The distribution and origins of acid groundwaters in the South West Agricultural Area

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The distribution and origins of acid groundwaters in the South West Agricultural Area
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Adam Lillicrap and Richard George

May 2010
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Please note earlier results published in Shand and Degens 2008 are shown Appendix I.

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Executive summary

Over a million hectares of the south-west of Western Australia are affected by dryland salinity and another 2–4 M ha have shallow or rising watertables. Deep rooted plants, a common tool recommended for salinity management, have not been as successful as forecast in the drier areas. Therefore land managers have looked to engineering solutions, such as deep open drainage, to lower groundwater levels and manage salinity. However, groundwaters in the region are highly saline and commonly acidic, