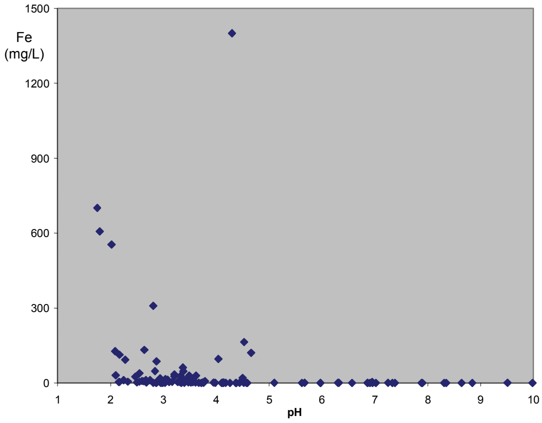

Figure 4.1 Dissolved Fe vs. pH for Wheatbelt waters.

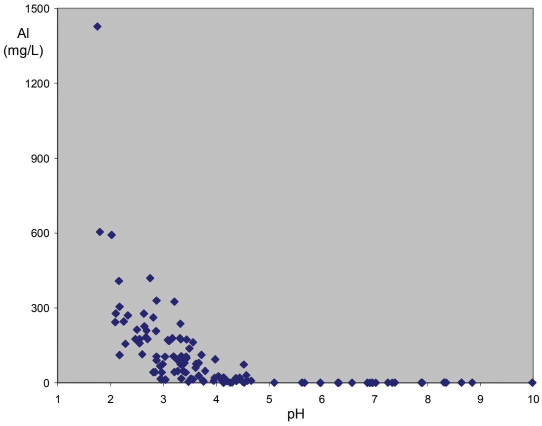

Figure 4.2 Dissolved Al vs. pH for Wheatbelt waters.

Acid transfer can also occur with the solid phase, whereby marcasite/pyrite can produce acidity during sulfide oxidation:

Equation 4.3 $2FeS_2 + 7O_2 + H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$

with additional acid production when the dissolved Fe also oxidises (Equation 4.1). These two stages of acid production could be effectively simultaneous if, for example, sulfide-rich material was exposed to air. Conversely, if sulfide was deep in the soil profile with oxidation limited by slow influx of O_2, these two processes could be laterally separated. The potential significance of these materials for storage of acidity and consequent release during aerobic conditions is indicated by 1 L of unbuffered water being acidified to pH 2 by oxidation of 0.3 g of marcasite i.e. sub-or low-percent concentrations of marcasite in soils can cause massive acidification from oxidation caused by water table decline.

Initial oxidation of secondary sulfides such as iron monosulfide (the blue-black phase commonly observed in drainage and lake sediments) does not produce acidity:

Equation 4.4 $\mathbf{2FeS + 4O_2 \rightarrow 2Fe^{2+} + 2SO_4^{2-}}$

though acid is produced with complete oxidation (0.44 g FeS taking 1 L to pH 2, in the absence of any neutralising agents):

Equation 4.5 $\mathbf{2FeS + 4\tfrac{1}{2}O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 2SO_4^{2-} + 4H^+}$

One postulate for the acidity of drainages is that sulfide minerals have been precipitated in the regolith as anoxic conditions moved up the profile with higher water tables following deforestation. With rapid oxidation of the top of the profile, due to dewatering from drainage channels, these minerals are being quickly oxidised, leading to groundwater acidity and highly acidic drainage waters. In general, naturally acidic groundwater systems such as those around Kalgoorlie have measured pH values no lower than 3.0, due to buffering by alumino-silicate dissolution:

Equation 4.6 $\mathbf{\underset{(kaolinite)}{3Al_2Si_2O_5(OH)_4} + 2K^+ + 4SO_4^{2-} + 6H^+ \rightarrow \underset{(alunite)}{2KAl_3(SO_4)_2(OH)_6} + 6SiO_2 + 3H_2O}$

In contrast, many ground- and drainage waters in the Wheatbelt have pH values below 3, suggesting that in the present-day Wheatbelt, acidification is occurring rapidly enough that such mechanisms are too slow to buffer groundwaters back to pH 3, though presumably this will happen with time.

Such an effect will only occur if these minerals were precipitated in the absence of secondary carbonates. In areas such as the Loveday disposal basin in Southern Australia, where sulfides are forming at surface (Lamontagne et al., 2006), the alkalinity caused by their formation (*e.g.*, Equation 4.3) leads to simultaneous precipitation of carbonate minerals, which buffers acidification from later oxidation. However, this appears not to have occurred in the Wheatbelt regolith, possibly because groundwaters were initially slightly to highly acidic (pH 6 – 3), and/or due to lateral separation of "acid forming" and "alkalinity storage" processes.

As evidence of the ongoing cycling of Fe, S, acidity and redox, secondary sulfides are forming in the drainage sediments as inflow of organic material is leading to reducing conditions within the unconsolidated sediments (Chapter 5). Presumably, these minerals could re-oxidise and re-release acidity with exposure to air, from lowered water flow or if sediments were dug out from the drains. Other minerals such as alunite, jarosite and schwertmannite can store acidity even in oxidised zones (though less than the sulfides, with 1 L of unbuffered water taken to pH 2 by 1.4, 1.7 and 3.9 g of these minerals, respectively) and could release acidity during flushing:

Equation 4.7 $\mathbf{\underset{(jarosite)}{KFe_3(SO_4)_2(OH)_6} + 3H_2O \rightarrow 3Fe(OH)_{3(S)} + K^+ + 2SO_4^{2-} + 3H^+}$

Equation 4.8 $\mathbf{\underset{(schwertmannite)}{Fe_8O_8(OH)_6SO_4} + 10H_2O \rightarrow 8Fe(OH)_{3(S)} + SO_4^{2-} + 2H^+}$

Thus, the complex reactions and mineral cycling within these drains and surrounding groundwaters, though still under investigation, are having a critical control on the release and storage of acidity. Given the precipitation of "acid-storing" minerals at the base of these drains, the sediment material in particular should be treated carefully in any amelioration program to avoid release of further acidity and increased environmental damage.

4.2 Metal mobilisation from the regolith

The extremely high acidities in Wheatbelt waters affect many elements, particularly base metals and rare earth elements (REE). In addition, the variation in redox conditions can have a major influence on the behaviour of redox sensitive elements, including Fe (as discussed above), Mn, As and U.

Results for Narembeen groundwaters (after Tapley et al., 2004) demonstrate strong pH control on the solubility of many elements, including base metals (e.g. Cu: Figure 4.3 and Zn: Figure 4.4), REE and chalcophile elements including As and U. Indeed, this includes many elements generally considered insoluble under "normal" acidic conditions (pH > 3) such as V (Figure 4.5) and As, due to enhanced precipitation or adsorption of negative charged species such as $VO_2(OH)_2^-$ or H_2AsO4^-, have enhanced solubility below pH 3, because they are forming positive aqueous species due to higher acidity (Figure 4.6).

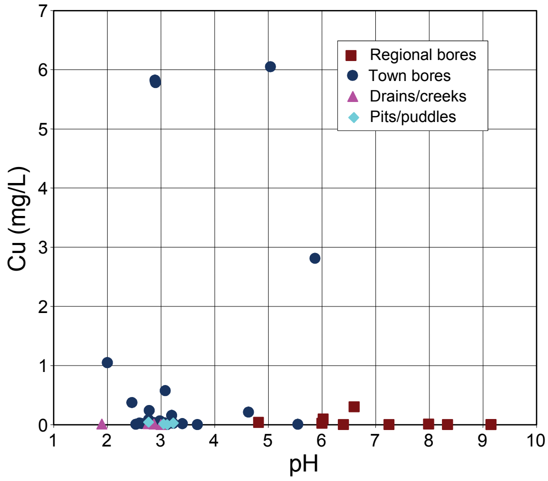

Figure 4.3 Dissolved Cu vs. pH for varying waters at Narembeen.

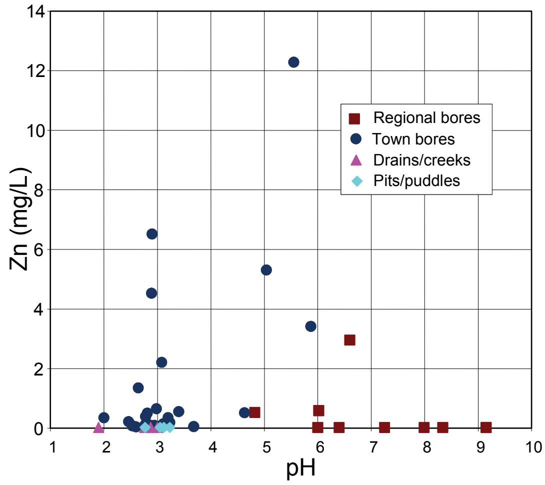

Figure 4.4 Dissolved Zn vs. pH for varying waters at Narembeen.

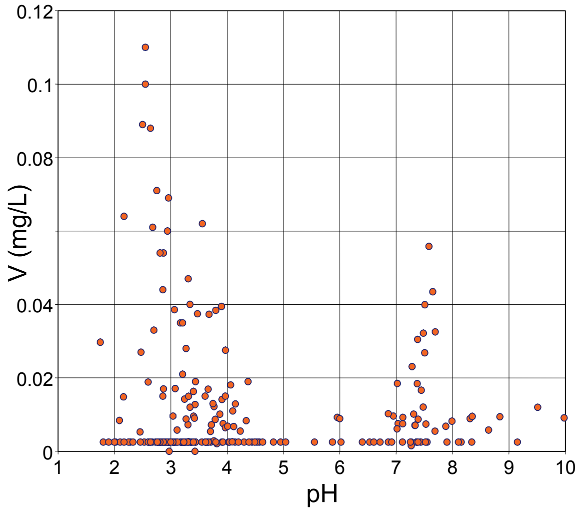

Figure 4.5 Dissolved V vs. pH for varying Wheatbelt waters.

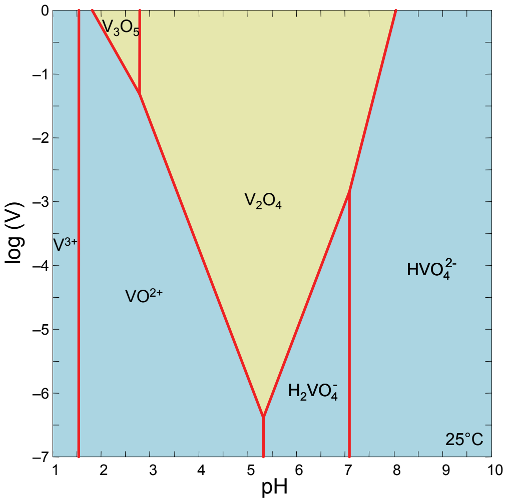

Figure 4.6 Vanadium speciation and solubility at 25°C/1 atm/0.16 V, indicating minimum solubility at pH 5.3.

The very high concentrations of various elements in these acidic groundwaters has potentially major environmental and health ramifications. However, many elements such as Cu (Figure 4.3), Zn (Figure 4.4) and As have much lower concentrations in surface drains than in the groundwaters, presumably due to co-precipitation with Fe minerals precipitated on the walls and base of the drains (Figure 4.7). Any subsequent changes in conditions (pH, salinity or redox) that results in dissolution of these minerals (Section 4.1) could see these elements released in high dissolved concentrations. Importantly, metals more weakly adsorbed by Fe oxides such as Mn and Pb appear to be readily released into surface drainage waters (Figure 4.7) and are an ongoing risk. This should be considered in any amelioration activities.

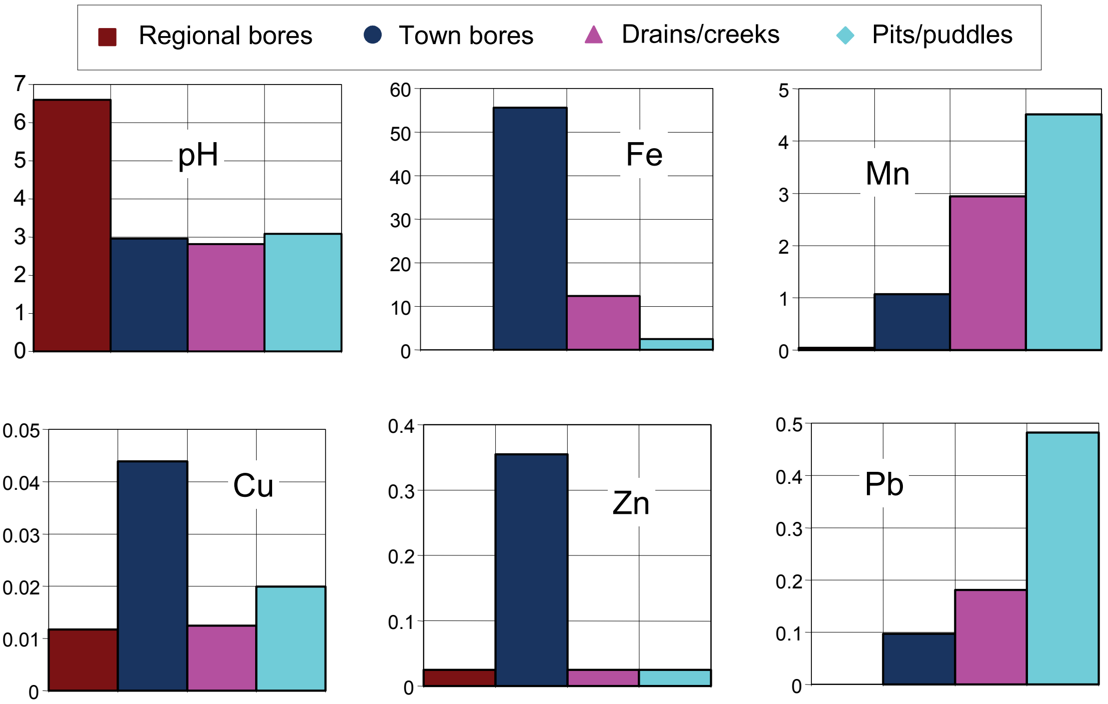

Figure 4.7 Median concentrations of various metals and pH for different water types at Narembeen, all metal concentrations in mg l^{-1} (after Tapley et al., 2004).

Ionic strength (c.f. salinity) also can influence solubilities, as the chemical activity of any particular solution phase is commonly affected by salinity. Increasing ionic strength commonly acts to reduce solubility e.g. the maximum solubility of Si in groundwaters (as controlled by precipitation as amorphous silica) decreases from 55 to 12 mg l^{-1}, going from fresh conditions to 18‰ salinity (Figure 4.8). Additionally, some elements are highly affected due to specific precipitation as salts of ions associated with saline conditions: e.g., Ba, which has very low concentrations in saline waters due to barite ($BaSO_4$) precipitation (Figure 4.9). There are similar, though weaker, effects for Ca and Sr.

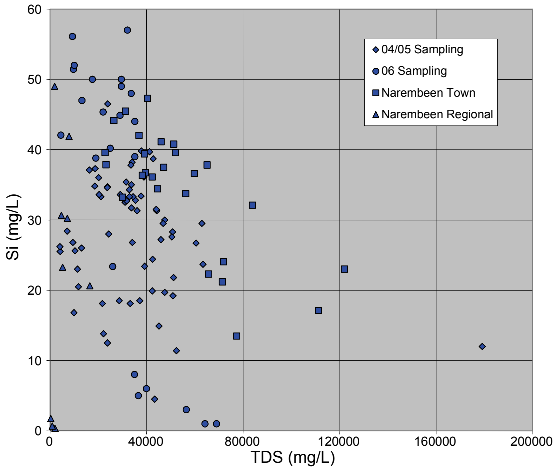

Figure 4.8 Dissolved Si vs. TDS for varying Wheatbelt groundwaters.

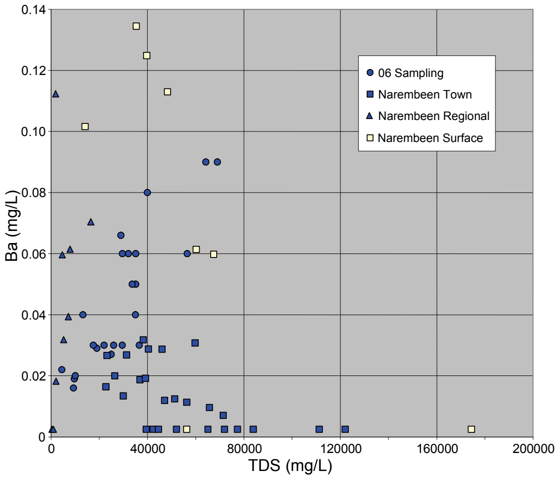

Figure 4.9 Dissolved Ba vs. TDS for varying Wheatbelt ground- (blue) and surface- (yellow) waters.

These ionic strength effects are more easily observed for Si and Ba, as these elements are generally only weakly affected by pH, except under alkaline conditions. Strong effects are also observed for Au (and potentially other metals such as Ag, Pt and Pd) which has enhanced solubility in saline conditions, due to oxidation to dissolved Au chloride. For most other elements, including base metals, REE, U and anionic chalcophile elements such as As and Sb, ionic effects are generally minor compared with effects such as pH variation.

4.3 Main findings

- Dissolved iron (either Fe^{2+} or Fe^{3+}) and aluminium play a major role in acidity transfer from groundwaters to drains.
- The mineral origins of the iron rich, acidic groundwaters are unclear.
- Low pH waters provide geochemical conditions that favour mobilisation of trace elements from the regolith, with local properties of the regolith influencing the composition of the trace elements.
- The varying salinity of waters in surface environments will have less influence on the behaviour of the trace elements, rare earths elements and chalcophile elements (such as As) than pH conditions though will greatly influence major constituents such as Na, Ca, Mg, K, SO_4 and Cl.

4.4 Management implications

- Management of acidity in acidic drainage waters will need to consider iron and aluminium in addition to trace elements
- Prediction of trace element composition of local acidic groundwaters (and therefore waters that might be intercepted by drains) may not be possible if these vary due to the composition of local regolith (deep soils).
- The pH of the waters will be more critical for management of trace elements than the salinity.

5. GEOCHEMICAL AND HYDROCHEMICAL PROCESSES OCCURRING WITHIN DRAIN ENVIRONMENTS IN THE AVON BASIN

Rob Fitzpatrick, Brad Degens, Andrew Baker, Mark Raven, Margaret Smith, Steve Rogers, Richard George and Paul Shand

5.1 Introduction

The geochemical risks associated with deep drainage include the potential to release metals and other elements and colloids into the landscape. Assessment of these risks requires consideration of the biogeochemical and mineralogical processes in the soils and sediments of drainage systems. This chapter presents the results of a sampling program in the Avon Basin to:

- Develop a robust field sampling program and experimental approach to characterise the soil, sediment, mobile colloids and waters in the drains and receiving playas.
- Develop detailed and generic conceptual models that encapsulate various soil-water processes to:
    - Assess impacts of deep open drains on the production, export and fate of leachate and minerals on receiving environments.
    - Recommend generalised principles that lead to implementation of "best management practices" for ameliorating identified categories of degraded drain sediments and soils.

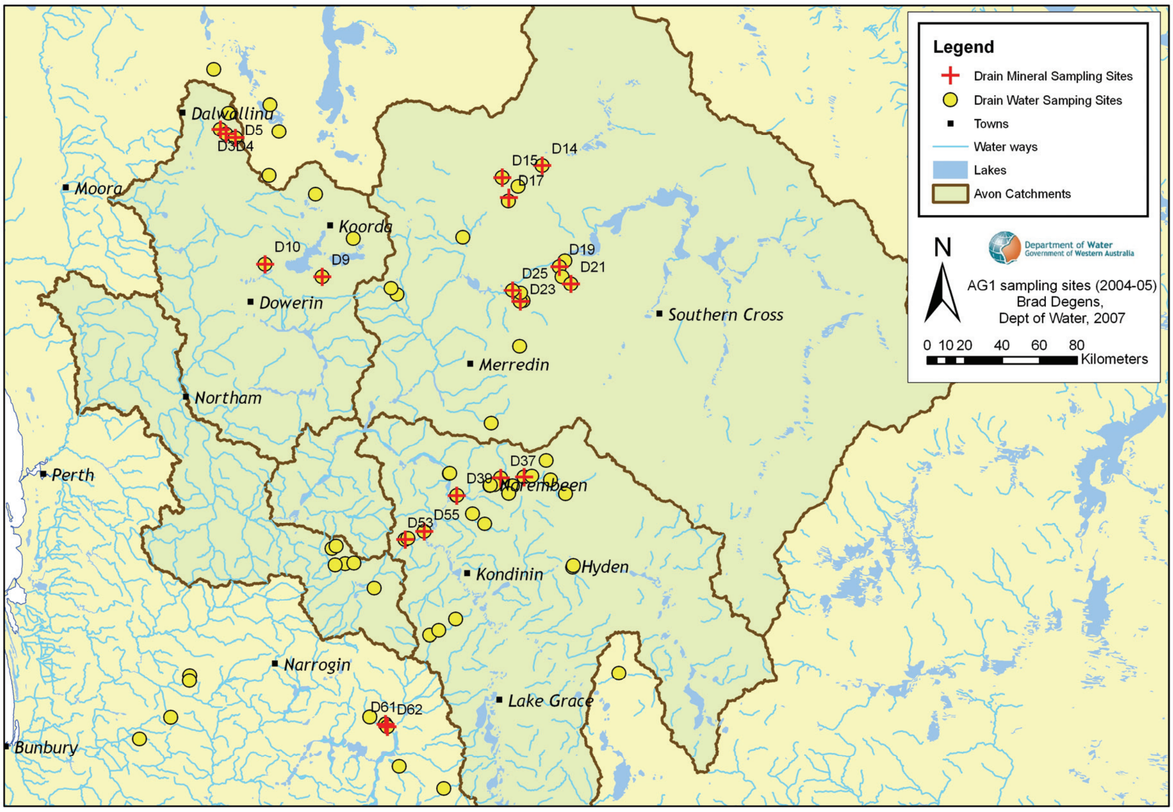

Figure 5.1 Locations of drain hydrochemistry and mineralogy sampling sites in the Avon catchment (WA).

5.2 Methods

Sediments and soil materials were surveyed at 19 representative acidic drain sites (January 2005), 8 receiving lake sites and 6 reference lake sites (February 2006) in the Avon catchment (Figure 5.1; site locations in Appendix 1). At each site, the following materials (over 300 samples) were described and sampled: sulfidic materials/sediments, sulfuric materials/sediments, gels, salt efflorescences, salt crusts, iron-rich crusts, soils (drain batters; and naturally occurring saline-sodic soils on the edge and adjacent of the drains). Samples were variously treated and fractionated (sub-samples) according to procedures outlined in the flow diagram (Figure 5.2).

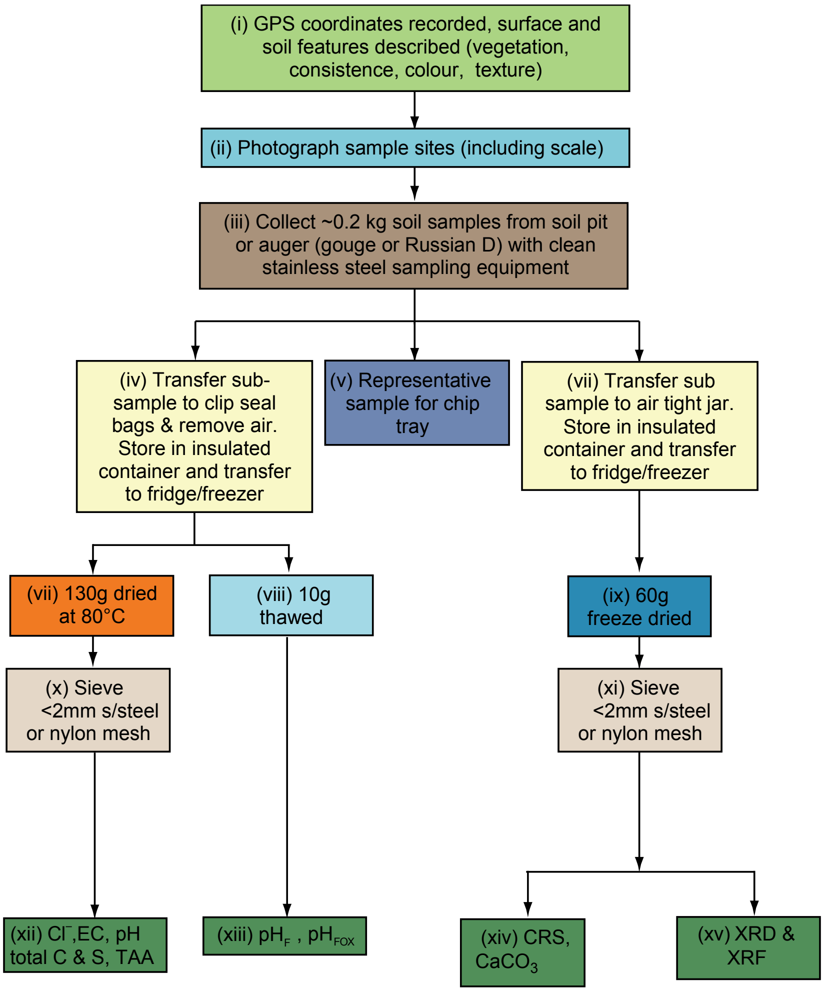

Figure 5.2 Flowchart for sample collection, preparation and analysis.

Specialised laboratory analyses (Figures 5.2 and 5.3) were conducted on selected sub-samples from each site using geochemical (XRF and ICP), mineralogical (XRD and scanning electron microscopy) and chemical methods to determine what biogeochemical and mineralogical processes were taking place in the drains and receiving environments. In addition, drain flows were estimated and waters were sampled for salinity, pH, major metals, trace elements, rare earth elements and other elements such as uranium (Chapter 2).

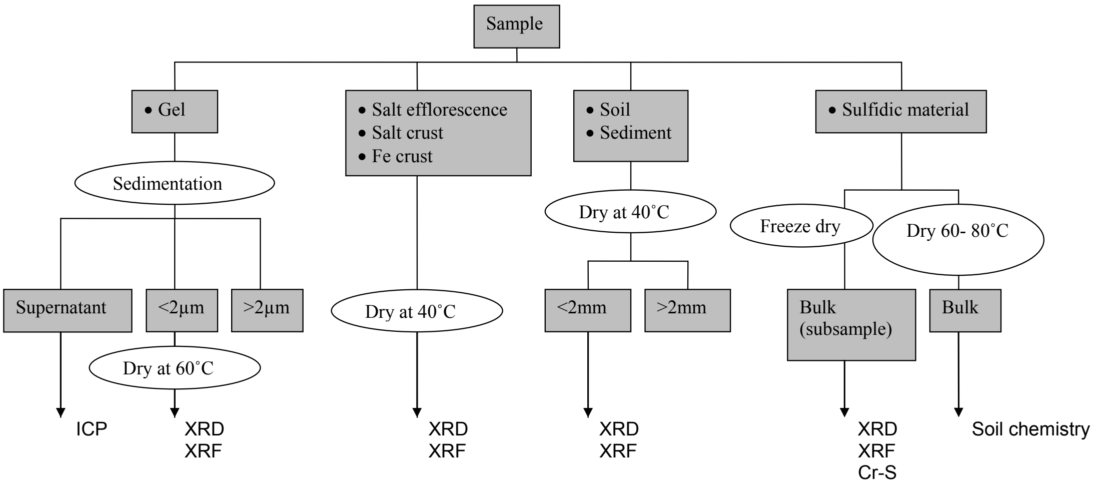

Figure 5.3 Flowchart summarising preparation and fractionation of various sub-samples and analytical methods used to characterise mineralogy, geochemistry and chemistry of sub-samples. Where: XRD = X-ray diffraction, XRF = X-ray florescence, ICP = Inductively Coupled Plasma analyses, Soil chemistry = pH, EC (Electrical Conductivity), organic carbon, carbonate content, exchangeable cations and SAR (Sodium Adsorption Ratio).

5.3 Results and Discussion

5.3.1 Systematic web-based approach for acquisition, collation and communication of soil-regolith data

All the descriptive field information and laboratory data were stored in a web-based data-base, specifically designed as a framework for the acquisition, collation and communication of all information (Baker and Fitzpatrick 2005; Fitzpatrick *et al.* 1996). The online database was constructed using Microsoft FrontPage 2003 to ensure that large data sets were structured and could be managed in a methodical way to allow rapid and effective communication of results. The visual information (e.g. landscape, soil profile and chip tray colour photographs) and data (field and laboratory including XRD data and XRD spectra) stored in the web-based data-base is shown in the flowchart in Figure 5.4. This new approach permitted the easy collation of geological, pedological, hydrological, geochemical and mineralogical data to help construct cross-section diagrams and mechanistic models of soil-regolith and hydrological processes for each case study site. For example, the locality map (Figure 5.4 (i)) is linked to all site summary pages, permitting rapid and simple navigation between sites and provides links to more detailed information. The location of each sample or group of samples, collected at each site is displayed on photographs in the site summary pages (Figure 5.4 (ii)). This provides an accurate record of sample locations and their spatial distribution in the drain and receiving environments. Each sample, group of samples or profile can then be investigated in more detail via a HTML link to a sample summary page (Figure 5.4 (v)). These pages provide more detailed information on each sample and their location within a profile or group of samples, with high quality colour photographs, including a scale, for each sample (e.g. Chip tray photos in Figure 5.4 (viii)). Interpretive toposequence models (Figure 5.4 (iv)) are included for each site. Data summary pages (Figure 5.4 (vi)) have direct HTML links to all the observations and data recorded in the field (colour, texture, pH, Eh etc.) and results from laboratory techniques (XRD, XRF, ICP-MS etc.). Spreadsheets containing geochemical data (e.g. XRD (Figure 5.4 (ix)) and XRF (Figure 5.4(x)) are made available for download, via the data site, without putting the original data at risk. Data, such as SEM images, are also made available (Figure 5.4 (vii)).

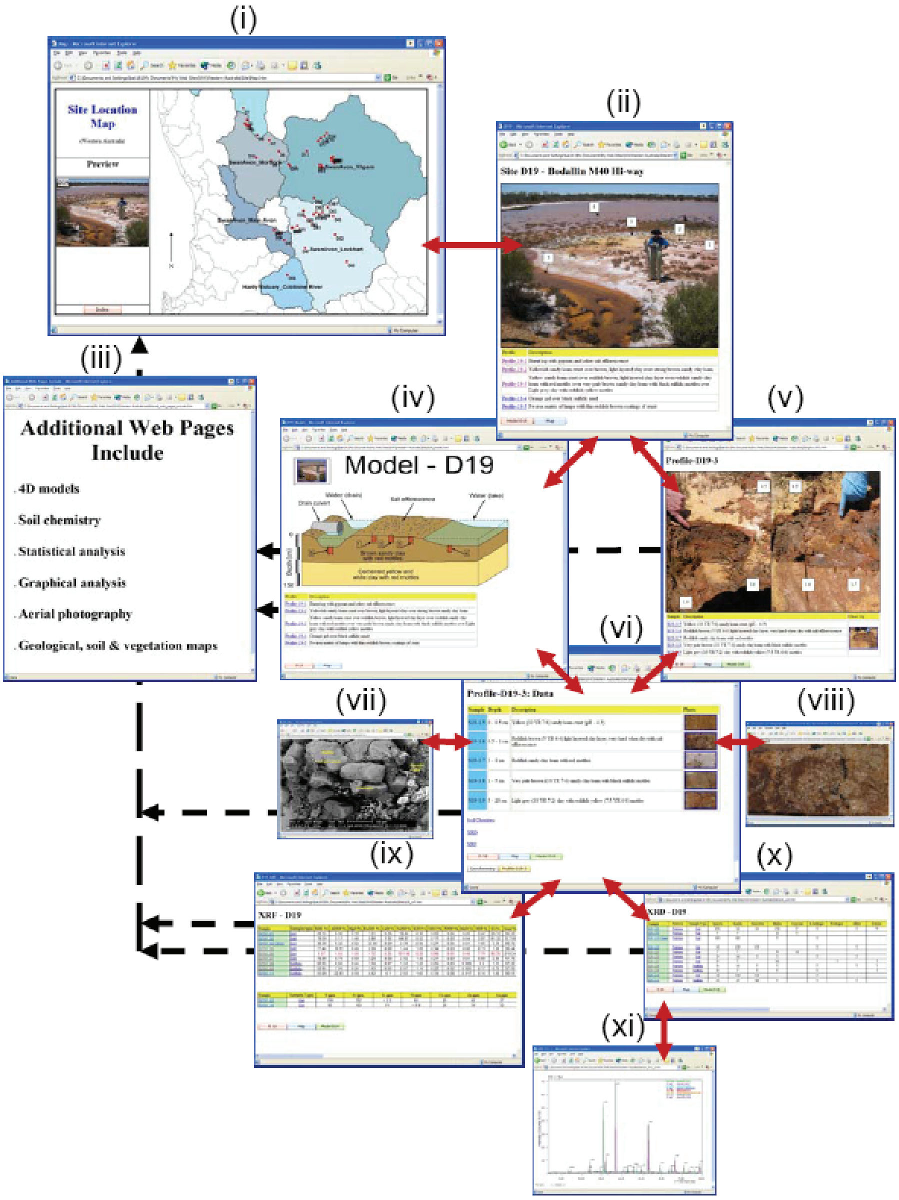

Figure 5.4 Flowchart constructed of web views from a typical acidic drain entering an acidic receiving lake site (D19: Boodarockin, Koorda-Bullfinch Rd see Figure 5.6) containing acidic water and acid sulfate soil web based data set. Views represent: (i) Site locality map of Avon basin, (ii) site summary web page, (iii) additional web pages that were included in the data set, (iv) 3-dimensional, interpretive model, (v) profile/sample summary page, (vi) data summary page, (vii) SEM photograph, (viii) chip tray photograph, (ix) XRF data, (x) XRD data, (xi) XRD spectra.

5.3.2 Acidic drain water salinity and acidity

Most drains were typically very saline at the time of sampling (January) with specific electrical conductance (SEC) in the range 60-100 mS cm^{-1} (approximating to TDS between 43,000 and 75,000 mg l^{-1}). Acidic pH was widespread, with more than half of the drains sampled in October 2004 having pH values less than 3. Drain pH decreased during the summer months, probably due to oxidation of ferrous iron in groundwaters, iron minerals in sediments and/or evaporation. Results indicated two broad groups of drain pH and salinity. The pH was lowest east of a line from Dalwallinu to Dumbleyung (pH less than 3.5) and highest (pH greater than 6) in the western and central part of the

Basin (see section 2, Fig 2.1), though there were few drains flowing in this area. Only a few flowing drains contained high pH (alkaline) waters, mostly in the western areas. The data showed that in most eastern drains with a low pH (less than 4.5), iron, aluminium, cobalt, copper, zinc, lead, uranium and a range of other trace elements and rare earth elements were all elevated (See chapter 2). The chemistry of the receiving and reference lakes is presented and discussed in Chapter 6.

5.3.3 Drain mineral environments

Several materials were generally evident within the drains and indicate different geochemical process zones. These materials broadly consisted of (from the original excavated base of the drain): unconsolidated saturated sediments including sulfidic materials, monosulfidic black oozes, sulfuric materials, saturated gels and precipitates, salt crusts overlying saturated sediments and salt crusts in the capillary zone above the drain waters. Not all materials were present within all drains. For example, in recently constructed drains (<3 years age) or drains with little sedimentation, there was minimal sediment profile, gel and precipitate development. The main materials and key processes that these indicate are discussed in the following sections.

5.3.4 Sulfidic materials

Sulfidic material occurred in almost all the drain sediments (Figures 5.5 b & c; and 5.12) as a thin horizon/layer (5 to 10 cm thick) representing a pool of stored acidity that could contribute to drain water acidity seasonally, or de-oxygenation in aged drains if exposed to oxygen. The sulfidic material mostly consists of accumulations of iron sulfide minerals, one of the end products of sulfate reduction (i.e. the use of SO_4^{2-} instead of O_2 during microbial respiration). Sulfate reduction is a natural process that occurs in virtually all the drains. However, the quantities or thickness of sulfidic material that accumulate in the drains is a function of many factors. The key requirements for high rates of sulfate reduction and sulfide accumulation are: (i) a high concentration of sulfate in surface or groundwater, (ii) saturated iron rich soils and sediments, saturated for periods long enough to favour anaerobic conditions, and (iii) the availability of labile carbon to fuel microbial activity. Saline groundwaters in the Wheatbelt generally contained quite high concentrations of sulfate and ferrous iron. Thus, drains that intercept saline groundwater should be expected to accumulate some sulfides in their sediments over time, especially if they are permanently flowing or waterlogged. Two forms of iron sulfide minerals are of importance from an environmental point of view: monosulfides (FeS) and pyrite (FeS_2). Soils and sediments rich in monosulfides (or “black ooze”) tend to be very dark and soft. Monosulfides can react rapidly (minutes to hours) when they are disturbed and exposed to oxygen (Sullivan et al. 2002). Pyrite will tend to occur as more discrete crystals in the sediment matrix and will react more slowly when disturbed (days to years). Layers of sulfidic material also occurred in receiving lakes (e.g. Figures 4.5 - in this case the sulfidic material has recently oxidised/transformed to sulfuric material). If flushed out of the drain as floodwaters scour drain channels, they will oxidise and may become acidic. However, in some drains, the ubiquitous presence of carbonates of calcium, magnesium and sodium in drain sediments and banks may neutralise drainage acidity. The extent to which this occurs, however, is dependent on whether the carbonates remain in contact with the acidic waters and are not armoured with precipitates or buried.

5.3.5 Monosulfidic black ooze

Monosulfidic Black Ooze (MBO) is readily observed in the surface sediments of most drains (Figures 5.5b and 5.5c) and in receiving lakes (e.g. Figure 5.6). The high nutrient environment, especially at the edges of drains and the activity of algae and micro-organisms cause reducing conditions to develop rapidly with the formation of black, smelly iron monosulfides and other sulfides. Erosion of organic rich topsoils and influx of saline groundwater, with low redox potential (reducing), into the drains are also likely to contribute to MBO formation. MBO is very reactive if exposed to oxygen, but provided that the materials remain anoxic and undisturbed they are relatively unreactive.

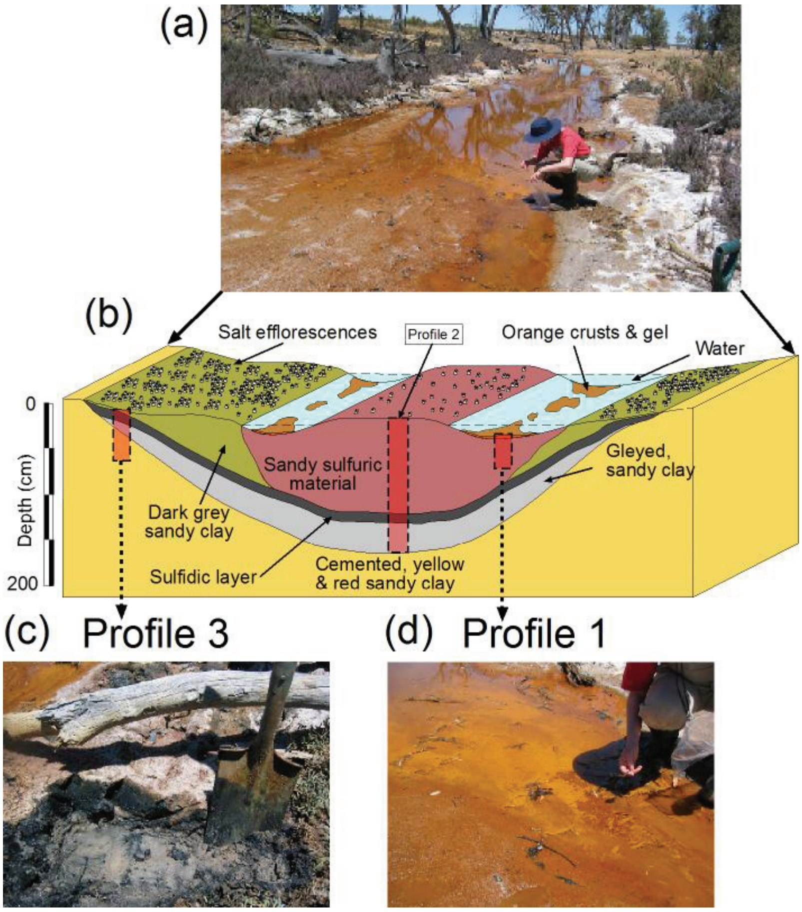

Figure 5.5 Schematic cross-section or hydro-toposequence (b) through a drain showing sulphuric soils with orange crusts and gels (a and d) comprising mostly of Fe-oxyhydroxides (akaganéite: β-FeOOH) and Fe-oxyhydroxysulfates (schwertmannite: $Fe_8O_8(OH)_6SO_4$) in surface waters overlying soil horizons consisting of: (i) reddish sulfuric material (pH <3.5), soft and sandy in Profiles 1 and 2, (ii) black sulfidic material (pH >4) friable and sandy clay in profiles 1, 2 and 3, (iii) greyish gleyed sandy clay and (iv) yellow matrix with red mottles, hard, sandy clay. White salt efflorescences occur on the sides of the drain in profile 3 overlying a mixture of uniform black, sulfidic material and monosulfidic black ooze, which in turn overlies mottles of black, sulfidic material in a yellowish-greenish-grey to olive mottled clay.

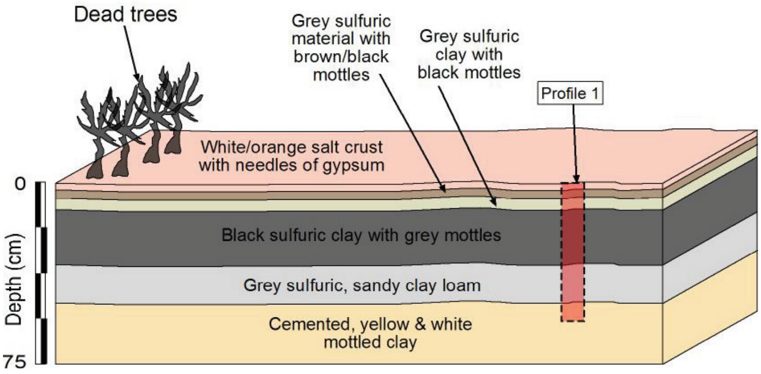

Figure 5.6 Schematic cross-section or hydro-toposequence through receiving lake D17 (Cunderdin Rd, Elachbutting) showing various white salt efflorescence crust with needles of gypsum overlying layers of black and grey sulfuric material (profile 1).

5.3.6 Sulfuric materials – including gels and precipitates

Subaqueous soil horizons and sediments in some drains and receiving environments are highly acidic (pH <3.5) and by definition classify as "sulfuric materials' according to Isbell (2002). Acidity can form through several mechanisms:

(i) primarily by iron hydrolysis reactions (e.g. (Mann 1983) or ferrolysis (Brinkman 1979) when anoxic ground water containing dissolved ferrous ions is exposed to air and ferrous ions are oxidised to the ferric ions, which reacts with water to form orange-brown precipitates, gels or crusts of ferric oxyhydroxides, releasing free hydrogen ions in the process.

(ii) When sulfidic materials are drained and exposed to air, they oxidise and produce sulfuric acid (e.g. Dent & Pons 1995). If the amount of acidity produced exceeds the buffering capacity of water and sediments, acidification occurs. Prior to draining, materials that can cause acidification by sulfide oxidation are called sulfidic materials (i.e. potential acid sulfate soil materials or PASS). Once sulfidic materials are drained, they may transform to sulfuric materials (i.e. actual acid sulfate soil materials or AASS).

In the WA Wheatbelt drains, the dominant source of acidity appears to be the acidic, oxidised, iron rich shallow groundwater discharging to the drains (where the water is acidic prior to drainage), though formation of secondary minerals in the drain sediments provides additional pathways of acid storage and release.

Mineral precipitates and gels present in the drains are indicative of specific geochemical conditions occurring (or having occurred). The occurrence of bright yellow natrojarosite mottles in some of the clay-rich sulfuric horizons are indicative of acidic conditions in the pH range 3.5-4. Similarly, the occurrence of orange coloured mottles, gels and crusts (Figures 5.5a & d) are indicative of schwertmannite and akaganéite, which forms from the oxidation of ferrous iron under acidic conditions in the range pH 4-5. Many of these minerals occurred in drains above groundwater level, indicating that there is a store of acidity in the soil profiles that could contribute to future, if not current drainage acidity. The minerals also present a reactive surface that can alter the solubility of trace metals in the drainage waters (see below). Saline and subaqueous soils with sulfuric material may occur in receiving lakes (e.g. Figures 5.6 and 5.7).

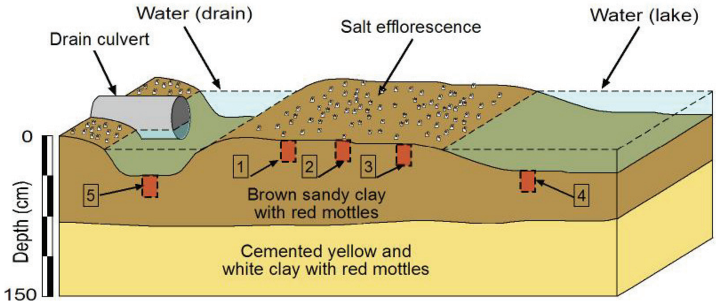

Figure 5.7 Schematic cross-section or hydro-toposequence through receiving lake D19 (Boodarockin, Koorda-Bullfinch Rd) showing: (i) acidic water overlying subaqueous soils with sulfuric material (profiles 4 and 5) and (ii) white salt efflorescences overlying sulfuric material (profiles 1, 2 and 3).

5.3.7. Salt crusts - Sulfate-containing salt efflorescences and oxyhydroxysulfate minerals

Soluble sulfate/chloride-containing minerals in efflorescences are produced by evaporation of groundwater and capillary waters. These evaporite minerals reflect the geochemical reactions resulting from the combination of groundwater, drainage water and drained soils in regions. For example, zones under:

> • alkaline conditions (e.g. surface soil horizons in the drain batters) where Na/Ca ratio >4, eugsterite, gypsum and thenardite (i.e. Na-Ca-sulfate salts) form.
>
> • acidic conditions (e.g. interface of groundwater and drain batter in the base of drains) where Na/Ca ratio <4; bloedite and pentahydrite (i.e. Na-Mg-sulfate salts) form.

A predominance of sulfate-containing evaporite minerals occur in the drains because of the specific chemical composition and pH of inflowing drainage waters containing Na, Ca, Mg, Cl, Ba and SO_4. This composition probably arises from saline groundwaters enriched in sulfate (with other elements sourced from mineralised zones) seeping through soils. Declines in pH of the waters (due to oxidation of ferrous iron) on exposure to air or mixing with oxygenated waters can cause additional mineral dissolution and contribute to precipitation of a range of sulfate-containing minerals, each reflecting different geochemical conditions in the drains. These minerals include:

- pentahydrite, starkeyite, bischofite, bassanite, carnallite, rozenite, barite, halite and gypsum in sandy sulfuric horizons with pH <3.0

- natrojarosite and jarosite in clay-rich sulfuric horizons with pH 3.5-4

- eugsterite, bloedite, thenardite, glauberite, gypsum, thenardite, mirabilite, schwertmannite, lepidocrocite, akaganéite and colloidal poorly crystalline, pseudoboehmite-like (white) precipitates in sulfidic materials with pH >5.

Movement and accumulation of soluble salts is typical in many drains but, the salt crusts in the Avon catchment contain an assemblage of sulfate-containing evaporite minerals as detected by X-ray diffraction and SEM previously unrecorded in Australia (Figures 5.8-5.10).

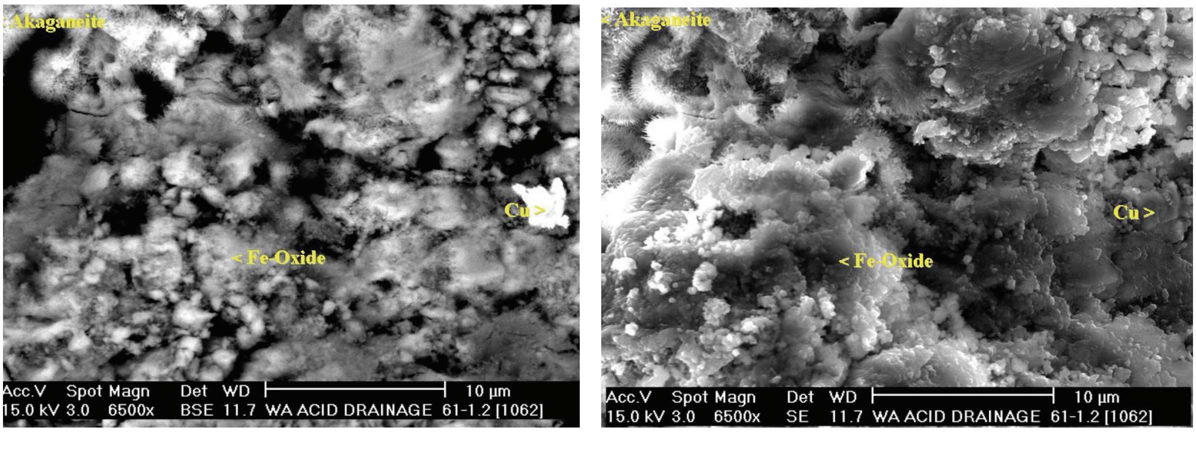

Figure 5.8 SEM images of orange coloured iron oxide crusts and gels in the soil profile 1 (d) near the centre of the drain shown in Figure 5.4. The crust and gel comprises mostly akaganéite with some minor schwertmannite, which scavenges dissolved metals (e.g. Cu).

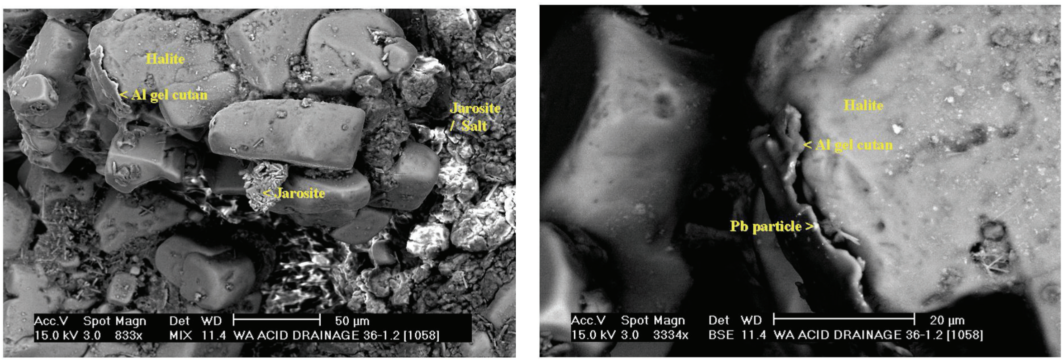

Figure 5.9 SEM images of salt efflorescence (halite and natrojarosite). The halite crystal has a coating (cutan) of Al-gel that contains small particles of lead (Pb).

The occurrence of these minerals is caused by the specific geochemistry of the drainage environment. The components of the evaporite minerals are generally derived by leaching of products due to the oxidation of iron sulfides and then precipitated as specific minerals at various stages during the drying/evaporation of the drained soils and sediments. Sulfate-containing salt minerals accumulate steadily in the lower parts of drains immediately below/under the carbonate-rich or calcrete layers and above the sulfidic layers (Figure 5.4d) because of limited lateral movement of water to carry the soluble salts away in the drains. It is likely that annual cycling of these salts occurs, with evapo-concentration and metal accumulation during the summer months followed by dissolution of the salts and transport in drainage waters during winter rainfall. A change in mineral composition will indicate a change in the nature of the salts entering the system from drain or ground waters.

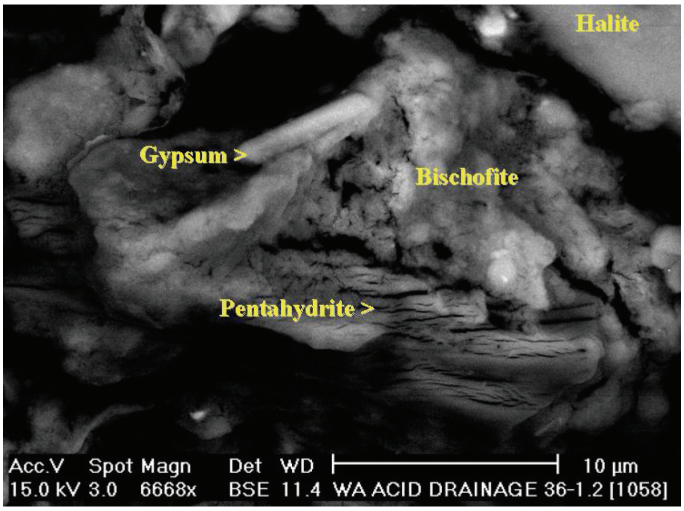

Figure 5.10 SEM image of a salt efflorescence in an acidic receiving lake (D19 - Boodarockin, Koorda-Bullfinch Rd) containing mixtures of halite (NaCl), gypsum ($CaSO_4$ $2H_2O$), pentahydrite ($MgSO_4.5H_2O$) and bischofite ($MgCl_2.6H_2O$) in close proximity to each other.

These minerals range in morphology from thin, powdery, and very transient efflorescences to thicker, more persistent, soil-cementing crusts (e.g. Figures 5.9 and 5.10). Formation of these complex sulfate salts of Fe, Al, Na, Pb, Ca, As, Zn, Mg, jarosites, oxyhydroxysulfates and oxyhydroxides are indicative of rapidly changing local environments and variations in Eh, pH and rates of availability of S and other elements. As such, these evaporite minerals are indicators of soil-water processes operating in specific landscapes. A detailed understanding of these minerals and biogeochemistry in acid sulfate soils and sediments reveals important dual applications for environmental land management and mineral exploration.

5.3.8 Concentrations of Major and Trace elements in Drain Materials

Gels: The gels were mainly composed of kaolin and smectite (probably derived from drain walls), locally with significant amounts of quartz and halite, and less commonly, gypsum and akaganéite. Trace to minor amounts of feldspars, carbonates, jarosite or anatase may occur as phases within the gels.

Compared with other sample types, the gels contain significantly higher concentrations of Ti, Al, Fe, Cr, I, Nb, Sn, Th and V (see selected box plots in Figure 5.11). Gels may also contain relatively anomalous concentrations of Mg, P, As, Cd, Cu, Mo, Pb, Rb and Y. Rare earth elements tend to correlate with each other and with Y, whereas Si is negatively correlated with most elements. Niobium and Ti correlate with each other, presumably reflecting their occurrence in anatase. Strontium, Ca and Mg tend to correlate with each other, indicating that they most likely occur in carbonates; Sr also correlates with Na, Br and Cl, suggesting some association with halides. Rubidium correlates with K, Ba, Cr, Ni and Zn, suggesting that these elements may be present in smectites.

Salts: Halite and gypsum were the dominant salts, but may be associated with significant amounts of quartz. Minor to trace amounts carbonates, clay minerals and sulfates or chlorides of Mg, Ca, K and Fe were also present.

The salts contain the most significant concentrations of Ca, Na, Cl, S and Sr, and may contain anomalous concentrations of Mg, Cd, Cu, I and Mo (see selected box plots in Figure 5.10). They contain the lowest concentrations of Ti, K, Co, Cr, Ga, Nb and Ni (Figure 5.10), suggesting that these elements are immobile in this environment. Sulfur correlates with Na, Ca, Sr and Cl (reflecting their occurrence in gypsum and halite), but are negatively correlated with elements found most commonly in silicates (especially Si, Ti, Al, Fe, K, Ba, Cr, Ga, Nb and Rb. Rare earth elements correlate with each other and with Th and Y.

Soils: The soils were mainly composed of quartz, kaolin and smectite, with minor to trace amounts of feldspar, carbonate, Fe oxides and mica. Variable amounts of halite and gypsum were also present in some samples.

Silicon exhibited a negative correlation with most other elements including Ti, Al, Fe, Mn, Mg, K, Ba, Cr, Ga, Nb, Ni, Pb, Rb, Th, Tl, V, Y and Zn which correlated with each other. Sulfur correlated with Mg, Na, Ca, Cl, Br and Sr, indicating their occurrence in halite, gypsum and carbonates; these elements are also negatively correlated with Si.

Sulfidic materials: The sulfidic materials are mineralogically similar to soils, except that Fe sulfides and oxides are more common. Sulfidic horizons contained anomalous concentrations of P, Ba and Pb (Figure 5.11), but were generally similar to soils in composition. Element associations are similar to those for soils, with most elements being negatively correlated with Si.

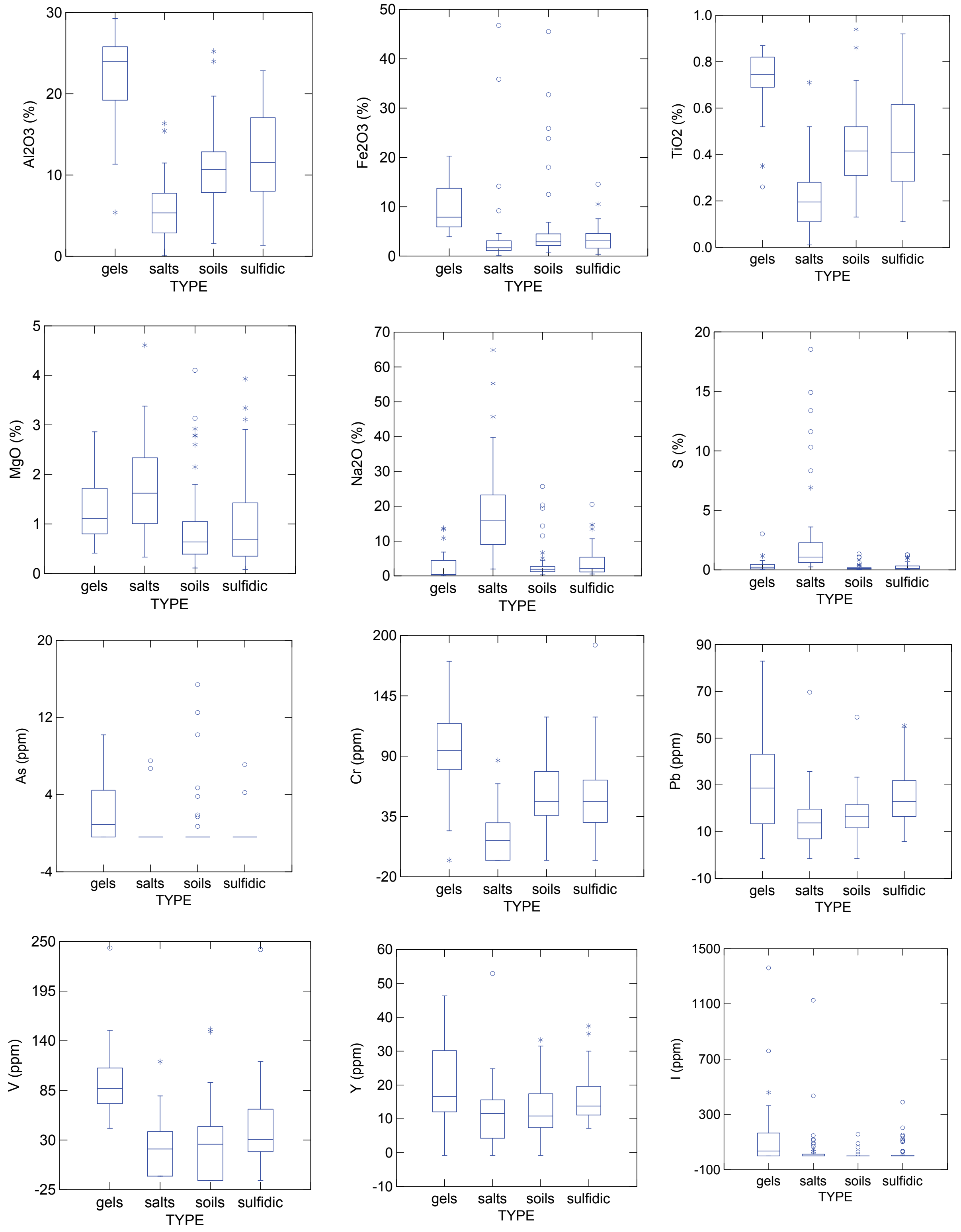

Figure 5.11 Concentrations of selected major and trace elements in gels, salts, soils and sulfidic materials in drains (box plots).

5.4 Conclusions

Sulfate-containing evaporite minerals found in salt efflorescences in drains and receiving lakes are an integrated indicator of the complex geochemical conditions in these environments and play a critical role in drain erosion processes by salt fretting. These minerals are a transient storage of ions (Na, Ca, Mg, Cl, Sr and SO_4), which will dissolve during rainfall and contribute to the formation of the saline monosulfidic black ooze in the drains, particularly sulfate. The metals concentrated within these salts (e.g. Al, Fe, Cd, Cu and Mo) also indicate a significant potential environmental risk since many are in a position to be flushed (potentially in ***concentrated*** pulses) into receiving environments by rainfall events. The latter risk applies to drains in both low flow and dry states.

Fine gels forming on the surface of sediments in drains and receiving lakes, and iron rich precipitates that form in and on the gels, can be efficient scavengers of trace metals (e.g. Cr, Sn, Th, V and occasionally As, Cd, Cu, Mo). Despite this, the fine colloidal nature of these materials places them at risk of being suspended and flushed from the drains by even low flow velocities. The detailed chemical association of the metals with the precipitates and gels is not known but it is conceivable that the materials could act as transporting media for metals from the drains if not well managed. Changes in water chemistry conditions (e.g. evaporation and further declining pH) could result in dissolution of trace metals associated with the gels and precipitates.

The accumulation of significant sulfidic materials in drain sediments increases the risk of additional acidification of drainage waters. The discharge of acidic, ferrous iron rich groundwater (Figure 5.5a & b) and subsequent oxidation appears to be the main processes causing low pH, however, the contribution of this source compared with sediment sources over the life of the drain is not clear. Acidification could conceivably be dominated by the release of stored acidity from sulfidic materials after cessation of groundwater discharge (and drying occurs) or if the materials are excavated or flushed from the drains. This acidification risk is greatest where carbonate minerals are absent or spatially separated from the sulfidic drain sediments.

Accumulations of metals within the sulfidic materials further compounds the geochemical risks posed by drains to receiving environments. In addition to lowering pH, disturbance and oxidation of sulfidic materials during flow events could lead to significant, short-term pulses in dissolved metal concentrations in surface waters, including aluminium, iron and other metals released from the sulfidic materials (e.g. Pb, Cu or Cr, see Figures 5.8 & 5.11). Drains sampled in eastern areas were typically acidic and contained large amounts of Fe, Al, salt, metals (Pb, Cr, Mn, As) and the rare earth elements e.g. lanthanum and cerium (see Section 2). The increase in solubility of metals in acidic environments may be more harmful to biota than the low pH itself.

Accumulations of iron precipitates on vegetation blown into the drains poses a risk to hydrological function, particularly if burnt. The effect of burning of vegetation residues at D14 (Elachbutting) is a dramatic example of where an intense fire resulted in the formation of an irreversibly fused, iron plug, which blocked a drain pipe (Figure 5.12).

The role of sediments and minerals associated with these in influencing the geochemical risks of drains to off-site environments will be increasingly important as drains age and as flows ebb or become seasonally intermittent. The drain environments surveyed in this study varied in age, though many were at least 3 years old. Furthermore, the flow regimes varied widely (at the time of sampling in summer), from no-flow with no pools to sluggish flows of <0.1L/s with considerable pooling to flows of up to 7 L/s (at the D19 site, Boodarockin drain on the Koorda-Bullfinch Rd). Conceptually, recently constructed (younger) drains tend to exhibit higher flows and have had less time for geochemical processes to occur that lead to mineral formation with acidity and trace metal accumulation. As drains age, increasing time for geochemical processes to occur is likely to lead to a greater role of these secondary minerals in influencing the timing of acid and trace metal export from drains, with this becoming more linked to disturbance and rain-fall runoff events.

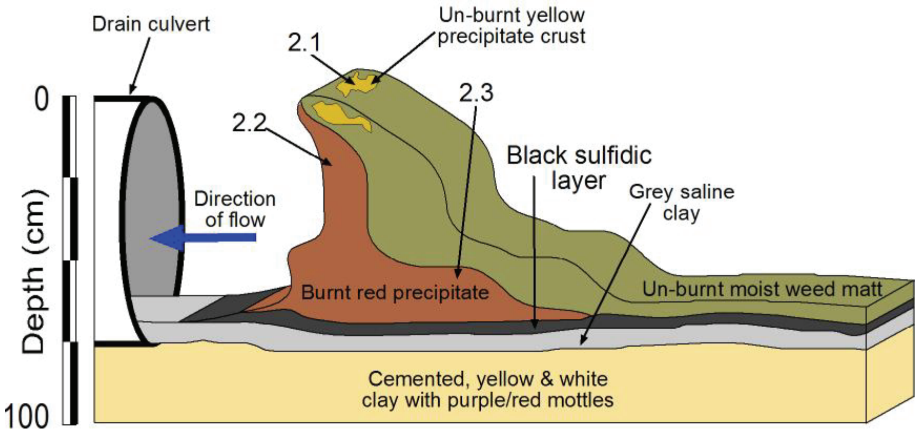

Figure 5.12 Schematic cross-section or hydro-toposequence through drain D14b (Elachbutting) showing: (i) black sulfidic layer in the base of the drain underlying a hard cemented (ceramic-like) burnt zone, which clogged the outflow pipe at the entrance of the drain culvert and (ii) un-burnt zone.

It is important for all landholders, community groups, drainage contractors and local governments in the Avon catchment to be aware of the many impacts that result from occurrence of sulfuric materials and disturbance of sulfidic materials, as these impact on potential geochemical risks. In other parts of Australia, disturbance and oxidation of sulfidic material resulting in creation of sulfuric materials has led to: the destruction of wetlands; acidification and deoxygenation of waterways; contamination of groundwater resources; reduction in public amenity of lakes and waterways; increased mobility and accumulation of heavy metals; corrosion and destabilisation of roads, concrete and steel infrastructure; decreased agricultural productivity of land; increased odour problems, and increased mosquito and arbovirus incidence. A range of management options have however been designed to mitigate or lessen the impacts of ASS in different environments.

5.4.1 Key findings

- Changes in soil geochemical characteristics in drains and receiving environments could be characterised by a rapid field survey procedure coupled with a series of key laboratory analysis methods for gels, salts, soils and sulfidic materials selectively sampled at each site.
- A systematic web-based data system was developed for acquisition, collation and communication of detailed data sets (e.g. soil morphology, chemistry and mineralogy) dealing with gels, salts, soils and sulfidic materials in drains and receiving environments.
- Identified that a range of soil formation processes occurred in the hypersaline soils of drain batters and sodic soils on the edge of drains.
- "Reddish-brown and orange-yellow precipitates or gels" in drains are ferric-oxyhydroxides and ferric-oxyhydroxysulfates that can which release free hydrogen ions in the process of formation. These precipitates form when the ferrous iron rich waters in the drains and receiving lakes containing dissolved ferrous ions are exposed to air and ferrous ions are oxidised to ferric ion minerals.
- Various types of hydrated oxyhydroxides (ferrihydrite), iron oxyhydroxysulfates (schwertmannite and akaganéite), oxyhydroxides (goethite) and oxides (hematite) occurred in various micro-environments in drains and receiving lakes. The minerals were indicative of a wide range of rapidly changing local environments and variations in Eh, pH, rates of availability of S and other

elements and temperature (e.g. burning). These minerals can be useful indicators of soil-water processes operating in these environments.

- Sulfidic and sulfuric materials (acid sulfate soil materials) occurred in drains and receiving environments. Disturbance by excavation or high flow scouring of sediments risks oxidation of the pyrite in the sulfidic materials with release of sulfuric acid and formation of sulfuric materials.
- Deduced that the specific types of salt efflorescences are an integrated indicator of complex biogeochemical conditions and transformations occurring in the drains and play a critical role in drain erosion processes by salt fretting. Salt efflorescences, especially the sulfate containing minerals, can cause detachment of soil during crystal growth and degradation of drain walls.
- Soluble sulfate/chloride-containing minerals in efflorescences (mainly on drain walls and dry sediments) play important roles in the transient storage of ions such as Na, Ca, Mg, Ba, Sr, Cl, Br, I and SO_4. These can rapidly dissolve during rainfall and contribute to formation of saline monosulfidic black ooze in drains and receiving environments.
- Gels and sulfuric horizons within the base of drains can contain elevated trace element and metal concentrations (Al, Cu, Pb, Cr, Pb, Zn, Mg and rare earth elements).
- The minerals, associated trace elements and spatial occurrence of these within drains highlight specific risks that point to key management strategies: some specific to drains: e.g. anthropogenic burning results in the formation of irreversibly fused, particulate and discrete iron-rich artefacts, which can block drain pipes.
- Several new assemblages of sulfate-containing evaporite minerals, oxyhydroxysulfate minerals and sulfides have been identified in the wide range of sulfuric and sulfidic soil environments that have formed in drains in the Avon catchment.

5.4.2 Management implications

- Drains need to be designed and managed to minimise turbulent flow in order to minimise the flushing of precipitates and gels (frequently containing trace metals) and disturbance of sulfidic sediments (being a store of acidity and trace metals). In particular, entry of surface waters from catchments to the drains should be avoided without measures to contain flow velocities.

- Drain design to maximise hydrological residence times and formation of precipitates will contribute to maximising retention of trace metals within the systems, though first flush from drains will need to be managed (see below).

- Containment (and or treatment) of flows after rainfall events would assist in reducing trace metal and acid fluxes from drains. Run-off from drain banks and walls is likely to mobilise trace metals and acidity associated with these zones, increasing drain water acidity and trace metal concentration. Mobilisation of precipitates on drain sediments (also containing acidity and trace metals) will also contribute to increased export of acidity and trace metals from drains during early stages of rainfall-runoff events.

- Management of trace metal mobility and acid release will need to be considered when maintenance cleaning of sediments from drains is carried out, since there are minerals in the drains that can release acidity and trace metals should these be disturbed. Appropriate management might include mixing of sediments with alkaline drain spoils (to neutralise acidity), placement within depressions on drain spoils (allowing drying and containment but including contact with alkaline spoils) or collection and containment in a site without risk of off-site impacts (i.e. outside of a surface flow pathways).

- Accumulated vegetation in drains (e.g. roly poly residues) is best removed using an excavator particularly where large compact accumulations of materials occur in conjunction with iron precipitates. Burning of residues can result in the formation of a cemented iron plug that can significantly impede flows.

6. GEOCHEMICAL RISKS ASSOCIATED WITH DISPOSAL OF ACIDIC WATERS TO LAKES

Brad Degens, Rob Fitzpatrick, Grant Douglas and Warren Hicks

6.1 Introduction

The geochemical risks associated with deep drainage highlight an urgent need to consider the geochemical processes occurring and potential impacts on receiving environments for these waters. Tracking of drainage flows from many deep drains sampled during earlier stages of the project (using GIS and on-ground checks) showed that many discharged to natural flood ways, with flows collecting in down-stream lakes or directly discharged to lakes closed to most surface inflows. Constructed evaporation basins were not widely used for disposal of waters from deep drains (with few examples identified involving acidic waters at the time of the survey), such basins being mainly used for waters from groundwater pumping schemes.

This section presents data from the sampling program to characterise geochemical processes and risks to drain receiving lakes including a comparison with sites not receiving deep drain discharge (both acidic and non-acidic).

6.2 Methods

Water samples were taken at sixty six lakes and one constructed evaporation basin between October 2005 and August 2006 (Figure 6.1). Thirteen of these sites were identified as receiving drainage waters from a GIS evaluation of surface flow paths from drain sites sampled in October 2004 (see chapter 5) using aerial photography and spatial data on watercourses and flow paths. Verification that drain flows discharged into lakes or that lakes were in the immediate flow-path downstream of drain discharge points was conducted as part of on-ground investigations. A similar process was used to identify reference lakes, which were control sites not receiving drainage or off-line from main water courses and containing water at the time of sampling.

Most sites were only sampled once. However, as a result of summer flooding in the Lockhart Catchment and the permanency of some water-bodies, it was possible to sample a number of these several times. Sampling of sediments for evaporite minerals and clastic sediments (chapter 5) was undertaken at fourteen sites during February 2006 to provide an indication of the dominant hydrogeochemical processes occurring within the lake environments including the fate of trace metals and acidity.

Observations of water depth, recent maximum filling depth, sediment characteristics, hydrological connectivity (open or closed to low flows upstream or from the localised catchment) and evidence of aquatic/faunal life were made, where possible.

Sediment samples were collected and analysed, as described in chapter 5, from 14 lakes (7 receiving lakes/sites and 7 reference lakes). Briefly, sediment samples were collected at a number of zones within each lake, selected to provide information on geochemical processes above the high-water mark (beach), in the evaporation zone and within the bed sediments. Localised variations in morphology, determined by colour, texture, mineral precipitates and depth of submersion, guided sampling within each zone.

In addition to hydrochemical analyses, potential (or stored) acidity was determined by analysis of sulphide-S using the chromium reducible S method (Ahern *et al.*, 2004) and existing acidity (total actual acidity) was determined by titration to pH 6.5 with NaOH in a 1M KCl suspension (standard acid sulfate soil analysis method 23F; Ahern *et al.*, 2004). These analyses allowed better understanding of the extent to which sediments had acidified that was not apparent from pH alone.

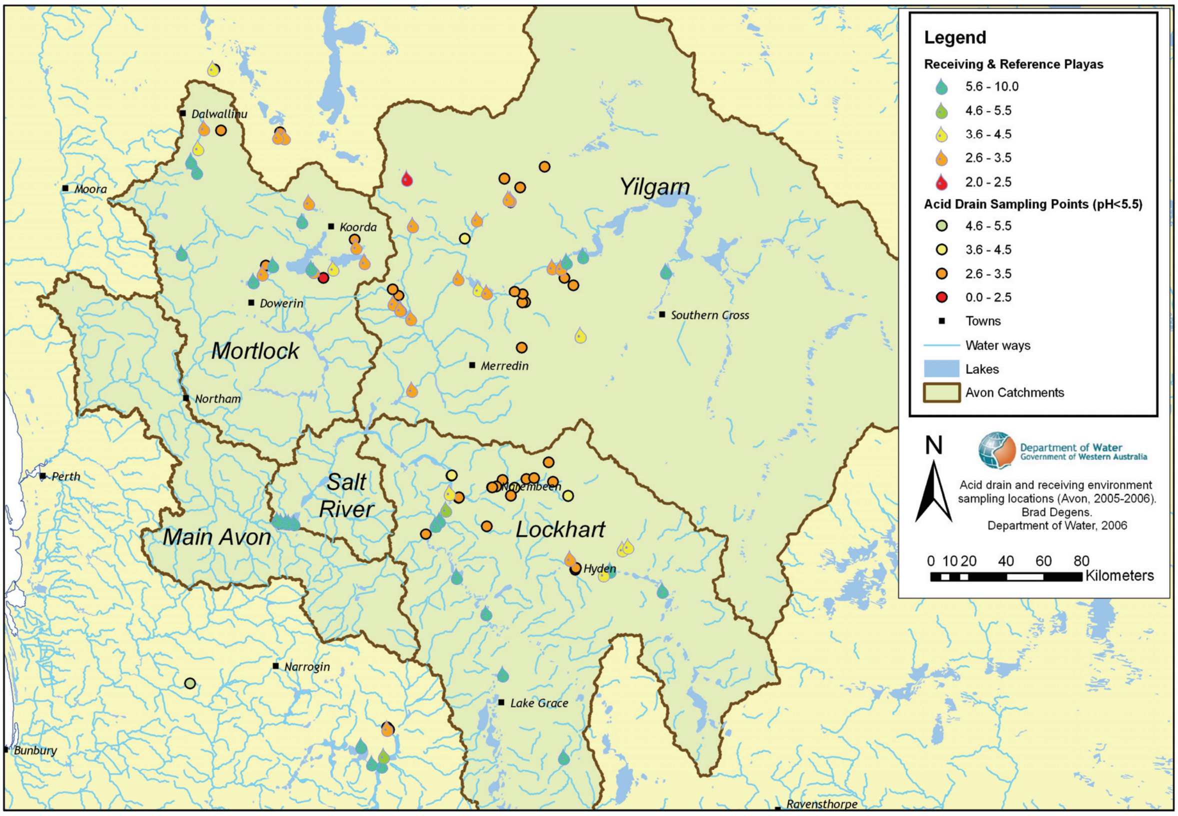

Figure 6.1 Outline map of reference and receiving lake sampling sites, drains discharging to the receiving lakes and the pH of these in the Avon catchment (WA) (site location details in Appendix 1).

6.3 Results and Discussion

6.3.1 Surface Water Acidity and Salinity

Surface waters within reference lakes ranged from acidic (pH<5.5) to alkaline (pH>7). Over 45% of reference lakes were alkaline (pH>6.5; Figure 6.1 and 6.2), particularly in upper Lockhart River and mid-North Mortlock catchments. However, there were numerous lakes with acidic water (the majority less than pH 4) in the upper North Mortlock and central Yilgarn catchments (Figure 6.1). There was no known evidence of discharge from deep drainage schemes currently affecting or having affected these sites in the past.

This survey indicates that acidic lakes may occur across a much larger area of the eastern WA Wheatbelt than previously recognised. Waters in lakes in the eastern Wheatbelt around Narembeen and Bruce Rock are considered to be naturally acidic (Halse *et al.*, 1993) and there are reports of acidic groundwaters interacting with lakes (Mann, 1983; McArthur et al., 1991), though some of these contained alkaline surface waters (Mann, 1983). Prior to clearing it was likely that there were localised discharges of acidic groundwaters on the margins of some lakes and from sand seeps (Bettenay *et al.*, 1964; McArthur *et al.*, 1991), however it is unlikely that significant acidity in surface waters was present over such are large spatial extent as has been found in this survey.

Discharge of regional acidic groundwaters may have contributed to the acidification of lakes that were acidic in the absence of drainage discharge and this may be increasing with on-going groundwater discharge. Many acidic reference lakes were not open to annual surface-water inflows (ruling out any possible unidentified drainage impacts) and were effectively closed basins primarily under the influence of rising regional groundwaters (Figure 6.3). Acidic groundwater is widely distributed (see chapters 2 and 3) and it is possible that discharge of this to lakes, floodways and creek lines with poor neutralising capacity would result in acidification of some of these water-features. The similar chemistry of acidic reference lakes and acidic drain receiving lakes (Figures 6.2 and 6.3) also indicates a similar acid origin. The titratable acidity of many acidic drainage receiving lakes was similar to that of acidic reference lakes (Figure 6.3) and is dominated by dissolved aluminium (see Figure 6.4).

Lakes into which acidic drains directly discharge (receiving lakes) or those immediately down-stream of deep drainage schemes all contained acidic waters (with pH<3.8; Figure 6.1) and over 75% contained waters with >50 000 mg l^{-1} TDS at the time of sampling (Figures 6.1 and 6.2). Lakes may have acidified as a result of discharge or were acidic prior to discharge (this was not readily distinguishable in all cases). If lakes were alkaline prior to discharge, it was clear that there is limited capacity of any lakes to neutralise acidic drainage waters.

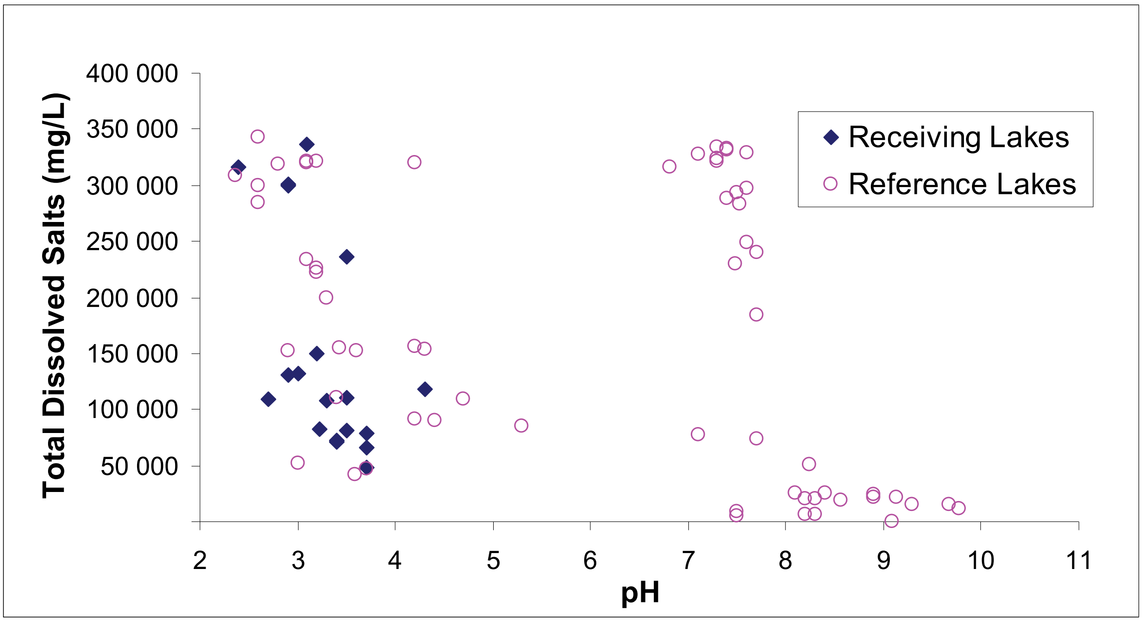

Figure 6.2 Lake pH and corresponding salinity (total dissolved salts; TDS) of waters in reference and receiving lakes in the Avon catchment, WA (at various stages of drying).

A wide range of salinity levels were found across all the sites, with many sites containing waters exceeding 150 000 mg l^{-1} TDS (Figure 6.2), which in many cases indicated that many lakes were in advanced stages of drying, reflecting limited rainfall in the months prior to sampling. Where lakes contained waters with less than 50 000 mg l^{-1} TDS, this was commonly due to recent filling by surface water inflows, either by high winter rainfall during 2005 or remnant-cyclone rainfall occurring during the summer of 2006.

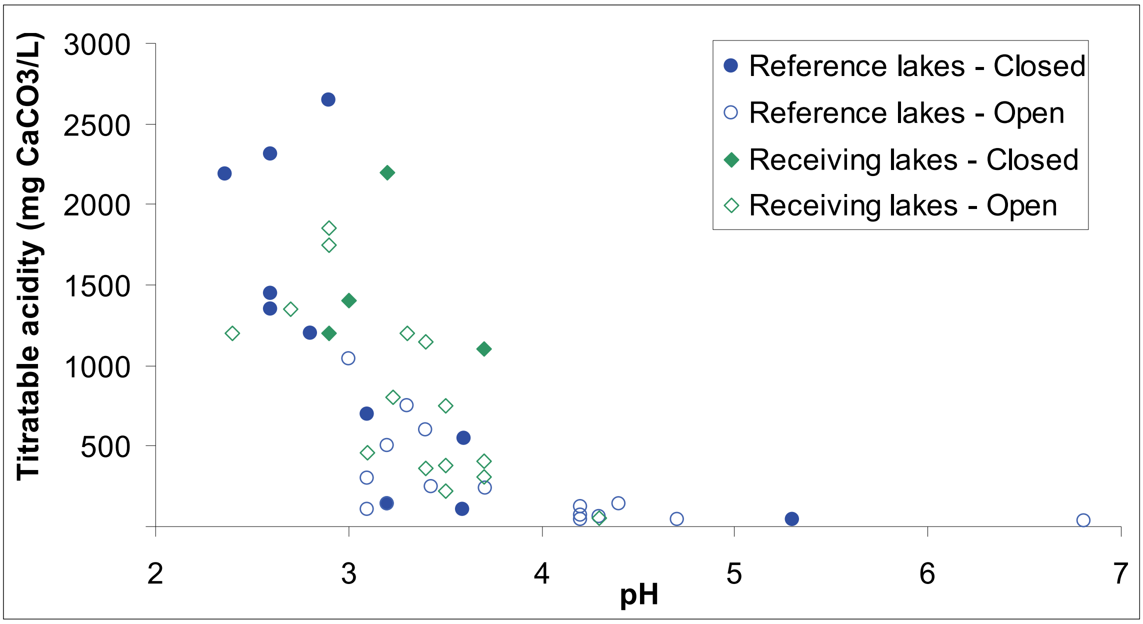

Figure 6.3 Lake pH and corresponding amounts of calcium carbonate needed to neutralise this (titratable acidity) for waters in reference and receiving lakes (where pH<7) in the Avon catchment, WA (distinguished by whether the lakes were deemed open or closed to regional surface water flows).

6.3.2 Trace elements in surface waters

The acidic lake waters contained high solute concentrations of some trace elements (including Al, Fe, Co, Ni, Pb, and the rare earth elements) at generally more than 10 times the concentrations occurring in non-receiving lakes with alkaline waters (Figure 6.4 and 6.5). Other trace elements such as As, Cu, Su, U and Zn were not dissimilar between acidic and alkaline reference lakes (Figure 6.4).

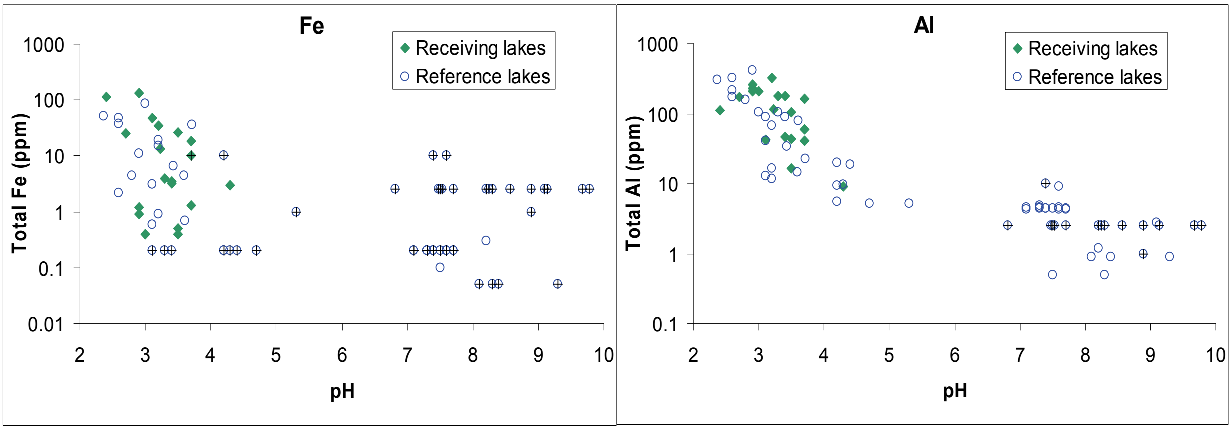

Figure 6.4 Similar concentrations of iron and aluminium in waters of reference and receiving lakes with corresponding pH. NB: Values below detection are plotted at the detection limit (marked with +) and concentrations are shown on a logarithmic scale.

The highest concentrations of trace metals such as Cu, Co, Ni, Pb, U and Zn occurred in waters in lakes receiving acidic drainage and were generally at least 1.2 times greater than the maximum concentrations in acidic reference lakes (Figure 6.4). However, the ranges across all acidic drain receiving environments were relatively similar. For example, Pb concentrations in waters of a receiving lake north of Bodallin contained concentrations of 2500 µg l^{-1} Pb, but a non-receiving lake at Beacon (100 km north-west) contained 2300 µg l^{-1} Pb. Similarities between the waters in receiving and non-receiving lakes may reflect the similar geochemical processes at the sites determining metal solubility (e.g. precipitation and adsorption driven by evapo-concentration and mineral precipitation processes). These may have masked any original differences that might be due to different rates of metal loading (from drains or direct regional groundwater discharge).

The risk posed by metals in lakes receiving acidic drainage and acidic reference lakes is unclear. Algae and aquatic crustaceans (e.g. *Paratemia spp*) were observed at a number of acidic reference sites (e.g. King Rocks Rd, East Hyden; McKay Rd, Pithara and Doodlakine-Kununoppin Rd lake, Trayning). The presence of these organisms presents the possibility that there may well be pathways by which bioaccumulation of some metals (e.g. Pb, U, Cd) could occur, thereby posing some risk to bird-life evident at many sites and reported to occur elsewhere (Goodsell, 1990). However, there has been very little investigation of ecotoxicological effects of metals in hyper-saline waters (Wang, 1987) and even less is known about the ecological impacts in temporary or ephemeral lake systems (Smith *et al.*, 2004). The high concentrations of Cl in seawater may reduce uptake of some metals by aquatic organisms (i.e. reduce bioavailability), although, in contrast there are some metals (e.g. Cd) where high Cl concentrations can increase uptake by aquatic organisms (Wang, 1987; Campbell, 1995).

6.3.3 Lake and shoreline sediments

Lakes (and the one new evaporation basin) receiving acidic saline waters (<pH 5.5; as sampled in spring, 2005) also contained acidic bed sediments (pH<5.5 in 1:5 deionised water). Likewise, reference sites with acidic waters also contained acidic bed sediments. Conversely, lakes with alkaline waters contained alkaline sediments.

Seepage of acidic drainage waters into alkaline sediments (pH>7 in 1:5 deionised water) was still evident at one receiving site (Gambles Rd, Cowcowing) where a thin layer of acidic surface sediments (pH<4, 0-1cm) overlay more alkaline bed sediments (pH>6.3, 1-30 cm). There were no free carbonates in the deeper sediments of this lake, though these may have been present at some time in the past, since the bed sediments of an adjoining reference lake (Ski Lake, Cowcowing) contained up to 9% by mass $CaCO_3$ within the surface 15 cm.

The surface waters in lakes contained significantly less acidity than the shallow sediments (<40 cm depth) in acidic reference and receiving lakes (Table 5.1). Some sites contained up to several thousand times more existing acidity in sediments than in waters at the time of sampling in spring 2005 (Table 5.1). These results indicate that neutralisation of acidic waters in acidic drain receiving lakes must take into account the acid store within the sediments since these will tend to buffer the pH of the system. The per hectare amounts of acid (as equivalent sulfuric acid) stored within the sediments can be used to indicate the quantities of pure lime (as $CaCO_3$) that would need to be added to treat the acidity in lake sediments and waters, since neutralisation of one kg of sulfuric acid requires one kg of pure lime (as $CaCO_3$). Notably, these estimates only indicate the more readily neutralisable acidity, generally present as exchangeable cations and soluble Al and Fe minerals, and do not include less reactive forms of acidity (McElnea *et al.*, 2002) that were present as iron (e.g. jarosite and natrojarosite) and aluminium hydroxysulfate (e.g. alunite) minerals at some sites.

Shallow soils in the beach zone of many acidic lakes contained greater amounts of existing acidity than the bed sediments (Table 5.1). The accumulation of acidity in these zones at most acidic reference lakes was probably due to concentration of acidity by evaporation of local groundwater discharge on the margins of the lakes. This process has also been reported in larger, less hydrologically disturbed salt lake systems in the goldfields (McArthur *et al.*, 1991) and is likely to be increasing with rising water tables in many lakes in the eastern Wheatbelt. Lateral leakage of acidic waters from the main lake (with evapo-concentration in surface soils) may also have contributed to the accumulation of acidity in the beach zone at some sites receiving acidic drainage discharge, but

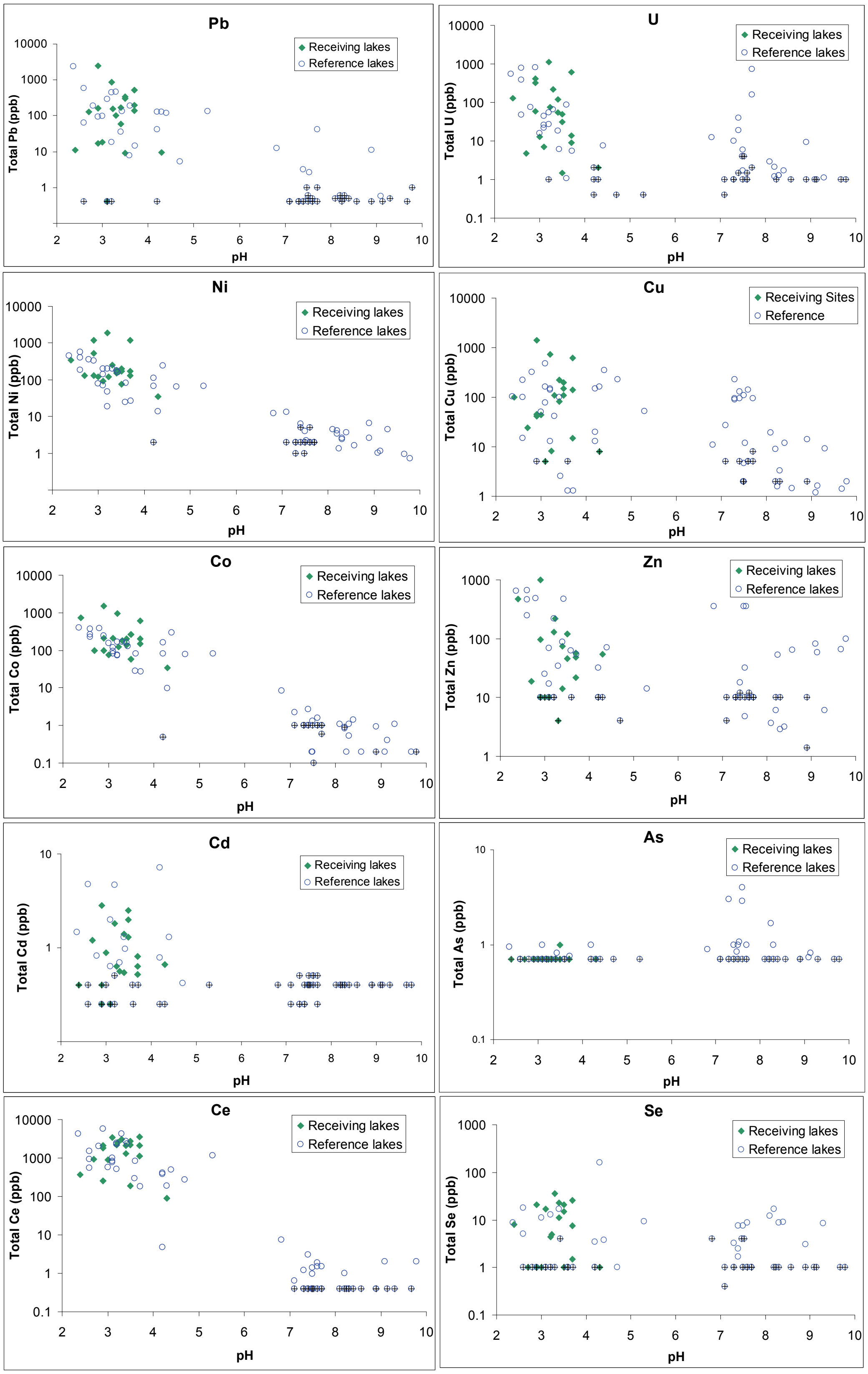

Figure 5.5 Concentrations of selected trace elements in reference and receiving lake waters of varying pH. NB: Values below detection are plotted at the detection limit (marked with +) and concentrations are shown on a logarithmic scale.

Site[1]	Acidity in ponded waters[2] (as equivalent kg H_2SO_4/ha[3])	Existing acidity[3] in lake bed sediments (as equivalent kg H_2SO_4/ha)	Existing acidity[3] in beach soils (as equivalent kg H_2SO_4/ha)	Acidity[4] stored as sulfides of lake-bed sediments (as equivalent kg H_2SO_4/ha)
McKay Rd lake, Pithara (Ref)	0.4	9	267	439
Carter Rd lake, Jibberding (RE)	0.9	833	1 454	11 776
Gambles Rd lake, Cowcowing (RE)	1.8	288	209	16 519
Doodlakine-Kununoppin Rd, Trayning (RE)	3.0	4 018	Not sampled	393
Doodlakine-Kununoppin Rd, Trayning (Ref)	1.2	5 165	3 039	0
Yilgarn lake, Boodarockin (RE)	0.9	7 879	26	0
Yilgarn lake, Boodarockin (Ref)	0.4	416	2 304	0
Bodallin Evaporation Basin (RE)	11.0	2 596	2 919	0
Lake Ardath (RE)	4.1	2 564	664	0
King Rocks Rd, East Hyden (Ref)	0.6	9 745	Not sampled	0
Lake Gounter, Hyden (RE)[5]	1.4	773	3 843	8 691

Table 5.1 Estimated acidity (as equivalent kg sulfuric acid (H_2SO_4) per ha) in different zones within lakes (ponded waters, sediments and beach zones) for acidic reference lakes and lakes receiving acidic drainage (see footnotes for explanation of acidity pools).

[1] Ref = reference site, RE = receiving site.

[2] Estimated from depth of water in lake at time of sampling in early October 2005 and titratable acidity.

[3] **Existing acidity** expressed as equivalent kg of H_2SO_4 estimated by summation of total actual acidity for all horizons in a profile (<40cm depth) calculated on a per hectare basis assuming a uniform bulk density of 1.5g/cm^3 for all materials (Note: this is a conservative estimate since bulk density of hydrated materials may be less, which would increase acid storage/ha). Total actual acidity is determined by titration to pH 6.5 of a 1M KCl-soil suspension (Ahern *et al*., 2004). Acidity is expressed as equivalent weight of H_2SO_4 (in kg) per hectare that would need to be neutralised to raise the pH of the soils to 6.5.

[4] Stored acidity = potential acidity within sulfides determined by chromium reducible S analysis (assuming no contribution of acidity from monosulfides). These were calculated as equivalent kg of H_2SO_4 and summed for all horizons in a profile and calculated on a per hectare basis assuming a uniform bulk density of 1.5g/cm^3 for all materials.

[5] Calculations for Lake Gounter focus on smaller permanently inundated NW corner of lake and not the larger eastern and SE flood fill zone (which was only occasionally inundated).

the effect is constrained to within 10's of metres of the lake edges. The beach zone at many sites included an area inundated by water during winter 2005 (a year when generally average rainfall fell across the Wheatbelt) and at all sites would certainly be inundated during flooding events (except for the Bodallin evaporation basin which is protected from the hydrological impacts of flooding). Acidity accumulated in Al- and Fe-bearing surface salt efflorescences (e.g. rozenite) would be rapidly washed into the main water body during most winters.

Acidity was also stored as sulfides in the bed sediments and occasionally beaches of eight receiving and reference environments (Table 5.1), as well as at three alkaline lake sites (not listed in the table). It was notable that the majority of acidic reference and receiving lakes did not contain sulfides. In the acidic lakes, the potential acidity in the sediment was generally more than an order of magnitude greater than that that present as titratable acidity in the profiles (Table 5.1). The acidity stored in the sulfide minerals does not pose a threat to the environment providing that the lake beds remain anoxic (waterlogged) and/or saturated and are not disturbed by excavation.

Sulfide minerals were generally concentrated in the shallowest 10 cm of bed sediments (up to 0.6% S) and often occurred with significant accumulations of organic matter (up to 2.4% organic C in some horizons). It is likely that sulfides accumulating in bed sediments of the smaller lakes (in particular) have formed due to microbial sulphate reduction fuelled by organic inputs to the lakes and maintenance of water-logged conditions in the early stages of secondary salinisation. Organic C inputs may have occurred as a result of algal and macrophyte blooms during past lake filling events (evident at some sites as dried macrophytic material deposited on shorelines during most recent lake filling events) and/or as deposition of sediments and organic residues washed from the topsoil of adjacent agricultural areas during flood events. Waterlogged conditions in bed sediments between these events were probably maintained by rising groundwater levels due to land-clearing. Sulfide minerals present in lakes with acidic waters and sediments (receiving and reference) were most likely formed prior to acidification, since sulfate reduction and sulfide formation is generally favoured in alkaline environments (Langmuir, 1997; Ward *et al*., 2004). Occurrence of sulfides in acidic reference lakes may be evidence that the lakes were alkaline in the past and have undergone acidification in recent times, most likely because of increased discharge of acidic groundwaters occurring after land-clearing.

Data from the initial sediment survey indicated that the concentrations of most trace metals in the bed sediments of most lakes receiving acidic drainage were not obviously elevated compared with the acidic reference lakes and two alkaline reference sites. However, there were frequently less than 4 sampling sites within each receiving or reference environment which might have failed to detect differences in metal accumulations due to large spatial variation in metal accumulation. Spatial variation in deposition of precipitates (and associated trace metals) in the lakes receiving acidic drainage may be uneven, particularly where prevailing winds result in re-suspension and deposition of precipitates on the leeward side of lakes. It is also possible that some receiving lakes were acidic prior to drain discharge and the magnitude of discharge impacts (i.e. accumulation of trace metals) was indistinguishable compared with trace metal accumulation from previous regional acidic groundwater discharge.

Drain discharge may increase surface concentrations of some trace elements. Elevated concentrations of some elements (e.g. Pb and U) were evident in surface horizons at several sites receiving acidic drainage (Doodlakine-Kununoppin Rd receiving lake, Trayning and Gambles Rd receiving lake, Cowcowing). Such an assessment was based on evidence of increasing concentrations of the metals in surface horizons relative to deeper horizons and comparison of concentrations of the trace metals with respect to horizons of a nearby reference lake. However, sediment concentrations of some elements may be similar in all environments. For example, Pb and U concentrations were generally similar (5-52 mg l^{-1}) in lake bed and beach sediments in an acidic reference lake, a lake receiving acidic drainage and an alkaline reference lake near Boodarockin. Notably, this survey identified concentrations of Pb that were frequently an order of magnitude greater than acid digestible metal concentrations in an earlier survey of sediments in WA lakes (Lyons et al., 1990), although Cu, Zn and Cd concentrations were generally within similar ranges.

The acidification of sediments in lake systems, from whatever cause, poses a significant risk to aquatic habitat and the long-term integrity of aquatic ecosystems. These impacts are in addition to those caused by changes in hydroperiod and increasing salinity (Halse, 2004). Loss of habitat through acidification of sediments may impact greatest on sites where resting stages of aquatic organisms can survive between lake filling events. Furthermore, while acidity in surface waters might be periodically neutralised by floodwaters or during lake filling events, this is less likely to occur for the acidity within bed and shoreline sediments. Neutralisation of acidic sediments during lake filling events is likely to be slow and limited because of restricted seepage and slow diffusion of alkaline waters. In a worse case scenario, the acidic sediments could result in progressive consumption of alkalinity of lake waters resulting in acidic conditions prevailing from the early part of the drying phase. This is a period during lake hydrological cycles that is commonly the most critical for aquatic ecosystems; when the lake is fullest, freshest and significant growth and reproduction of aquatic organisms occurs (Smith *et al.*, 2004).

Mobilisation of trace metals from acidic sediments to water columns may also be increased under certain conditions, for example formation of anoxic bottom waters after lake filling resulting in reductive iron dissolution and release of trace metals (see chapter 5). A similar situation can occur if bottom waters become acidic due to acidity emanating from bottom sediments.

6.4 Conclusions

Acidic drainage discharge to lakes can result in acidification of surface waters and the sediments and soils immediately surrounding the lakes, compared with lakes not receiving drainage discharge. However, in some cases lake waters and sediments may have been acidic prior to discharge in which case the impacts would dependent on the magnitude of drain discharge compared with regional groundwater discharge. Concentrations of Al, Fe and trace metals including Pb, Ni, Co and U appear to be increased in the surface waters of sites receiving acidic drainage, particularly when compared with alkaline lakes. This acidification and associated increased trace metal solubility may result in impacts on aquatic ecosystems, including loss of habitat and reduced ecosystem functioning during lake filling events.

Lakes can be acidic in the absence of drainage discharge, most likely due to the discharge of regionally acidic groundwaters. Numerous acidic lakes occurring in the upper reaches of the Lockhart, Mortlock and Yilgarn catchments were found to be acidic with no evidence of deep drainage discharge. These lakes may have been acidic since before land clearing began, however, there is sedimentary evidence that some lakes may have become acidic since land clearing. Notably, the acidic reference lakes exhibited geochemical conditions similar to those in lakes receiving acidic drainage.

Preliminary results indicate that acidic drain discharge does not necessarily result in readily distinguishable elevated accumulations of trace metals compared with lakes not receiving acidic drainage. However, the sampling density was too sparse for this to be certain. Further, more detailed investigations will be required to predict which drains are likely to result in increased accumulation of trace metals in receiving environments compared with acidic reference lakes. These investigations should involve comparisons of paired lakes (acidic reference and acidic drain receiving lakes) as well as before-after investigations of trace metal accumulation in environments receiving acidic saline drainage.

Initial overflows from acidic lakes (both receiving lakes and non-receiving lakes) following a rainfall events are likely to be laden with high concentrations of dissolved aluminium and iron and potentially high concentrations of trace metals. In this context, the first flush from such environments will require greatest management intervention.

6.5 Main Findings

1. A random survey found that surface waters in more than 45% of lakes were alkaline ($pH>6.5$), with the remaining lakes containing acidic waters, frequently at $pH<4$.
2. Lakes that contain acidic waters not attributed to drainage discharge are likely to have been acidified by regional groundwater discharge or were naturally acidic prior to rises in regional groundwaters.
3. Some existing alkaline lakes will be under on-going acidification pressure if discharge of regionally acidic groundwaters continues to occur. For current acidic lakes, this will result in increasing acidification and accumulation of trace elements (determined by rates of groundwater discharge). For current alkaline lakes this could result in acidification.
4. Acidic drainage to lakes can result in acidification of lake waters, sediments and the soils in the beach-zone surrounding the lakes.
5. Containment of acidic saline discharge results in formation of highly acidic sediments in receiving environments (artificial and constructed).
6. Drain/bore discharge to lakes within the central floodway can result in accumulation of salts, acidity and trace metals in surface sediments and adjoining flood-zones that carries the risk of being exported in concentrated flushes to down-stream lakes during moderate flow events.
7. Surface waters within acidic drain receiving lakes can contain significant concentrations of dissolved Al and Fe which may form significant concentrations of Al species (e.g. $Al(OH)^{2+}$, $Al(OH)_2^+$) that can be toxic to aquatic to some aquatic biota and iron floc (smothering benthic communities) on mixing with neutral/alkaline floodwaters. The greatest risk of this is likely to occur during the first flush part of flood-flows and for small rainfall events that result in localised lake filling, and therefore concentration of discharge, in the Avon.
8. Naturally occurring alkalinity occurs in shallow soils surrounding receiving environments and may offer some capacity to neutralise acidic waters and sediments.
9. Alkaline flood flows may not have significant capacity to neutralise acidic sediments in acidic lakes (natural and drainage created) due to the limited capacity for overlying waters to seep into and interact with acidic sediments below the surface layers and the significant volumes of water that might be required (See chapter 5).

6.6 Management Implications

1. Acidic lakes that occur due to regional groundwater discharge (i.e. not drainage) may require management of geochemical risks including acidity and soluble trace metals to protect alkaline down-stream environments.
2. Acidic groundwater discharge is best managed by containment and/or treatment in sites with minimal risk of down-stream transport which may be difficult to achieve which discharge to lakes in the central floodway.
3. Where drains discharge acidic waters to sites with poor containment, management of geochemical risks to down-stream environments will need to focus on acid and metal mobilisation occurring during the first flush.
4. Containment of acidic saline discharge may require treatment with neutralising agents (e.g. Agricultural Lime) at regular intervals, depending on the risk to down-stream environments. This periodic treatment of accumulated acidity may be more cost effective than continuous treatment of drain discharges, which can be difficult in remote sites.
5. Soils with carbonates surrounding receiving environments could be mixed into the sediments or used to line lakes to provide some capacity to neutralise acidic waters and sediments.
6. Use of alkaline flood flows to neutralise acidic sediments in acidic lakes may only be possible with significant volumes of water and extended periods of flooding.

7. CASE STUDY ASSESSMENTS OF REGIONAL DRAINAGE GEOCHEMICAL RISKS USING GEOCHEMICAL MODELLING

Grant Douglas and Brad Degens

7.1 Introduction

A geochemical model has been constructed using the geochemical package PHREEQC for Windows (v2.12.05, Parkhurst and Appelo, 2006) to simulate mixing and evaporation of acidic saline waters (present in deep drains) with surface waters in receiving basins (*e.g*. lakes or playas) or in stream channels in the Western Australian Wheatbelt (Figure 7.1). Where one tributary discharges into another, and mixing takes place in the stream channel, the process can be equated to a simple batch mixing model, assuming sufficient turbulent flow and path length for complete mixing to occur and where mineral equilibration times are short relative to the previous two parameters. In a lake, however, parameters such as the existing volume of water, inflow volumes, and the total volumes resident after mixing require consideration on a case by case basis. In addition, the scenario of complete mixing in a simple batch mixing model may not be sufficient, with factors such as the morphology of the lake or internal stratification decreasing the extent to which waters mix, being important. Furthermore, an evaporative term may have to be incorporated to account for changes in lake receiving environment surface area and volume (both of which will change and modify evaporation as this progresses).

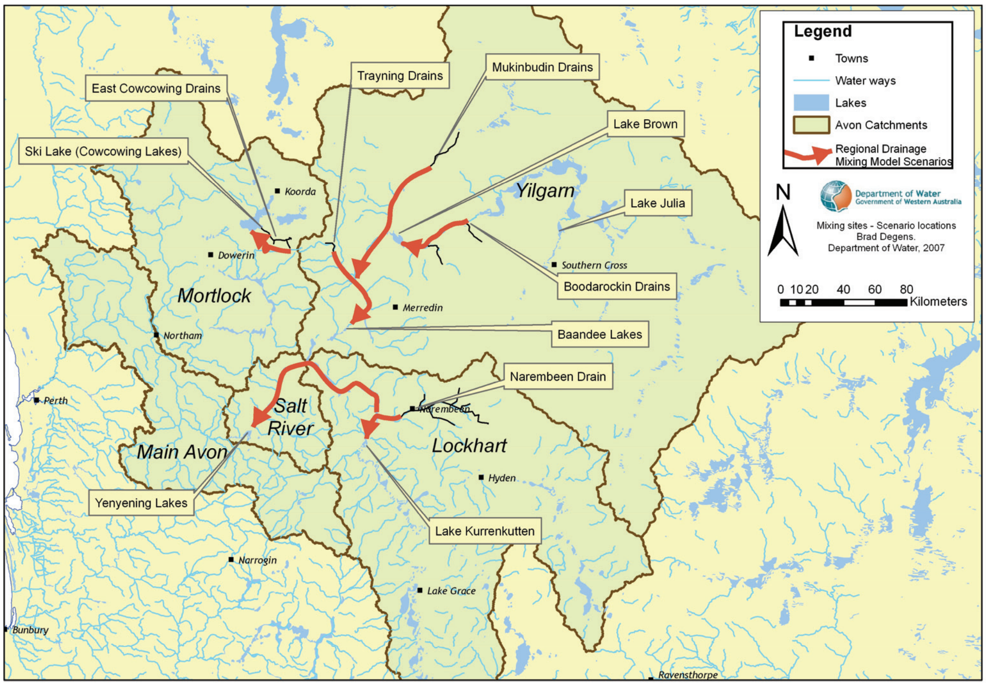

Figure 7.1 Locations of selected drainage and lake sites used to represent different scenarios modelling regional acidic drainage mixing with alkaline surface waters.

A major challenge in the mixing model being developed here is to adequately explain the variation in water quality where salinities may typically encompass three orders of magnitude and hydrogen ion concentration (pH) up to seven orders of magnitude in acidic and alkaline waters within the Western Australian Wheatbelt. A number of empirical factors and geochemically-based assumptions are also inherent in the mixing model. These are outlined below, highlighting some of the limitations of the assumptions:

- **All mixing occurs with well aerated waters:** It is assumed that all waters are in equilibrium with atmospheric O_2 and CO_2 and remain so during mixing reactions. Whilst this assumption may be valid in some mixing and evaporation scenarios in many shallow lakes, when prolonged density stratification occurs within a receiving environment (principally lakes with deep pools in the main lake bed (*e.g.* Lake Kurrenkutten) this may lead to a change in the water chemistry of the deeper water layers (*e.g.* Fe^{2+} release form the bottom sediments). Future versions of the model will allow for user-friendly variation of these parameters.

- **Mixing does not include interaction with sediments:** The modelling only focuses on behaviour of surface waters and suspended precipitates or evaporates that may form in these and does not include interaction with acidic or alkaline bed sediments in creek lines and lakes. This is critical for some of the mixing scenarios where the mixing environment may already be acidic prior to drain discharge offsetting some of the neutralising capacity of the alkaline waters or for receiving environments where sediments may be alkaline prior to acidic discharge.

- **Single water samples are used to represent water chemistry from acidic drains and alkaline surface waters:** The mixing model essentially involves mixing two types of waters, thereby assuming that the a single set of water chemistry can be used to define each water sample. Due to a lack of temporal data in drains, often only one sample is used to represent the average water chemistry over the life of a drain. Where available, multiple samples were mixed to provide an improved average water chemistry. In general, only single samples of water chemistry were available and were used to represent the alkalinity of flood waters. In many cases the only alkaline surface water samples available were from the drying phase of lakes.

- **Modelling was conducted using a simplified set of minerals:** A mineral suite comprising five major groups: carbonates, chloride and sulfate salts, Al-minerals, Fe-minerals, and two accessory minerals have been chosen to represent relevant drain, soil and sediment mineralogy interacting with the drain and lake waters. These mineral suites are summarised in Appendix 3. The minerals contained in the carbonate suite are known to be common in the Western Australian regolith, while the chloride salt suite was selected on the basis of the major drain precipitate and efflorescence mineralogy identified by Fitzpatrick *et al.* (2005). Both Fe- and Al-mineral suites are commonly found in acid mine drainage which has a similar geochemical character to many of the waters encountered in this study, albeit generally less saline (Douglas and Degens, 2006). The two accessory minerals, fluorite and amorphous silica, are usually regarded as being influential in regulating F and Si concentrations in a variety of surface and groundwaters.

- **Trace metals can only interact with one simple iron-oxide analogue:** An amorphous Fe-oxyhydroxide phase equivalent to ferrihydrite has been designated as the sole adsorptive phase for trace elements in this study. While other phases (identified in Section 5) may be influential in the adsorption or co-precipitation of trace elements, there is generally little well-validated data that allows incorporation of these other minerals (*e.g.* schwertmannite, alunite) into this model. The interactions of trace metals with these other minerals may well be significantly different from that used in this simple model, hence trace metal concentrations may only broadly reflect those occurring in the field. At present the trace element suite is limited to Cu, Pb and Zn but this suite will be expanded during further model development in the next phase of this project.

- **Two background chemical databases were used to support the model, to partially overcome the limitation that neither could cover the full range of salinity for all elements:** The choice of database used in the mixing and evaporation model is critical. PHREEQC for Windows offers a range of databases with the two most relevant to this model being the default phreeqc.dat (phreeqc) and pitzer.dat (pitzer). Both the intent and function of these databases varies substantially. The phreeqc database contains a wide range of elements and minerals and

> is generally used for low ionic strength solutions. However, it has sometimes been used for solutions up to approximately twice seawater salinity. In contrast, pitzer can be used at substantially higher ionic strength, albeit with a vastly reduced range of elements and mineral phases, most notably Fe- and Al-minerals. Thus, in choosing the database (and as a consequence the breadth of information that is output) the ionic strength of the mixing components must be considered. In certain cases, where the mixing and evaporation of Wheatbelt waters is well validated (*e.g.* by empirical laboratory simulations) the parallel use of both databases may represent a reasonable approach.

The basis of the geochemical mixing model developed here is represented by four separate modules of PHREEQC code; mineral saturation index (SI), estimation of trace element adsorption, a mixing module and an evaporation module. These are explained in detail in Appendix 4.

7.2 Modelling of Wheatbelt mixing and evaporation

In consultation with the project team, five mixing and evaporation scenarios were examined to complement modelling of regional drainage options in the Avon catchment of the WA Wheatbelt. The scenarios were specifically selected to represent the range of situations where acidic drainage waters might discharge to lakes and the possible flood-waters that these might subsequently mix with. The scenarios represent examples in the Avon catchment where existing localised deep drainage occurs (containing acidic waters) and where future regional drainage has been proposed in the eastern Avon catchment, where shallow acidic groundwaters are known to occur (Figure 7.1). Input data for the modelling was selected from the compiled database and the modelled mixing proportions are outlined below. Results of the mixing of various proportions of acidic and alkaline waters expressed as the estimated pH using both the phreeq and pitzer geochemical databases are shown. After mixing, evaporation was modelled using the proportions 50:50 and 99:1 alkaline:acid water.

7.2.1 Mixing and evaporation: upper Yilgarn example

A specific example of the PHREEQC model output is given in detail for major elements and mineral saturation indices in addition to pH in the case of mixing alkaline lake waters (pH 7.1; Lake Julia sample R29YR) with waters in a lake containing acidic drainage discharge waters (pH 2.9; sample R25YR), which might occur for drainage in the Upper Yilgarn agricultural zone. The effects of evaporation were also simulated after mixing with waters mixed in 50:50 and 99:1 ratios. Examples comparing the use of the different geochemical databases (phreeq and pitzer) are presented for pH estimation when different proportions of alkaline and acidic waters are mixed and for pH during evaporation of the mixed waters.

This example illustrates differences in the model output using the phreeq and pitzer databases. The output for both databases is similar at low pH and mixing proportions up to approximately 50:50 (Figure 7.2). Where near neutral water is the predominant component of the mixture the pH estimated using the pitzer database increases more rapidly than that estimated using the phreeq database. As an example, to attain a pH of 6 using the pitzer estimate, near neutral to acid water in the approximate proportion of 95:1 is required, whereas using the phreeq database the proportion is approximately 99:1.

At the high ionic strength of these waters, the model output using the pitzer database is probably the most appropriate database for mixing varying proportions of the near neutral and acidic waters. However, at present the pitzer database does not include Fe or Al minerals. Both Fe and Al minerals such as jarosite or alunite may be particularly important in regulating pH, and thus their absence may explain some of the discrepancy between the output from the two databases used in this mixing simulation. Further lab-based mixing experiments of representative waters from the Avon are in progress along with the results from these being used to further refine the model development.

The saturation indices (SI) of a suite of minerals that are likely to precipitate within WA Wheatbelt waters are shown in Figure 7.3. These SI's have been estimated using the phreeq database which allows the inclusion of important Fe, Al and Si minerals. Alunite and amorphous silica are at or near saturation irrespective of the proportion of acidic or alkaline water. In contrast, magnesite, amorphous Fe-hydroxide (ferrihydrite) and gibbsite only become saturated at near neutral pH, consistent with a high proportion of Lake Julia water.

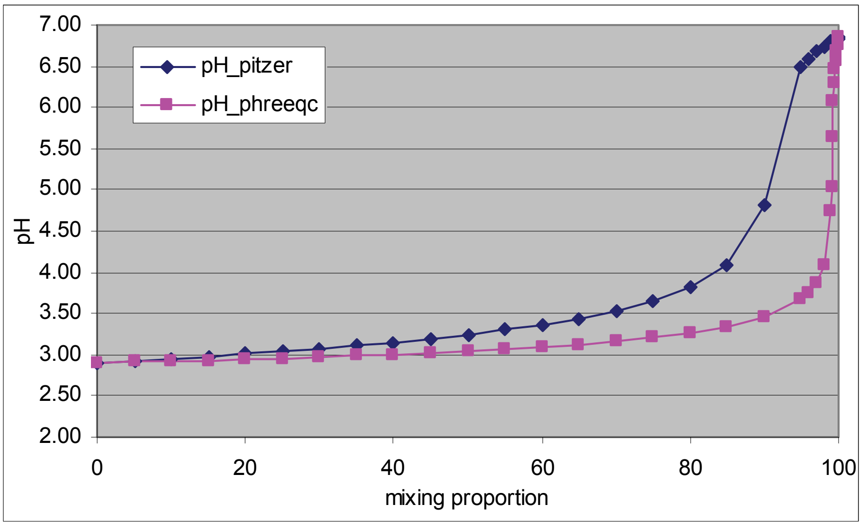

Figure 7.2 Estimated pH after mixing alkaline waters (Lake Julia sample R29YR) with acidic drainage discharge (stored within a playa on the Yilgarn River: sample R25YR) in varying proportions.

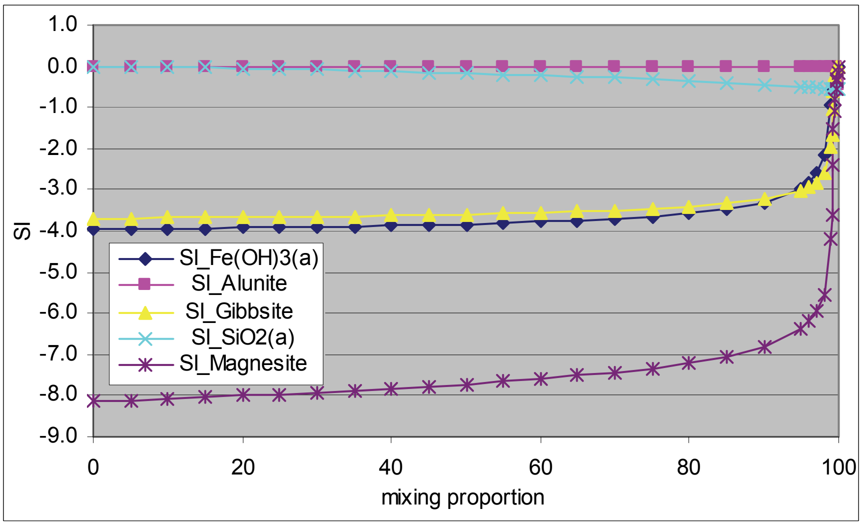

Figure 7.3 Estimated Saturation Indices (SI) of a range of minerals after mixing alkaline waters (Lake Julia sample R29YR) with acidic drainage discharge (stored within a playa on the Yilgarn River: sample R25YR) in varying proportions. (NB: Mixing proportions begin with 0 parts alkaline waters mixed with 100 parts acidic waters).

Concentrations of Cu and Zn from mixing of a sample from Lake Julia (sample R29YR) with an acidic playa lake on the Yilgarn River (sample R25YR) are shown in Figure 7.4. A linear relationship for Cu and Zn (and for Pb, not shown) exists between the mixing of the two waters as a consequence of there being no ferrihydrite and therefore no reactive minerals to interact with the waters over almost the entire range of mixing proportions (see plot above of ferrihydrite SI). Hence, a theoretical substrate does not exist as defined in the geochemical mixing model to adsorb trace metals. Inclusion of other iron minerals (e.g. schwertmannite, akaganéite) that have been found to occur in the acidic waters may modify the trace metal concentrations modelled here.

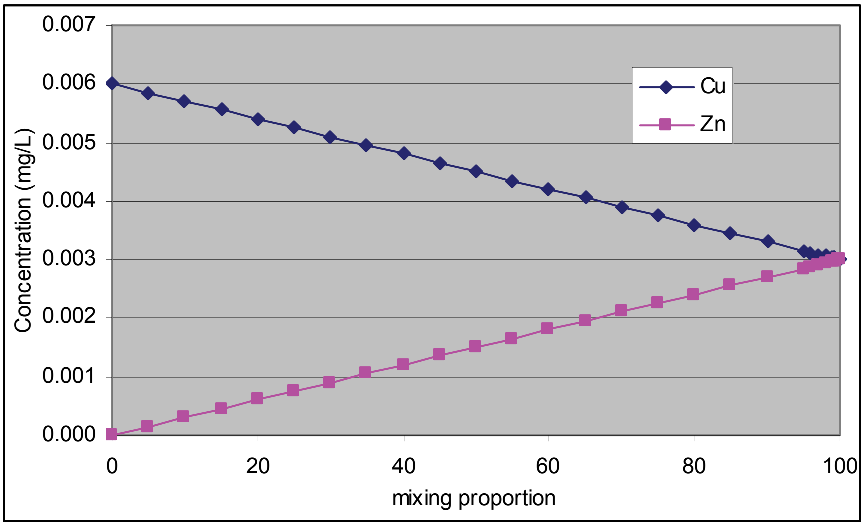

Figure 7.4 Estimated Cu and Zn concentrations after mixing alkaline waters (Lake Julia sample R29YR) with acidic drainage discharge (stored within a playa on the Yilgarn River: sample R25YR) in varying proportions (NB: Mixing proportions begin with 0 parts alkaline waters mixed with 100 parts acidic waters).

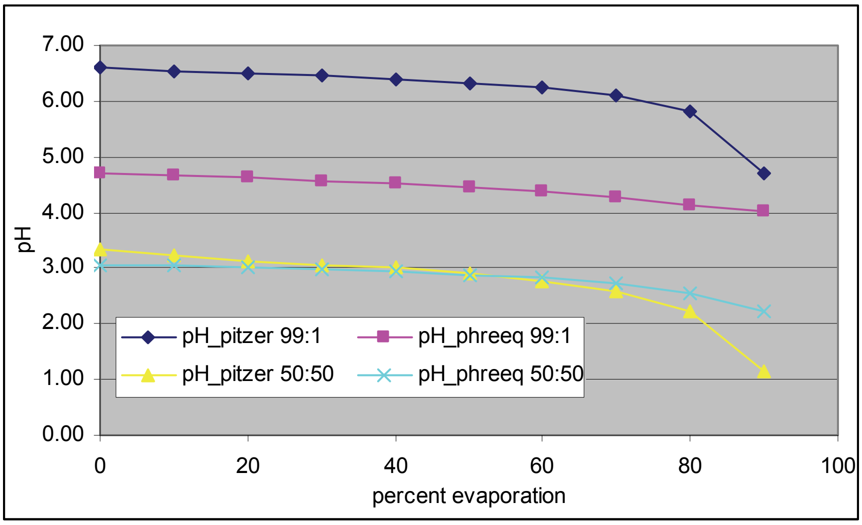

Figure 7.5 Estimated pH after mixing alkaline waters (Lake Julia sample R29YR) with acidic drainage discharge (stored within a playa on the Yilgarn River: sample R25YR) in 50:50 and 99:1 proportions and evaporation.

The estimated solution pH as a function of the evaporation of mixtures of near neutral and acidic waters in the proportions of 99:1 and 50:50 are shown below (Figure 7.5). In the 50:50 solution of acidic to near neutral water both the pitzer and phreeq databases yield a similar output for a large portion of the evaporation sequence. There is a gradual decline in pH up to approximately 70% evaporation which becomes progressively large in the pitzer estimate leading to a pH approximately one unit lower at 90% evaporation. In the 99:1 solution of near neutral to acidic water the initial pH of the waters calculated using the two databases differ by approximately two pH units. This difference may reflect the consumption of a large portion of the alkalinity by equilibrating minerals not present in the pitzer dataset as outlined above.

Mineral precipitation was estimated using a suite of minerals identified as common in the WA Wheatbelt drains (Fitzpatrick *et al*., 2005). During evaporation of near neutral and acidic waters in the proportion of 99:1 there is the progressive precipitation of a suite of minerals (Figure 7.6) in the order: magnesite ($MgCO_3$), halite ($NaCl$), gypsum ($CaSO_4.2H_2O$), starkeyite ($MgSO_4$:$4H_2O$) and carnallite ($KMgCl_3$:$6H_2O$).

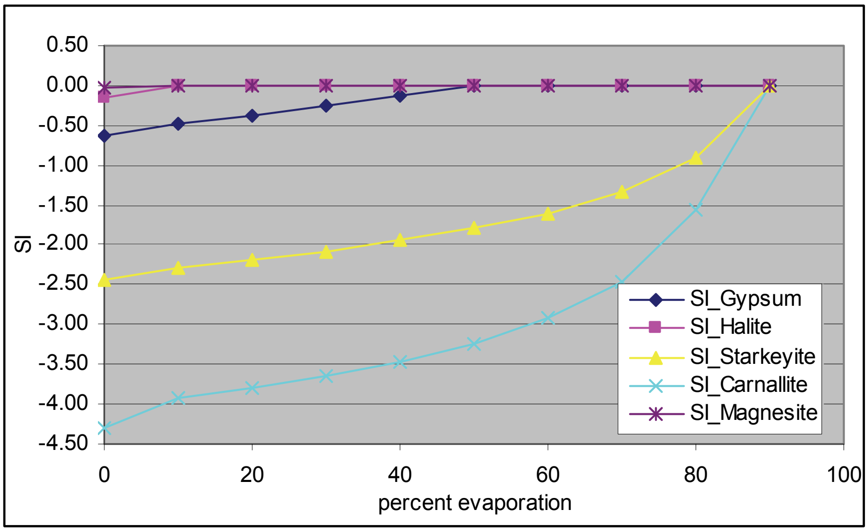

Figure 7.6 Estimated Saturation Indices (SI) of a range of minerals after mixing alkaline waters (Lake Julia sample R29YR) with acidic drainage discharge (stored within a playa on the Yilgarn River: sample R25YR) in the proportion 99:1 and evaporation.

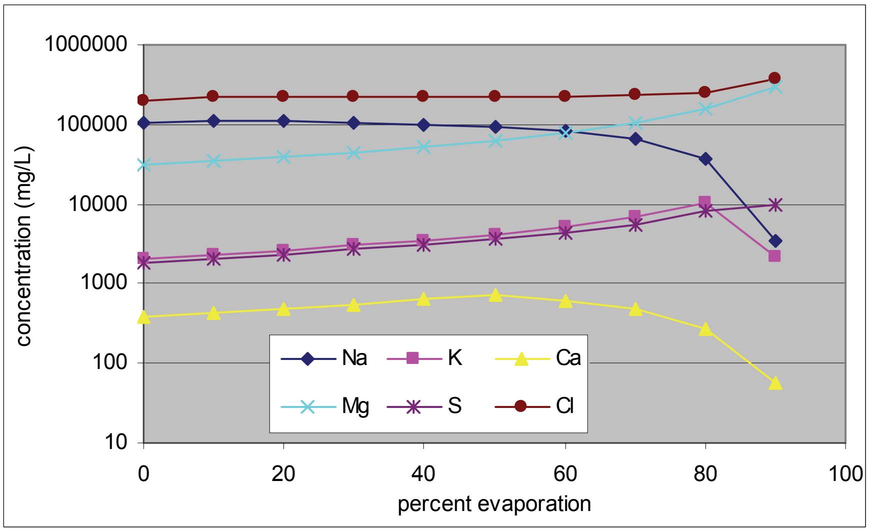

Figure 7.7 Estimated major ion concentrations after mixing waters in Lake Julia (sample R29YR) with acidic drainage discharge (stored within a playa on the Yilgarn River: sample R25YR) in the proportion 99:1 and evaporation.

Corresponding to the precipitation sequence of the mineral suite described above, progressive changes are also predicted to occur in the relative proportions of major ions (Figure 7.7). The estimates were made using the pitzer database as this is the most appropriate under the high ionic strength generated during evaporation. The most substantial changes occur for Na relative to Cl during the simultaneous process of evaporation and halite precipitation due to the higher initial chloride concentration. Calcium also decreases in concentration relative to sulfate due to the same processes described above but in this case due to the precipitation of gypsum. Ultimately, the solution attains a composition similar to that of a Mg-Cl bittern typically formed during the evaporation of seawater.

7.2.1 Mixing: Other Avon scenarios

A number of other possible mixing scenarios for waters of the Western Australian Wheatbelt are investigated below and include mixing of deep drainage waters in the Yilgarn, Lockhart and East Mortlock rivers with alkaline flood flows (Figure 7.1). Comparisons of pH only have been made using the phreeqc and pitzer databases.

The scenarios include:

- **Acidic drainage waters mixing with alkaline lake waters.**
    - Expanded Boodarockin drains directly mixing with alkaline flood-waters originating in the Upper Yilgarn (represented as flood overflow from Lake Julia). Mixing occurs in Lake Campion or Lake Brown,
    - Extended deep drainage from Trayning mixing in the Baandee Lakes with alkaline flood-waters originating in the Upper Yilgarn (represented as flood overflow from Lake Julia),
    - Expanded regional deep drainage from Mukinbudin mixing in the Baandee Lakes with alkaline flood-waters originating in the Upper Yilgarn (represented as flood overflow from Lake Julia),
    - Mixing of drainage from the Cowcowing-Wallambin catchments with alkaline lakes waters on the margins of the Cowcowing-Wallambin lakes system.
- **Acidic drainage waters mixing with alkaline flood-waters.**
    - Discharge from the Narembeen drains mixing with alkaline (flood-fill) waters in Lake Kurrenkutten,
    - Regional discharge of deep drainage in the lower Lockhart and Salt Rivers (represented by waters from the Narembeen drain) mixing with flood-flow water in the Yenyening Lakes

The results of modelling these mixing scenarios (Figures 7.8, 7.9, 7.10, 7.11, 7.12 and 7.13) outline a common pattern in that neutralisation of all acidic drainage waters require at least 10 times (up to 100 times) the volume of alkaline waters. Neutralisation of acidic sediments would therefore require significantly greater volumes of alkaline waters (see Chapter 6). In the case of sites such as Lake Brown/Lake Campion or the Baandee Lakes with existing acidic waters (and most likely acidic sediments), mixing modelling does not account for the additional acidity, hence greater volumes of alkaline waters are likely to be required to neutralise acidic drain waters in these environments.

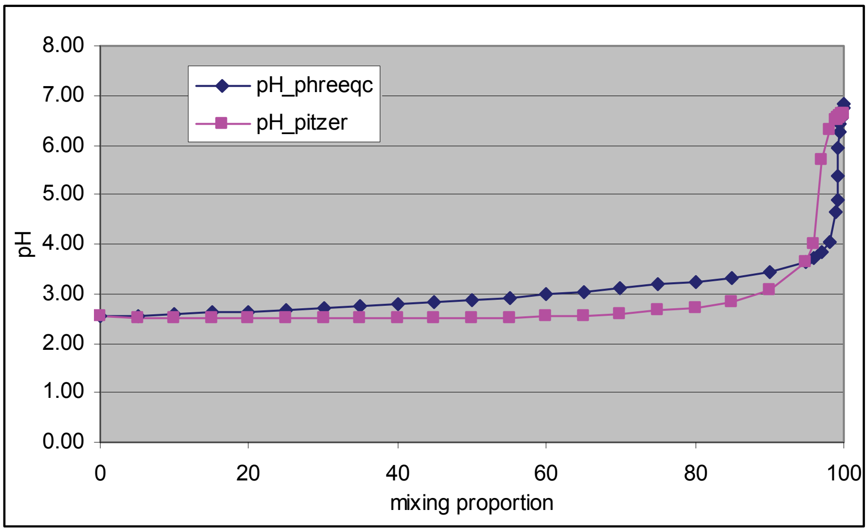

Figure 7.8 Estimated pH after mixing acidic saline drainage waters from Boodarockin (spring sample WADGC 19-A and summer sample WADGC 103) with alkaline lake waters (represented by water in Lake Julia, sample R29YR).

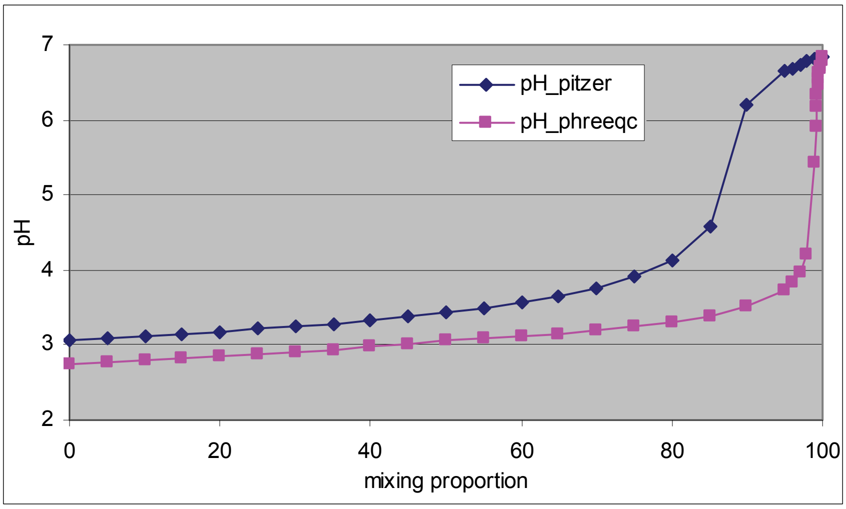

Figure 7.9 Estimated pH after mixing discharge from drainage SE of Trayning (sample WADGC 11-A) in varying proportions with alkaline lake waters (represented by water in Lake Julia, sample R29YR).

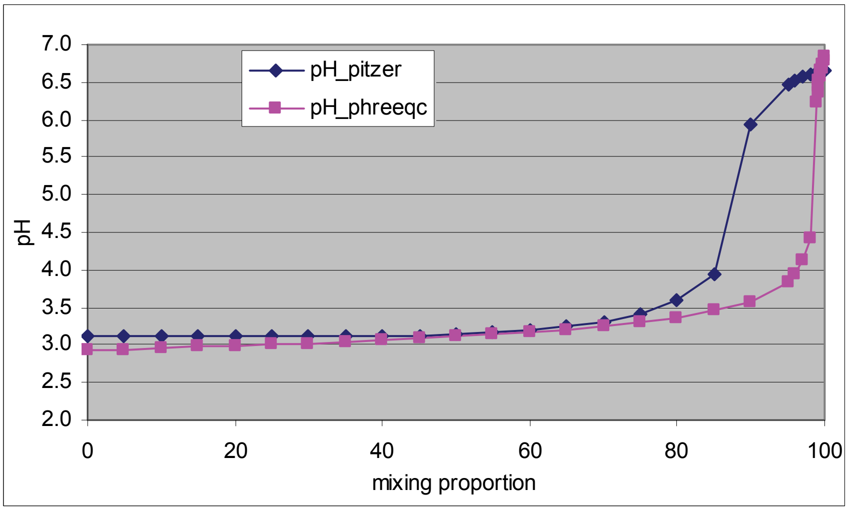

Figure 7.10 Estimated pH after mixing deep drainage discharge from the Mukinbudin area (Elachbutting sample WADGC-16 A) in varying proportions with alkaline lake waters (represented by Lake Julia, sample R29YR).

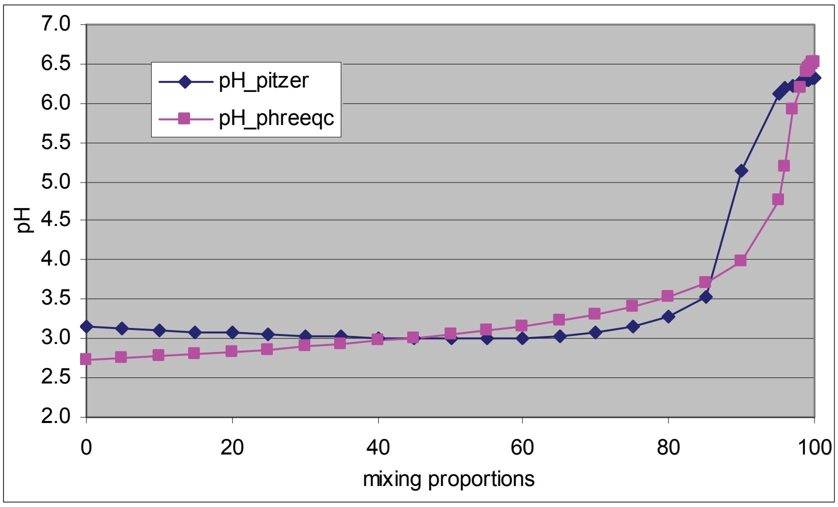

Figure 7.11 Estimated pH after mixing deep drain discharge (represented by East Cowcowing drain sample WADGC 09-A) in varying proportions with alkaline lake waters (represented by an average of Ski Lake spring R15 EM and summer samples R15EM240206).

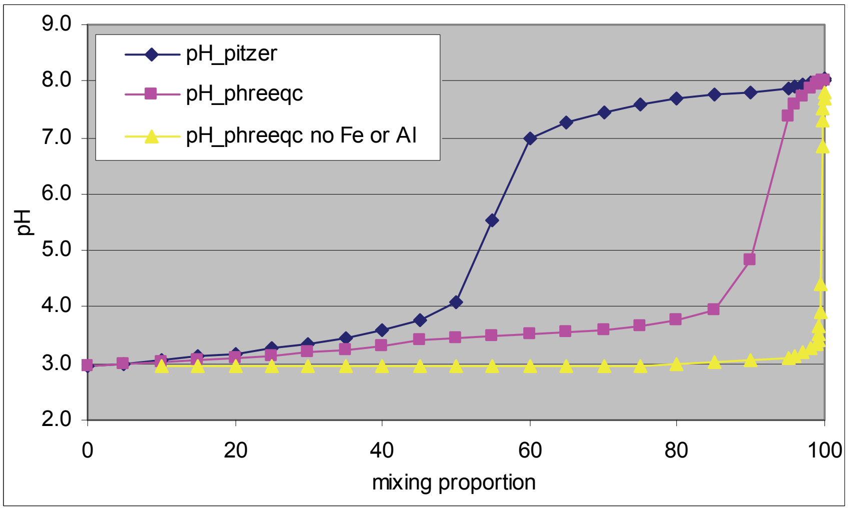

Figure 7.12 Estimated pH after mixing discharge from deep drainage at Narembeen (samples WADGC- 39A, D39210206 and LL10 2/8; all taken at Boundary Rd) with flood-waters in Lake Kurrenkutten (summer 2006 sample R35LR200206). Also shown is the estimated pH of the mixed waters using the phreeqc database without the presence of Fe or Al in solution, and thus not allowing Fe or Al minerals to precipitate.

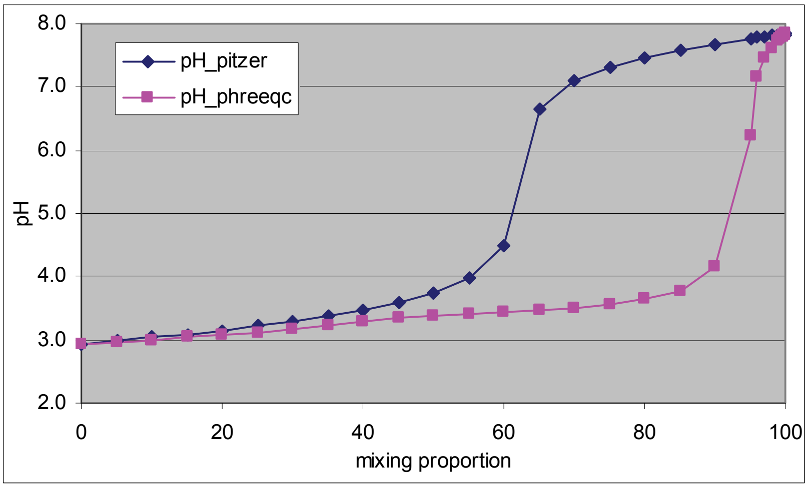

Figure 7.13 Estimated pH after mixing discharge from deep drainage at Narembeen (samples WADGC- 39A, D39210206 and LL10 2/8; all taken at Boundary Rd) with flood-waters in the Yenyening Lakes (represented by Beverly Ski Lake summer 2006 sample YY6010310).

7.2 Discussion

The simple mixing and evaporation scenarios modelled here illustrate the broad behaviour of low pH, saline waters on mixing with alkaline surface waters key areas of the Avon catchment where deep drainage is in place and could conceivable be expanded. The limited data available at each site restricted modelling to mixing of representative water chemistries (often based on single samples). In the case of the water chemistry representing acidic drainage, these appear to encompass the wide spatial and physico-chemical range (Chapters 2 - 5) of waters occurring in drains across the Western Australian Wheatbelt.

A common theme that emerges, irrespective of location and water chemistry, is that in order to achieve a near neutral to neutral pH, mixing ratios of typically between 99:1 (or greater) using the phreeq database and 3-5:1 using the pitzer database of near neutral to slightly alkaline water to acidic water is commonly required. A more detailed mixing model currently under construction will better constrain the actual pH derived from the mixing of various proportions of alkaline and acidic water. Nonetheless, it is likely that large relative proportions of alkaline water will be required to neutralize acidic drain discharge. Thus, in a typical scenario where there is an acidic water influx into an alkaline receiving basin it is likely that the residual buffering capacity of the receiving basin will be readily exceeded.

Near neutral to neutral pH of final mixed waters will be required to treat via adsorption or co-precipitation mechanisms many (but not all) of the trace metals that can be present in the discharge of some deep drains (see Chapters 2-6). The modelling process highlighted that significant geo-scientific gaps exist in reliably predicting the outcomes of mixing saline, acidic drainage waters with saline, alkaline waters. Priorities include a more detailed spatial and temporal understanding of the distribution of acidity and alkalinity in the WA Wheatbelt, and an improved understanding of the behaviour of trace elements in acidic, hypersaline waters. In particular, there is a need to determine the temporal pattern of water chemistry in drains and undertake sampling to define the alkalinity of surface flood waters.

Evaporation of waters after mixing can have significant impacts on water quality with a general decline pH predicted to occur during evaporation. Decreases in pH during evaporation will have will have significant impacts on trace metal solubility. Similar decreases in pH would also be expected to occur for acidic waters stored prior to mixing and may result in pH as low as 1.5. In such cases, however, storage and/or evaporation of waters would result in greater interaction of acidic waters with sediments and the likelihood of the sediments becoming acidified (See Chapter 6).

As described above, further validation of the mixing and evaporation modules will require at the minimum a set of laboratory-based experiments to assess the utility and robustness of the individual modules. In addition, the results of the laboratory-based experiments (see discussion below) may assist in possible parameter-fitting to increase the range of elements and/or general applicability and utility of the mixing and/or evaporation modules.

Continuing research and model development

A key to the eventual use of the PHREEQC model as a modelling tool will be the laboratory-based experimental validation of the theoretical modelling exercises. Such a validation exercise will provide an indication of the degree of robustness of the model under a range of conditions. The validation process will be achieved using a range of empirical mixing experiments which will combine a suite of typical Wheatbelt waters in various proportions to examine the resultant geochemistry. In addition, selected samples of these waters will be evaporated under controlled laboratory conditions to simulate evaporative processes. In the specific case of trace elements, which due to their low concentration and often inherently more variable geochemistry as described above, an optimisation model will be incorporated in an attempt to explain their behaviour as a function of water chemistry.

Eventually it is envisaged that a Graphical User Interface (GUI) will be constructed for the mixing and evaporation modules. This GUI and the underlying PHREEQC code will eventually allow the wider use of the mixing and evaporation model by end users such as State Government Agencies to assist in the planning of water management by simulation of mixing and evaporation scenarios in natural and artificial drainages and receiving basins.

7.3 Main Findings

1. Mixing of between 3-5:1 and 99:1 alkaline waters with acidic drain waters is required to achieve neutralisation.
2. Evaporation of mixed waters can result in at least 1 unit decrease in pH, with waters at initially pH 3 decreasing to less than pH 1.5. This effect would also occur with acidic waters stored prior to mixing.

7.4 Management Implications

1. Large volumes of alkaline waters (up to 99 times that of acidic waters) will be required to neutralise acidic drainage waters, assuming that the acidity remains present within surface waters and does not become embodied within sediments or precipitates.
2. Evaporation of acidic waters can result in further formation of waters with very low pH.

8. CONCLUSIONS

Brad Degens and Paul Shand

This investigation has found that there are significant geochemical risks associated with drainage of shallow saline acidic groundwaters. High concentrations of trace elements can occur in acidic drainage waters (such as Al, Cd, Cu, Fe, Mn, Ni, Pb, U and Zn), though this is not the case for all elements in the drains. The risk of deep drainage generating acidic waters is greatest mainly in the flat or gently sloping palaeodrainage systems east of the Meckering Line. Discharge of such metal-bearing, acidic drainage water may pose potential risks to aquatic and riparian ecosystems. Disposal of acidic saline waters will require careful management comprising treatment or containment to mitigate the risks.

Acidic groundwaters occur across a much larger area of the eastern WA Wheatbelt than previously recognised. Synthesis of historical groundwater records for salinity and pH with new data has shown that acidic saline shallow groundwaters are widespread in the Avon catchment in the WA Wheatbelt (Lillicrap and George, 2008). Across the whole agricultural zone, 23% of the 3032 groundwater observation sites had a pH of less than 4.5 with the median of this group being pH 3.6. The palaeodrainage systems of the eastern and northern Avon basin are the areas with the greatest likelihood of shallow acidic groundwaters. At local scales, these waters occur mostly in lower landscape positions, but can also underlie upland landscapes in some areas.

Although geology, regolith and depth to watertable play some role in explaining the spatial patterns of acidic groundwater, these do not sufficiently explain enough variation to be useful in reliably mapping the spatial distribution of the groundwaters. Further variation may be explained by exploring whether soil or vegetation variables provide better predictive power. However, without a conceptual understanding of the origins of the acidic groundwaters or understanding of spatial factors providing indications of acidic groundwater risk, this will be an entirely empirical approach and may only be useful in mapping acidic groundwater risk at catchment scales (10’s square km units). Mapping scales in the order of identifying 5-10 hectare units might be required for drainage planning.

Acidic groundwaters are most likely a natural regolith phenomenon, and existed in many agricultural areas well before the land was cleared and drains installed. The oxidation of ferrous iron appears to play a major role in the transport of acidity in the groundwaters intercepted by the drains, though the geochemical origin of the acidic iron-rich groundwaters is the subject of on-going work. Secondary processes occur within the sediments of drains that are likely to influence acid storage and release during the life of drains. ‘New’ sediment profiles are often evident within months of construction, in which cycling of iron and sulfur become important features within drains. Iron sulfide minerals form that effectively store acidity and can release this through sulfide oxidation if drain sediments dry out or are disturbed.

The discharge of regional acidic groundwaters may be acidifying lakes in some parts of the Avon, “naturally acidic” lakes were found, mostly in the agricultural zone of the upper Mortlock and Yilgarn Rivers. Although over 45% of reference lakes in this survey were alkaline (pH>6.5), there were lakes with naturally acidic waters (pH<4.5) with no evidence of acidic drain inflows. This may partly be biased by sampling time, mostly capturing lakes in the final stages of drying during low rainfall years, whereas a greater proportion of lakes are likely to be alkaline in wetter years or after flood events. Although a number of lakes may have been acidic since before vegetation clearance began, a number of lakes showed evidence of being previously alkaline and have been acidified in recent decades, most likely by discharge of acidic groundwaters. Given that shallow acidic groundwater is widespread, and that groundwater rise and increased discharge is likely to continue in much of the Avon for coming decades, it is likely that more lakes may become acidic. In most cases, however, this would be preceded by significant impacts from secondary salinity such as increasing salt accumulation and water-logging.

Construction of deep open drains intercepts shallow saline acidic groundwaters and enables increased transport of these waters through inland agricultural areas of the Avon catchment. Over 45% of baseflows in deep drains of the central eastern Wheatbelt (east of a line from Dumbleyung to Dalwallinu) were found contain acidic (pH<4.5), saline (at least 40 000 mg l^{-1} TDS) waters. This broadly mirrored areas where acidic groundwaters have been identified during the sampling of monitoring bores. Over half of the drains contained high concentrations of soluble iron (>5 mg l^{-1} and up to >200 mg l-1), aluminium (>80 mg l^{-1} and up to >200 mg l^{-1}) and manganese (>5 mg l^{-1} and up to >40 mg l^{-1}), mostly linked with the low pH conditions. Although less frequent, trace metals such as Pb, Cu, Zn, Ni, U and rare earth elements (La, Ce) were also present in high concentrations (>0.5 mg l^{-1}). Alkaline drainage waters generally contained significantly lower concentrations of trace elements, though occasionally contained high Se and As. Similar concentrations of elements were found in regional groundwaters.

Drain mineral surveys indicated that these environments are complex geochemical "factories" that are likely to be sensitive to changes in flow, evaporation or disturbance of sediment (e.g. by drain cleaning). Detailed studies of the sediments, salts and mineral precipitates in drains indicated that a range of geochemical processes could occur over the scale of a few millimetres. Salts accumulating on drain walls may contain acidity and trace metals, as well as the ubiquitous halite and gypsum salts. New sediments also formed in the base of drains that could include surface gels and precipitates rich in trace metals at the sediment-water surface, in addition to stored acidity in sulfide minerals in underlying sediments. In a study at Narembeen, concentrations of several trace elements were lower in drainage waters compared with surrounding groundwaters indicating that these are being removed by adsorption onto Fe and/or Mn oxyhydroxides within the drains (Tapley et al., 2004). The minerals accumulating within drains present risks in terms of acid and trace metal storage that could potentially be at risk of flushing. To minimise this, drain management options should include aiming to retain such minerals, by minimising scouring flows or runoff from the walls of drains.

Management of drain discharge will need to account for temporal changes in drain geochemistry. For example, acidity commonly increases during sediment drying in summer, probably due to oxidation and precipitation of iron minerals in drain sediments coupled with evaporation of drainage waters. Trace metal mobility will be strongly affected by variations in pH and to a lesser degree by variation in salinity. Geochemical modelling also confirmed that significant declines in pH are expected to occur during evaporation, with evaporation of 80% of water from drainage waters of approximately pH 3 resulting in a final pH of less than 2. There was some evidence that drain geochemistry can also vary with the drain age as sediments accumulate, flows ebb and increased contact occurs between sediment and drain waters.

The disposal of acidic drain waters to lakes or floodplains offers limited opportunity to 'neutralise' the acidity from drains or immobilise many trace elements. All lakes (and other environments) receiving acidic saline drain discharge were acidic (with pH<3.8) indicating limited capacity to neutralise acidity or that sediments were acidic prior to drainage discharge. Over 75% contained waters with total dissolved salts >50 000 mg l^{-1}, reflecting the dominance of evaporation in the disposal sites. Lakes with acidic drainage waters appeared to be geochemically similar to acidic reference lakes (considered to be "naturally" acidic). This may reflect the similar geochemical processes at the sites.

Geochemical modelling has indicated that large volumes of neutral-alkaline waters will be required to neutralise acidic drain waters by mixing. Every cubic metre of acidic drainage water could require up to 100 cubic metres of alkaline waters, which might only be achieved during large flood events. Given that these are likely to be infrequent (at least several years between events); waters will most likely evaporate with much of the acidity becoming "stored" within the sediments. Neutralisation of this acidity may then depend on whether flood waters remain contained for sufficiently long periods to allow neutralisation of these sediments. In the absence of such volumes of alkaline waters being continuously available, it will be necessary to implement further remediation strategies.

Further factors to consider using flood-water neutralisation are the amount of alkalinity that might be present within flood waters and whether the treated site remains alkaline. There were limited opportunities to obtain water samples for flood-flows during this investigation and those used in the geochemical modelling were either flood-fill waters in alkaline lakes or waters from lakes in the final stages of drying. These were often non-turbid waters and could contain significantly different alkalinity than that of turbid flood-waters. A final factor to consider is whether the neutralisation site will remain alkaline after treatment. Removal of many (but not all) trace metals from acidic waters during neutralisation can be dependent on pH sensitive adsorption or co-precipitation mechanisms. Periodic acidification by drain discharge in intervening times may result in repeated adsorption and desorption of trace metals, potentially resulting in increased concentrations in surface waters.

Disposal of acidic waters to lakes will result in significant storage of acidity in the bed sediments and soils of the beach zone. Shallow soils in the beach zone commonly contained greater storage of soluble acidity than the bed sediments. The accumulation of acidity in this zone at most acidic reference playas was probably due to concentration of acidity by evaporation of local groundwater discharge on the margins of the lakes. Preliminary results indicate that acidic drain discharge does not necessarily result in readily distinguishable elevated accumulations of trace metals compared with playas not receiving acidic drainage. However, the sampling density was too sparse for this to be certain. Further, more detailed investigations will be required to predict which drains are likely to result in increased accumulation of trace metals in receiving environments compared with acidic reference playas. These investigations should involve comparisons of paired playas (acidic reference and acidic drain receiving playas) as well as before and after investigations of trace metal accumulation in environments receiving acidic saline drainage.

8.1 Key findings

Distribution

- Acidic groundwater is widespread across all agricultural regions and increases in occurrence from the higher rainfall, steeper areas to the drier, flatter areas.
- Geology, regolith and depth are important in explaining the spatial patterns of acidic groundwater. However, there are other as yet unidentified factors needed to explain acidic groundwater occurrence.
- Groundwaters in the Wheatbelt show a distinct bi-modal distribution in pH with a large acidic population (pH<4.8).

Characteristics of acidic groundwater and drain waters

- Acidic drain waters contain high concentrations of iron and aluminium that play a major role in acidity transfer from groundwaters to drains.
- The mineral origins of the iron-rich, acidic groundwaters are unclear.
- Low pH waters provide geochemical conditions that favour mobilisation of trace elements from the regolith, with local properties of the regolith influencing the concentration and distribution of the trace elements.
- The varying salinity of waters in surface environments will have less influence on the behaviour of the trace elements, rare earths elements and chalcophile elements (such as As) than pH, although the different forms (or species) of some elements may vary.

Drain geochemistry

- Changes in soil geochemical characteristics in drains and receiving environments could be characterised by a rapid field survey procedure coupled with a series of key laboratory analysis methods for gels, salts, soils and sulfidic materials selectively sampled at each site.
- A systematic web-based data system was developed for acquisition, collation and communication of detailed data sets (e.g. soil morphology, chemistry and mineralogy) dealing with gels, salts, soils and sulfidic materials in drains and receiving environments.
- A range of soil formation processes occurred in the hypersaline soils of drain batters and sodic soils on the edge of drains.
- Several new assemblages of sulfate-containing evaporite minerals, oxyhydroxysulfate minerals and sulfides have been identified in the wide range of sulfuric and sulfidic soil environments that have formed in drains in the Avon catchment.
- Reddish-brown and orange-yellow precipitates or gels in drains are ferric-oxyhydroxides and ferric-oxyhydroxysulfates that can which release free hydrogen ions in the process of formation or dissolution.
- Various types of hydrated oxyhydroxides (ferrihydrite, goethite), iron oxyhydroxysulfates (schwertmannite and akaganéite), oxyhydroxides and oxides (hematite) occurred in various micro-environments in drains and receiving lakes. The minerals were indicative of a wide range of rapidly changing local environments and variations in Eh, pH, rates of availability of S and other elements and temperature. These minerals can be useful indicators of soil-water processes operating in these environments.
- Sulfidic and sulfuric materials (acid sulfate soil materials) occurred in drains and receiving environments. Disturbance by excavation or high flow scouring of sediments risks oxidation of the pyrite in the sulfidic materials with release of sulfuric acid and formation of sulfuric materials.
- Specific types of salt efflorescences are an integrated indicator of complex biogeochemical conditions and transformations occurring in the drains and play a critical role in drain erosion processes by salt fretting. Salt efflorescences, especially the sulfate containing minerals, can cause detachment of soil during crystal growth and degradation of drain walls.
- Soluble sulfate/chloride-containing minerals in efflorescences (mainly on drain walls and dry sediments) play important roles in the transient storage of ions such as Na, Ca, Mg, Ba, Sr, Cl, Br, I and SO_4.
- Gels and sulfuric horizons on the margins or within the base of drains can contain elevated trace element and metal concentrations (Al, Cu, Pb, Cr, Pb, Zn, Mg and rare earth elements).
- The minerals, associated trace elements and spatial occurrence of these within drains highlight specific risks that point to key management strategies: some specific to drains: e.g. anthropogenic burning results in the formation of irreversibly fused, particulate and discrete iron-rich artefacts, which can block drain pipes.

Receiving environments

- A random survey found that surface waters in 45% of lakes were alkaline (pH>6.5), with the remaining lakes containing acidic waters, frequently with pH<4.
- Lakes that contained acidic waters not attributed to drainage discharge are likely to have been acidified by regional groundwater discharge or were naturally acidic prior to rises in regional groundwater tables.
- Some existing alkaline lakes will be under on-going acidification pressure if discharge of regionally acidic groundwaters continues to occur. For current acidic lakes, this will result in increasing acidification and accumulation of trace elements (determined by rates of groundwater discharge). For current alkaline lakes this could result in acidification.
- Acidic drainage to lakes can result in acidification of lake waters, sediments and the soils in the beach-zone surrounding the lakes.
- Containment of acidic saline discharge can result in formation of highly acidic sediments in receiving environments (artificial and constructed).

- Acidic drain/bore discharge to lakes within the central floodway can result in accumulation of salts, acidity and trace metals in surface sediments and adjoining flood-zones that carries the risk of being exported in concentrated flushes to down-stream lakes during moderate flow events.
- Surface waters within acidic drain receiving lakes can contain significant concentrations of dissolved Al and Fe which may form significant concentrations of Al species (e.g. Al^{3+}) that can be toxic to some aquatic biota and, during neutralisation, iron floc (smothering benthic communities). The greatest risk of this is likely to occur during the first flush part of flood-flows and for small rainfall events that result in localised lake filling, and therefore concentration of discharge.
- Alkalinity present in shallow soils surrounding receiving environments may offer some capacity to neutralise acidic waters and sediments.
- Alkaline flood flows may not have significant capacity to neutralise acidic sediments in acidic lakes (natural and drainage created) the significant volumes of water that might be required (See chapter 5).

Neutralisation and evaporation behaviour

- Mixing ratios of between 3:1 and 99:1 (alkaline waters: acidic drain waters) is typically required to achieve neutralisation.
- Evaporation of mixed waters can result in at least 1 unit decrease in pH, with waters at initially pH 3 decreasing to less than pH 1.5. This effect would also occur with acidic waters stored prior to mixing.
- The modelling completed highlighted that significant data gaps exist in reliably predicting the outcomes of mixing saline, acidic drainage waters with saline, alkaline waters. There are challenges in predicting the minerals that form during mixing and the behaviour of trace metals under saline conditions.

8.2 Management implications

Drainage planning and design

- The broad geographical extent of acidic groundwater highlights that consideration must be given to its occurrence for any activity involving pumping or drainage of groundwater in the palaeodrainage systems of the Avon catchment.
- Soils, groundwater geochemistry and pilot excavations should be assessed by sampling of fresh groundwater inflow before drain construction to determine the risk of acidic groundwater and trace element issues.
- Drains need to be designed and managed to minimise turbulent flow to minimise the flushing of precipitates and gels (frequently containing trace metals) and disturbance of sulfidic sediments (being a store of acidity and trace metals). In particular, entry of surface waters from catchments to the drains should be avoided without measures to contain flow velocities.
- Design drain to maximise hydrological residence times and formation of precipitates will contribute to maximising retention of trace metals within the systems, though first flushes from drains will need to be managed (see below).
- Containment (and or treatment) of flows after rainfall events would assist in reducing trace metal and acid fluxes from drains. Run-off from drain banks and walls is likely to mobilise trace metals and acidity associated with these zones, increasing drain water acidity and trace metal concentration as well as sediment erosion. The mobilisation of precipitates on drain sediments (also containing acidity and trace metals) will also contribute to increased export of acidity and trace metals during rainfall events.

Planning safe disposal

- For mixing options, large volumes of alkaline waters (up to 99 times that of acidic waters) will be required to neutralise acidic drainage waters, unless acid neutralisation processes occur with well buffered sediments.
- Acidic groundwater discharge is best managed by containment and/or treatment in sites with minimal risk of down-stream transport, although this may be difficult to achieve for drains which discharge to lakes in the central floodway.
- Where drains discharge acidic waters to sites with poor containment, management of geochemical risks to down-stream environments will need to focus on acid and metal mobilisation occurring during the first flush.
- Containment of acidic saline discharge may require treatment with neutralising agents (e.g. agricultural lime) at regular intervals, depending on the risk to down-stream environments. This periodic treatment of accumulated acidity may be more cost effective than continuous treatment of drain discharges, which can be difficult in remote sites.
- Evaporation of stored or disposed acidic waters can result in further formation of waters with very low pH. This will need to be avoided when managing trace elements in disposal environments to ensure that elements removed from solution by neutralisation or treatment are not subsequently remobilised.
- Soils with carbonates surrounding receiving environments could be mixed into the bed or used to line lakes to provide some capacity to neutralise acidic waters and sediments.
- The use of alkaline flood flows to neutralise acidic sediments in acidic lakes may only be likely with significant volumes of water and sufficient time of flooding to allow seepage of alkalinity into sediments.

Drain management

- Management of trace metal mobility and acid release will need to be considered when maintenance cleaning of sediments from drains is carried out, since there are minerals in the drains that can release acidity and trace metals. Appropriate management might include mixing of sediments with alkaline drain spoils (to neutralise acidity), placement within depressions on drain spoils (allowing drying and containment but including contact with alkaline spoils) or collection and containment in a site without risk of off-site impacts (i.e. outside of a surface flow pathways).
- Accumulated vegetation in drains (e.g. roly poly residues) is best removed mechanically particularly where large compact accumulations of materials occur in conjunction with iron precipitates. Burning of residues can result in the formation of a cemented iron plug that can significantly impede flows.

Regional salinity management issues

- Acidic lakes due regional groundwater discharge (i.e. not drainage) may require management of geochemical risks including acidity and soluble trace metals to protect alkaline down-stream environments.
- Additional lakes may be acidified in future decades by continued groundwater table rise across the Avon.

8.3 Recommendations for further work

This study has detailed the distribution of acidic groundwaters and drains in the Avon catchment at a regional scale. However, a conceptual geochemical model describing the origin of the acidity and the role that acid generation during groundwater discharge plays, are poorly understood. More detailed studies at a local scale, incorporating both surface water and groundwater, would help to resolve these problems. The approach presented should also be applied to the other catchments of the Wheatbelt, which are likely to governed by similar hydrogeochemical processes.

A further recommendation is that the results from the project should be combined with the outcomes of an EEI funded CSIRO Land and Water project evaluating regional drainage options for the Avon catchment. This will allow for a more quantitative assessment of risk.

Practical solutions to the remediation of acidic drainage are well established in the field of acid rock drainage. The scale of acidic drainage across the Wheatbelt and the remoteness of much of the landscape means that solutions may not be easily transferable or feasible. Low cost and low maintenance solutions may be a more feasible option for the Wheatbelt and should be assessed using field trials.

ACKNOWLEDGEMENTS

We are grateful to Clare Wright, Jason Kirby, Adrian Beech and other staff at the CSIRO laboratories in Adelaide for water analysis. We are also thank Peter Geste (Department of Environment and Conservation, WA) and Geoff Sadgrove (Department of Water, WA) for undertaking groundwater sampling, Ms Claudia Hadlow (WA Channel Management Group Executive Officer, 2004) for selected lake and drain samples and Dr Riasat Ali and John Byrne (CSIRO, Land and Water) for additional samples of Narembeen drain and adjoining groundwaters. Shahram Sharafi (DAFWA) sampled groundwaters for North Baandee, Wallatin Creek, Koorda, Warralackin, Bodallin and Bruce Rock.

REFERENCES

ABS (2003). Salinity and land management on Western Australian farms. Western Australian Statistical Indicators Bulletin No. 1367.5, June 2003. Australian Bureau of Statistics, Canberra.

Ahern, C.R., Sullivan, L.A. and McElnea, A.E. (2004). Laboratory Methods Guidelines 2004 – Acid Sulphate Soils. In: 'Queensland Acid Sulphate Soil Technical Manual'. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Ali, R., Hatton, T., George, R., Byrne, J. and Hodgson, G. (2004a). Evaluation of the impacts of deep open drains on groundwater levels in the Wheatbelt of Western Australia. *Australian Journal of Agricultural Research*, 55, pp 1159-1171.

Ali, R., Hatton, T., Lambert, T., Byrne, J., Hodgson, G. and George, R. (2004b). An assessment of the quality and quantity of discharge from deep open drains in Narembeen: Wheatbelt of Western Australia. In: *1st National Salinity Engineering Conf., 9-12 Nov., 2004, Perth Australia*. 84-88.

ANZECC and ARMCANZ (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality – Aquatic Ecosystems. Australian and New Zealand Environment and Conservation Council (ANZECC) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ).

Baker A.K.M. and Fitzpatrick R.W. 2005. A systematic web-based approach for the acquisition, collation and communication of soil-regolith data. In 'CRC LEME regional regolith symposia 2005'. (Ed. Roach I.C.). (CRC LEME: Adelaide) Australia.' Water and Rivers, Report No. SLUI 20.

Bettany, E., Blackmore, A.V., Hingston, F.J. (1964). Aspects of the hydrologic cycle and related salinity in the Belka Valley, Western Australia. *Australian Journal of Soil Research* **2**, 187-210.

Brinkman R. 1979. Ferrolysis, a soil-forming process in hydromorphic conditions. In 'Agricultural Research Reports 887'. (PUDOC: Wageningen).

De Broekert, P.P. and Coles, N.A. (2004).Wetland basins for saline drainage water disposal: Bodallin and Elachbutting Catchments, Eastern Wheatbelt, Western Australia. Department of Agriculture WA, Resource Management Technical Report 290. October 2004.

Campbell, P.G.C. (1995). Interactions between trace metals and aquatic organisms: a critique of the free-ion activity model. In: Metal Speciation and Bioavailability in Aquatic Systems (Tessier, A., and Turner, D.R., eds). IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. Volume 3. John Wiley and Sons, Chichester. Pp 45-102.

Clarke, C.J., George, R.J., Bell, R.W. and Hatton, T.J. (2002). Dryland salinity in South-Western Australia: its origins, remedies and future research directions. *Australian Journal of Soil Research*, 40, 93-113.

Degens, B.P. and Muirden, P.D. (2006). An emerging pattern of acidic base-flow conditions in waterways of the inland Avon basin. INTERACT Conference 2006 Proceedings. Perth, Western Australia September 24-28, 2006.pp 160.

Dent D.L. & Pons L.J. 1995. A world perspective on acid sulphate soils. *Geoderma* 67, 263-276.

Dogramaci S. and Degens B. (2003). Review of Engineering and Safe Disposal Options, Western Australia. Water and Rivers, Report No. SLUI 20.

Douglas, G. and Degens, B. (2006). A synopsis of potential amendments and remediation techniques for the neutralization of acidic drainage waters in the Western Australian Wheatbelt. CRC LEME Open File Report 209, 22 pp.

Dzombak, D.A. and Morel, F.M.M. (1990). Surface complexation modelling: hydrous ferrous oxide. Wiley Interscience, 393 pp.

Fitzpatrick, R.W., Baker, A.K.M., Raven, M., Rogers, S., Degens, B., George, R. and Kirby, J. (2005). Mineralogy, biogeochemistry, hydro-pedology and risks of sediments, salt efflorescences and soils in open drains in the Wheatbelt of Western Australia. *In*: Roach I.C. ed. 2005. Regolith 2005 – Ten Years of CRC LEME, 97-101.

Fitzpatrick R.W., Fritsch E. and Self P.G. 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes; V, Development of saline sulfidic features in non-tidal seepage areas. Geoderma 69, 1-29.

Fitzpatrick R.W., Merry R.H., Cox J.W., Rengasamy P. and Davies P.J. 2003 'Assessment of physico-chemical changes in dryland saline soils when drained or disturbed for developing management options.' CSIRO Land and Water, Technical Report 02/03, http://www.clw.csiro.au/publications/technical2003/tr2-03.pdf.

George, R.J., Nulsen, R.A., Ferdowsian, R., and Raper, P. (1999). Interactions between trees and groundwaters in recharge and discharge areas - A survey of Western Australian sites. *Agricultural Water Management* 39:91-113.

Goodsell, J.T. (1990). Distribution of waterbird broods relative to wetland salinity and pH in south-western Australia. Australian Wildlife Research, 17, 219-229.

Halse, S.A. (2004). Biological impacts of drainage disposal in wetlands of the Western Australian Wheatbelt. In, S. Dogramaci & A. Waterhouse (eds.), 1st National Salinity Engineering Conference, November 2004, Burswood International Resort, Perth, Western Australia. Institution of Engineers, Australia, Canberra. pp. 373-378

Halse, S.A., Williams, M.R., Jaensch, R.P. and Land J.A.K. (1993). Wetland characteristics and waterbird use of wetlands in south-western Australia. *Wildlife Research* 20, 103-126.

Heath, R. and George, R. (2007). Groundwater trends in the central agricultural region. FARMNOTE, No. 208. Department of Agriculture and Food. January 2008.

Isbell R.F. 2002. The Australian soil classification. Rev., CSIRO Publishing, Collingwood, VIC, Australia, 144 pp.

Kingwell, R. and Cook, S. (2007). Farmers' attitudes and investment intentions regarding land drainage in a salinising Australian landscape. *The International Journal of Interdisciplinary Social Sciences,* 2, 169-185.

Lamontagne, S., Hicks, W.S., Fitzpatrick, R.W., & Rogers, S. 2006 Sulfidic materials in dryland river wetlands. *Marine and Freshwater Research*, 57(8), 775-788.

Langmuir, D. (1997). Iron and Sulfur Geochemistry (Chapter 12). In: "Aqueous Environmental Geochemistry". Prentice Hall, New Jersey. Pp 431-485.

Lee, S.Y. and Gilkes, R.J. (2005). Groundwater geochemistry and composition of hardpans in southwestern Australian regolith. *Geoderma*, 126, 59-84.

Lillicrap, A.M. and George, R.J. (2008) The distribution and origins of acid groundwaters in the Southwest Agricultural Area. Natural Resource Management Technical Report, Department of Agriculture and Food Western Australia (in press).

Mann, A.W. (1983). Hydrogeochemistry and weathering on the Yilgarn Block, Western Australia – ferrolysis and heavy metals in continental brines. G*eochim. Cosmochim. Acta*, 47, 181-190.

Mazor, E. and George, R. (2005) Marine airborne salts applied to trace evapotranspiration, local recharge and lateral groundwater flow in Western Australia. *Journal of Hydrology*, **139**, 63-77.

McArthur, J.M., Turner, J.V., Lyons. W.B., Osborn, A.O. and Thirlwall, M.F. (1991). Hydrochemistry on the Yilgarn Block, Western Australia: Ferrolysis and mineralization in acidic brines. G*eochim. Cosmochim. Acta*, 55, 1273-1288.

McFarland, D. J., George, R.J and Caccetta, P.A. (2004). The extent and potential area of salt-affected land in Western Australia estimated using remote sensing and digital terrain models. In: *1st National Salinity Engineering Conf., 9-12 Nov., 2004, Perth Australia*. 55-60.

Parkhurst, D.L. and Appelo, C.A.J. (2006). PHREEQC for Windows v2.12.05, a hydrogeochemical transport model. PHREEQC program (freeware) can be downloaded at: http://www.geo.vu.nl/~posv/phreeqc/download.html

Paterson, J. (2005). Saline water disposal next step in drainage debate. Farming Ahead, No. 159, pp 55-57, April 2005.

Ruprecht, J.K., Ali, R. and Hatton, T. (2004). Regional drainage evaluation – Avon River Basin. In: *1st National Salinity Engineering Conf., 9-12 Nov., 2004, Perth Australia*. 331-336.

Smith, R., Jeffree, R., John, J. and Clayton, P. 2004. Review of methods for water quality assessment of temporary stream and lake systems. Australian Centre for Mining Environmental Research, Kenmore, Queensland. Australia.

Sullivan L.A., Bush R.T. and Fyfe D. 2002 Acid sulfate soil drain ooze: Distribution, behaviour and implications for acidification and deoxygenation of waterways. In 'Acid sulfate soils in Australia and China'. (*Eds* Lin C., Melville M.D. &Sullivan L.A.) pp. 91-99. (Science Press: Bejing, China).

Tapley, I., Pirlo, M.C. and Gray, D. (2004). Spectral mineralogy, soil and water chemistry associated with the Narembeen drain network and Seagroatt Nature Reserve. CSIRO Exploration and Mining, Exploration and Mining Report 1235R for Dept. Conservation and Land Management, WA.

Wang, W. (1987). Factors affecting metal toxicity to (and accumulation by) aquatic organisms – overview. Environmental International, 123, 437-457.

Ward., N.J., Sullivan, L.A. and Bush, R.T. (2004). The response of partially oxidised acid sulphate soil materials to anoxia. *Australian Journal of Soil Research*, 42, 515-525.

APPENDICES

Appendix 1: Site numbers, names and GPS co-ordinates (GDA 94).

Groundwater Geochemistry Sampling Sites

SITE_ID	SITE_NAME	ZONE	EASTING	NORTHING
00KO07D	Koorda	50	534833	6612497
00KO09D	Koorda	50	535025	6611017
00KO09S	Koorda	50	535029	6611017
00KO10D	Koorda	50	534893	6608936
00KO10S	Koorda	50	534890	6608934
00KO11D	Koorda	50	535442	6606925
00KO13D	Koorda	50	535873	6606964
00NE01	Warrachuppin	50	657937	6567230
00NE02D	Warrachuppin	50	670136	6567978
00NE02S	Warrachuppin	50	670139	6567977
00NE13	North Bodallin	50	687569	6558731
00NE22D	Bodallin	50	692376	6510220
00NE22S	Bodallin	50	692377	6510221
00NE24D	Bodallin	50	692116	6497325
00NE24M	Bodallin	50	692117	6497325
00NE28D	Bodallin	50	693417	6498629
00NE28S	Bodallin	50	693417	6498627
6.2	Richards Pump	50	535500	6449400
AB04	Bruce Rock	50	620280	6485218
AB04B	Bruce Rock	50	620281	6485219
B1D	Narembeen	50	654069	6456537
B2D	Narembeen	50	653960	6455907
B3D	Narembeen	50	653862	6455683
B3S	Narembeen	50	653860	6455684
B4D	Narembeen	50	653851	6455667
B4S	Narembeen	50	653849	6455666
B5D	Narembeen	50	653759	6455485
B5S	Narembeen	50	653758	6455485
B6D	Narembeen	50	653621	6455238
BC001D	Beacon	50	577666	6633736
BC001S	Beacon	50	577666	6633736
BC002	Beacon	50	577690	6633743
BC003	Beacon	50	577740	6633756
BC006	Beacon	50	578033	6633822
BC007D	Beacon	50	575935	6638181
BC007S	Beacon	50	575935	6638181
BC013D	Beacon	50	574316	6641909
BC013S	Beacon	50	574316	6641909
BC019D	Beacon	50	574622	6646673
BC019S	Beacon	50	574622	6646673
BC025S	Beacon	50	578592	6632367
BN02S	Beacon	50	574468	6643784
BN05	Beacon	50	577590	6649757
DSPD	Narembeen	0	671655	6446954
DSPS	Narembeen	0	671655	6446962
JD2D	Narembeen	0	671379	6446464
JD2S	Narembeen	0	671378	6446466
JD3D	Narembeen	0	671476	6446639
JD3S	Narembeen	0	671475	6446639

SITE_ID	SITE_NAME	ZONE	EASTING	NORTHING
JD4D	Narembeen	0	671481	6446655
JD4S	Narembeen	0	671478	6446655
JD5D	Narembeen	0	671550	6446940
JD5S	Narembeen	50	671549	6446940
JD7D	Narembeen	50	671596	6447178
JD7S	Narembeen	50	671596	6447178
L1D	Narembeen	50	633717	6451241
L1S	Narembeen	50	633717	6451235
L2D	Narembeen	50	633643	6451074
L2S	Narembeen	50	633643	6451076
L3D	Narembeen	50	633622	6450778
L3S	Narembeen	50	633620	6450778
NB04B (NB9)	North Baandee	50	585065	6524882
NB04c (NB10)	North Baandee	50	585068	6524879
NB06B (NB14)	North Baandee	50	586219	6526585
NB06C (NB13)	North Baandee	50	586220	6526581
PT001D	Pithara	50	491375	6637562
PT001S	Pithara	50	491375	6637562
PT007D	Pithara	50	491896	6638119
PT007S	Pithara	50	491896	6638119
PT012D	Pithara	50	495149	6637193
PT012S	Pithara	50	495149	6637193
PT014	Pithara	50	495220	6637160
PT018D	Pithara	50	495134	6636863
PT018S	Pithara	50	495134	6636863
PT026	Pithara	50	488370	6640296
PT027	Pithara	50	488610	6640511
PT029	Pithara	50	490823	6639706
PT033	Pithara	50	490298	6640479
PT035	Pithara	50	488111	6640648
W03	Wallatin Creek	50	582964	6517184
W04	Wallatin Creek	50	581367	6514010
W05	Wallatin Creek	50	581240	6512560
W06	Wallatin Creek	50	581235	6512562
W07	Wallatin Creek	50	581237	6512561
W08	Wallatin Creek	50	581202	6512309
W09	Wallatin Creek	50	581204	6512305
W10	Wallatin Creek	50	581204	6512303
W53	Wallatin Creek	50	573600	6523244
W54	Wallatin Creek	50	573632	6523121
W55	Wallatin Creek	50	573756	6522923
W56	Wallatin Creek	50	573758	6522921
W57	Wallatin Creek	50	573750	6522645
W61	Wallatin Creek	50	571762	6523154
W62	Wallatin Creek	50	572378	6523032
W63	Wallatin Creek	50	572353	6523010
W64	Wallatin Creek	50	572355	6523005

Drain Geochemistry Sampling Sites

SITE_ID	SITE_NAME	ZONE	EASTING	NORTHING
90	Belka Valley, Narembeen-Merredin Rd	50	632111	6484159
61	Beynon Rd Drain confluence, Doradine creek	50	575740	6323406
62	Beynon Rd Drain, Doradine creek, Dumbleyung-Lake Grace Rd.	50	576685	6322120
41	Billericay, Browns Rd	50	628676	6430323
40	Billericay, Cheethams Rd	50	622181	6435777
22	Boodarockin, Bennett Rd	50	649014	6549420
21	Boodarockin, Boodarockin East Rd	50	674492	6558595
18	Boodarockin, Boodarockin North Rd	50	671304	6570855
20	Boodarockin, Daddow Rd	50	669808	6562435
19	Boodarockin, M40, Koorda-Bullfinch Rd.	50	668444	6567807
91	Bulyee, Avon South Branch, Bulyee Rd	50	548900	6408400
80	Bulyee, Brookon-Corrigin Rd	50	549300	6418300
48	Bulyee, Brookton-Corrigin Rd	50	549300	6418300
49	Bulyee, Dwarlaking Rd	50	547154	6417004
24	Buracoppin, Begley North Road	50	647677	6553850
23	Buracoppin, Begley Road	50	647515	6549109
6	Burakin, Kirwan Rd	50	513629	6616432
55	Corrigin drains terminus, Nambadilling Rd, East	50	596343	6426062
54	Corrigin drains, Nambadilling Rd, East	50	587711	6422436
53	Corrigin drains, Nambadilling Rd, West	50	586119	6421867
50	Corrigin, Lomos Rd (Cross Rd South)	50	554183	6408972
51	Corrigin, Rafferty Road	50	558868	6409413
9	Cowcowing, Wyalkatchem-Koorda Rd	50	541880	6562524
2	Dalwallinu, Dalwallinu-Kalannie Rd	50	491957	6649597
60	Datatine, Robson Road	50	582985	6300809
59	Doradine Creek, Filmers - Ward Road	50	567363	6327344
63	Doradine, Temby Road Crossing	50	567363	6327344
10	Edjanding, Dowerin-Kalannie Rd	50	511451	6569021
93	EEI Morowa drain, Holder Road	50	406083	6795698
3	EEI Pithara drain, Birdwood Rd	50	487565	6640994
5	EEI Pithara drain, Petrudore Rd	50	495628	6636536
4	EEI Pithara drain, Pithara East Rd	50	490687	6638569
16	Elachbutting - Elsewhere Rd	50	646404	6610522
15	Elachbutting Rock-Road crossing	50	637997	6615191
15	Elachbutting Rock-Road crossing	50	637997	6615191
17	Elachbutting-Cunderdin Rd	50	641376	6604572
14	Elachbutting-Masefield Rd	50	659254	6621460
14	Elachbutting-Masefield Rd	50	659254	6621460
33	Hyden, Hyden-Lake King Rd	50	675834	6408033
32	Hyden, Kalgarrin Rd	50	675551	6407250
1	Jibberding, Jibberding Hall Rd	50	484212	6673020
30	Jitarning, Jitarning Rd	50	599355	6370867
BAT1D1	Kalannie, Goodlands Rd	50	514164	6654137
NIX1D1	Kalannie, Nixons Drain	50	518893	6639864
8	Koorda, Breakell Rd	50	558486	6582640
47	Kulin, Commonwealth Rd	50	613104	6379360
13	Mukinbudin, Manuel Rd	50	616996	6583168
YR46B	Mully Gully, Goldfields Rd	50	647190	6525330
39	Narembeen, Boundary Rd	50	613696	6445518

SITE_ID	SITE_NAME	ZONE	EASTING	NORTHING
43	Narembeen, Kiely, Dixon Rd	50	661390	6464111
38	Narembeen, Lockhart River drain, Ardath Rd	50	609842	6457107
34	Narembeen, Mt Walker Road	50	663690	6453770
45	Narembeen, Mt Walker/Calzoni Rd	50	671691	6446508
37	Narembeen, Soldiers Road	50	637056	6454773
35	Narembeen, Town	50	631419	6450848
36	Narembeen, Bailey Road	50	649603	6455292
Baily drain A	Narembeen, Baily drain, Swartz Rd	50	653661	6455827
Deluis drain A	Narembeen, Deluis drain, Emu Hill Rd	50	641477	6446640
Latham drain A	Narembeen, Latham drain, Off Mt Walker Rd	50	633709	6451293
42	Narembeen, Mt Walker Rd - Wilsons X	50	643341	6450632
31	NE Jitarning, Kulin-Dudinin Road crossing	50	604147	6373457
7	Newcarlbeon, Koorda-Kulja Rd	50	538355	6606297
46	Newdegate-Eastern Rd	50	700103	6350734
57	Nyabing, Kukerin Road	50	606722	6288971
25	Rabbitproof Fence Road, Walgoolan	50	643383	6555097
12	Trayning, Gent Rd	50	578747	6556338
11	Trayning, Lee Rd	50	581756	6553016
23	Walgoolan, Begley Road North	50	647515	6549109
83	Williams, Coolaking Gully, Williams-Collie Rd	50	461100	6327200
84	Williams, Lemon Rd, Lemon experimental catchment	50	444600	6315600
82	Williams, Off Zilko Rd - House drain	50	471200	6346800
81	Williams, Off Zilko Rd - North drain	50	471300	6349500
52	Yealering, Elsegood Rd	50	569606	6395980

Drain and Receiving/Reference Environment Mineralogy Sampling Sites (Note: Further details of receiving or reference environment sites in table below).

SITE_ID	DRAIN ID	SITE_NAME	ZONE	EASTING	NORTHING
3	D3	EEI Pithara drain, Birdwood Rd	50	487565	6640994
4	D4	EEI Pithara drain, Pithara East Rd	50	490687	6638569
5	D5	EEI Pithara drain, Petrudore Rd	50	495628	6636536
9	D9	Wyalkatchem-Koorda Rd, Cowcowing	50	541880	6562524
10	D10	Edjanding, Dowerin-Kalannie Rd	50	511451	6569021
14	D14	Elachbutting-Masefield Rd	50	659254	6621460
15	D15	Elachbutting-Elachbutting Road	50	637997	6615191
21	D21	Boodarockin, Boodarockin East Rd	50	674492	6558595
23	D23	Begley Road North, Walgoolan	50	647515	6549109
25	D25	Rabbitproof Fence Road, Walgoolan	50	643383	6555097
36	D36	Narembeen drain, Bailey Road	50	649603	6455292
37	D37	Narembeen drain, Soldiers Road	50	637056	6454773
53	D53	Corrigin drains, Nambadilling Rd, West	50	586119	6421867
55	D55	Corrigin drains terminus, Nambadilling Rd, East	50	596343	6426062
61	D61	Beynon Rd Drain confluence, Doradine creek	50	575740	6323406
62	D62	Beynon Rd Drain, Doradine creek, Dumbleyung-Lake Grace Rd.	50	576685	6322120
93	D1	EEI Morowa drain, Holder Road	50	406083	6795698

39	D39	Narembeen drain, Boundary Rd	50	613696	6445518
R30YR	N/A	Bodallin Evaporation Basin, Bodallin North Road	50	678504	6532165
R14EM	N/A	Gamble Rd receiving site, Upper Cowcowing	50	537001	6566447
R16YR	N/A	Doodlakine-Kununoppin Rd, Receiving Playa East	50	583320	6545907
R23YR or D17	N/A	Cunderdin Rd, d/s Elachbutting drain	50	640244	6604850
R25YR	N/A	Koorda-Bullfinch Rd, Warrachuppin, Yilgarn R Playa	50	663509	6568356
R33LR	N/A	Lake Ardath (ski lake), Old Beverly Rd	50	609093	6448321
R40CR	N/A	Lake Gounter, Mt Walker Rd	50	672910	6413045
R8NM	N/A	Carter Rd, Jibberding, open playa	50	483567	6673818
D19	N/A	Boodarockin, M40, Koorda-Bullfinch Rd	50	668444	6567807
R26YR	N/A	Koorda-Bullfinch Rd, Warrachuppin, Off road playa	50	668093	6568050
R38CR	N/A	King Rocks Rd, Playa south of Cashmore Rd	50	700802	6418142
R17YR	N/A	Doodlakine-Kununoppin Rd, west	50	582871	6545927
R15EM	N/A	Wyalkatchem North Rd, Ski Lake, Upper Cowcowing	50	535731	6567703
R27YR	N/A	Boodarockin North Rd, west side of road	50	671035	6571302
R6NM	N/A	McKay Rd, open playa	50	475635	6631644

Receiving and Reference Environment Sampling Sites

Site_Id	Site Type	Site Name	Zone	Easting	Northing
R10YY	Receiving	Nixon Natural Evaporation Basin 2 - 8 years old	50	521570	6637276
R30YR	Receiving	Bodallin Evaporation Basin, Bodallin North Road	50	678504	6532165
R9YY	Receiving	Nixon Natural Evaporation Basin 1 - 10 years old	50	517945	6637590
R11EM	Receiving	East Boundary Rd, receiving playa, North Wallambin	50	559430	6578985
R14EM	Receiving	Gamble Rd receiving site, Upper Cowcowing	50	537001	6566447
R16YR	Receiving	Doodlakine-Kununoppin Rd, Receiving Playa East	50	583320	6545907
R23YR or D17	Receiving	Cunderdin Rd, d/s Elachbutting drain	50	640244	6604850
R25YR	Receiving	Koorda-Bullfinch Rd, Warrachuppin, Yilgarn R Playa	50	663509	6568356
R33LR	Receiving	Lake Ardath (ski lake), Old Beverly Rd	50	609093	6448321
R40CR	Receiving	Lake Gounter, Mt Walker Rd	50	672910	6413045
R8NM	Receiving	Carter Rd, Jibberding, open playa	50	483567	6673818
R50EM	Receiving	Off Chown Tank Rd, NW Koorda, Receiving Playa	50	534321	6602897
D19	Receiving	Boodarockin, M40, Koorda-Bullfinch Rd	50	668444	6567807
R12EM	Reference	Trayning Rd (East Wallambin)	50	563934	6571215
R24YR	Reference	Clamp Rd, CALM Reserve	50	623531	6593646
R26YR	Reference	Koorda-Bullfinch Rd, Warrachuppin, Off road playa	50	668093	6568050
R2NM	Reference	Dowerin-Kalannie Rd, small playa	50	509758	6565165
R36LR	Reference	Healy Rd, eastern playa	50	603795	6433833

Site_Id	Site Type	Site Name	Zone	Easting	Northing
R38CR	Reference	King Rocks Rd, Playa south of Cashmore Rd	50	700802	6418142
R39CR	Reference	Graham Rock Rd, playa north off road	50	694190	6407061
R7NM	Reference	Wilgie Hill Rd, Closed playa	50	478723	6642450
RBR1	Reference	Askews Lake, Beacon-Bencubbin Road	50	586394	6615449
RKR	Reference	Forbes Rd, Non-receiving playa	50	703847	6419739
R17YRA	Reference	Stapleton Rd Playa, Trayning	50	579151	6549037
R17YR	Reference	Doodlakine-Kununoppin Rd, west	50	582871	6545927
C1	Reference	Gnowangerup Rd, Playa upstream of Kwobrup Swamp	50	593512	6267603
C2	Reference	Wagel Rd, Kwobrup Swamp	50	588147	6271891
C3	Reference	Lake Coyrecup outflow	50	576142	6269089
C4	Reference	Lake Ewlymartup	50	568151	6271281
C5	Reference	Playa north side Coblinine R, Bibkin Bridge	50	567858	6304716
C6	Reference	Lake Dumbleyung (north bank), Lake Rd	50	562182	6313966
C7	Reference	Lake Coomelburrup, Flats Rd	50	573165	6303458
C8	Reference	Dongolocking Playa, West off Flats Rd	50	574071	6308646
C9	Reference	Beynon Rd, Doradine Creek Crossing	50	575973	6322970
LA	Reference	Lake Austin, Austin Downs	50	565321	6964471
LC17	Reference	Graham Rock Rd	50	690860	6405070
R13EM	Reference	Lackman Rd, South Wallambin	50	547333	6567654
R15EM	Reference	Wyalkatchem North Rd, Ski Lake, Upper Cowcowing	50	535731	6567703
R18YR	Reference	Purdy Rd Playa	50	588579	6541165
R19YR	Reference	Cornish Rd, downstream playa, d/s Lake Brown	50	613754	6562590
R1NM	Reference	Koombelkine North Road, Playa (west bank)	50	504957	6561079
R20YR	Reference	Lake Brown (east), Off Chandler Rd	50	624395	6556548
R21YR	Reference	Lake Campion (west) off Stockton Rd	50	628795	6554994
R27YR	Reference	Boodarockin North Rd, west side of road	50	671035	6571302
R28YR	Reference	Baladjie Rock Playa	50	679791	6574321
R29YR	Reference	Lake Julia, railway service track	50	723813	6566021
R32YR	Reference	Ski Lake Rd, Lower Baandee Lake	50	589025	6502992

Site_Id	Site Type	Site Name	Zone	Easting	Northing
R34LR	Reference	Babkin Rd, southern playa off Marshall Rd	50	607063	6439524
R35LR	Reference	Lake Kurrenkutten	50	601490	6431256
R37LR	Reference	Kondinin Lake (west), Kondinin Lake Rd	50	612800	6403707
R3NM	Reference	East Edjanding Rd, Open playa	50	515326	6569530
R4NM	Reference	Northam-Pithara Rd, Damboring South Lakes	50	475057	6619074
R5NM	Reference	Damboring West Rd, Open playa	50	471940	6624520
R6NM	Reference	McKay Rd, open playa	50	475635	6631644
R9NM	Reference	Lake Ninan, Wongan-Callingiri Rd	50	466950	6575720
RBR2	Reference	Lake McDermott Playa (main lake)	50	589542	6590522
RK2A	Reference	Badjerin Rock-SE Playa, Koorda Wongan Hills Rd	50	530842	6592752
RLB	Reference	Lake Bryde	50	669625	6308055
RLC	Reference	Lake Carmody (South), Holland Track	50	721983	6396404
RLJ	Reference	Lake Jilakin	50	628415	6384280
RLP1	Reference	Salt Lake, Lake Grace Road	50	637376	6351888
YY1	Reference	Western Shore Channel Lakes (Yenyening)	50	526718	6432405
YY2	Reference	Swan Lake (Yenyening)	50	523807	6432616
YY3	Reference	Rocky Lake (Yenyening)	50	522442	6432742
YY5	Reference	Ossigs Lake (Yenyening)	50	519699	6433141
YY6	Reference	Beverley Ski Lake (Yenyening)	50	517731	6433907

Appendix 2: Analyte suite for water samples collected during the project.

Major Elements/Compounds	
Name	**Symbol**
Aluminium	**Al**
Ammonia	**NH_4**
Bromide	**Br**
Boron	**B**
Calcium	**Ca**
Carbon (organic C - dissolved)	**C**
Chloride	**Cl**
Fluoride	**F**
Iron	**Fe**
Magnesium	**Mg**
Manganese	**Mn**
Nitrate/Nitrite	**NOx**
Nitrogen (total)	**N**
Potassium	**K**
Phosphorous (total)	**P**
Phosphate	**PO_4**
Silica	**Si**
Sodium	**Na**
Sulfate	**SO_4**
Sulfur	**S**

Trace Elements	
Name	**Symbol**
Antimony	**Sb**
Arsenic	**As**
Barium	**Ba**
Cadmium	**Cd**
Cobalt	**Co**
Copper	**Cu**
Chromium	**Cr**
Molybdenum	**Mo**
Lead	**Pb**
Nickel	**Ni**
Selenium	**Se**
Silver	**Ag**
Strontium	**Sr**
Tin	**Sn**
Titanium	**Ti**
Vanadium	**V**
Yttrium	**Y**
Zinc	**Zn**

Rare Earth/Actinide/Lanthanide Elements

Name	Symbol
Cerium	**Ce**
Dysprosium	**Dy**
Erbium	**Er**
Europium	**Eu**
Gadolinium	**Gd**
Hafnium	**Hf**
Holmium	**Ho**
Lanthanum	**La**
Lutetium	**Lu**
Neodymium	**Nd**
Praseodymium	**Pr**
Samarium	**Sm**
Terbium	**Tb**
Thorium	**Th**
Thallium	**Tl**
Thulium	**Tm**
Uranium	**U**
Ytterbium	**Yb**

Appendix 3: WA Wheatbelt PHREEQC modelling mineral suite (those minerals with an asterisk denote a subset used in pitzer.dat calculations only).

Carbonates
*Calcite
$CaCO_3 \rightarrow CO_3^{2-} + Ca^{2+}$ log_k -8.48
*Gypsum
$CaSO_4{:}2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$ log_k -4.58
*Dolomite - allow dolomite oversaturation - slow kinetics (systems often strongly oversaturated)
$Ca,Mg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{+2} + 2CO_3^{2-}$ log_k -17.09
*Magnesite
$MgCO_3 + H^+ \rightarrow HCO_3^- + Mg^{2+}$ log_k 2.29
*Hydromagnesite - calcite + hydromagnesite often best represents the Ca-Mg-CO_3 system
$Mg_5(CO_3)_4(OH)_2{:}4H_2O + 6H^+ \rightarrow + 4HCO_3^- + 5Mg^{+2} + 6H_2O$ log_k 30.85

Chloride and sulfate salts
*Halite
$NaCl \rightarrow Na^+ + Cl^-$ log_k 1.58
*Bischofite
$MgCl_2{:}6H_2O \rightarrow Mg^{+2} + 2Cl^- + 6H_2O$ log_k 4.46
*Hexahydrite
$MgSO_4{:}6H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 6H_2O$ log_k -1.64
*Pentahydrite
$MgSO_4{:}5H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 5\ H_2O$ log_k -1.29
*Thenardite
$Na2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$ log_k -0.18
*Starkeyite
$MgSO_4{:}4H_2O \rightarrow + Mg^{2+} + SO_4^{2-} + 4H_2O$ log_k -1.00
*Carnallite
$KMgCl_3{:}6H_2O \rightarrow K^+ + Mg^{2+} + 3Cl^- + 6H_2O$ log_k 4.33

Fe-minerals
Jarosite-Na
$NaFe_3(SO_4)_2(OH)_6 + 6H^+ \rightarrow Na^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O$ log_k -5.28
Jarosite-K
$KFe_3(SO_4)_2(OH)_6 + 6\ H^+ \rightarrow K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6\ H_2O$ log_k -9.21
Schwertmannite
$Fe_8O_8(SO_4)_2(OH)_4 + 6SO_4^{2-} + 20H^+ \rightarrow 8Fe^{3+} + 8SO_4^{2-} + 12H_2O$ log_k 18.5
Ferrihydrite [$Fe(OH)_3$(am)]
$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$ log_k 4.89

Al-minerals
Jurbanite
$AlSO_4OH + H^+ \rightarrow Al^{3+} + SO_4^{2-} + H_2O$ log_k -3.23
Basaluminite
$Al_4SO_4(OH)_{10}{:}5H_2O + 10H^+ \rightarrow 4Al^{3+} + SO_4^{2-} + 15H_2O$ log_k 22.70
Alunite
$KAl_3(SO_4)_2(OH)_6 + 6H^+ \rightarrow K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$ log_k -1.35
Gibbsite
$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$ log_k 8.77

Miscellaneous minerals
Fluorite
$CaF_2 \rightarrow Ca^{2+} + 2\ F^-$ log_k -10.60
SiO_2 (am)

$SiO_2 + 2H_2O \rightarrow H_4SiO_4$ log_k -2.71

Fe surface master species (data from Dzombak and Morel, 1990)

Strong binding sites - Hfo_sOH	Weak binding sites - Hfo_wOH
Hfo_sOH = Hfo_sOH	Hfo_wOH = Hfo_wOH
log_k 0.0	log_k 0.0
Hfo_sOH + H^+ = Hfo_sOH$_2^+$	Hfo_wOH + H^+ = Hfo_wOH$_2^+$
log_k 7.29 = pKa$_1$,int	log_k 7.29 = pKa$_1$,int
Hfo_sOH = Hfo_sO- + H^+	Hfo_wOH = Hfo_wO- + H^+
log_k -8.93 = -pKa$_2$,int	log_k -8.93 = -pKa$_2$,int

Appendix 4: Geochemical mixing model modules

The geochemical mixing model developed here is represented by four separate modules of PHREEQC code;

- calculation of the mineral saturation index (SI)
- estimation of trace element adsorption
- a mixing module
- an evaporation module

Saturation Index: The saturation index (SI) for a given mineral as listed in Appendix 2 can be simply defined as:

$$SI = \log IAP/K_{sp}$$

where IAP = ion activity product of the chemical species involved in the reaction, and

K_{sp} = the solubility product for the designated mineral

The saturation index gives an estimation of the degree of over (>0), under (<0) or equilibrium (=0) saturation of a particular mineral phase for the prevailing solute chemistry and physicochemical conditions. The saturation index is commonly plotted as a function of solution pH or element concentration to examine the effect of pH or concentration on mineral equilibria and hence, saturation/solubility. Hence this module of PHREEQC code allows an estimate to be made of the thermodynamic stability of a particular mineral phase. No estimate is made of reaction kinetics. An example relevant to this study is the precipitation of dolomite: waters are commonly found to be 10 to 100 times oversaturated (SI = 1 to 2) with respect to the prevailing solution chemistry, but it is not precipitated due to slow reaction kinetics.

Estimate of trace element adsorption: As outlined above, an estimate of trace element adsorption can be achieved using ferrihydrite as a model adsorptive substrate. The role of precipitated ferrihydrite in the model can be outlined as follows. During mixing of two or more waters (and if evaporation occurs) the mass of precipitated ferrihydrite is calculated by the model. Using this mass term and a range of default surface areas, strong and weak site complexation parameters and sorption constants for individual elements, the proportion of adsorbed metals can be estimated. In addition to the use of default sorption parameters, two other avenues are available to investigate the adsorption of trace elements. The first involves the use of a parameter optimisation model to internally fit sorption parameters to field data. The second avenue involves the fitting of sorption parameters to empirical results derived from laboratory-based mixing and/or evaporation experiments. It is envisaged that both methods will be investigated during the next phase of the project to optimise parameters for trace element adsorption.

Mixing: The mixing of two solutions is modelled as a simple batch mixing process. The default used is that the most acidic solution is the primary solution into which other waters are mixed. This batch mixing sequence simulates the addition of alkaline to acidic water that might occur during either remediation or a large inflow of flood-water into a receiving environment. The mixing assumes perfect mixing of acidic water with inflow water and infinite time for the reactions to occur. Notwithstanding, however, are the complexities associated with factors that may lead to incomplete mixing as described above. The alkaline water is mixed in batch mode with the acidic water in 5% increments up to 95% (0-95%). Thereafter, the more alkaline solution is added in batch mode in 1% increments up to 95% (95-99%). From 99% onwards the alkaline solution is mixed in batch mode with the acidic solution in 0.1% increments (99-99.9%). This degree of resolution at the higher proportion of alkaline water provides additional information during the greatest rate of change of pH (discussed later).

Evaporation: This module allows the simulation of evaporation scenarios within WA Wheatbelt waters. The extent of evaporation is infinitely variable, but when sufficient evaporation has occurred the use of the pitzer database may be required to yield more reliable estimates of major ion concentration and pH with the concurrent loss of information for a range of trace ions relative to the phreeqc database. Typically, the evaporation module may be invoked to simulate the evaporation of receiving basins or the ponding and evaporation within natural or artificial drainages.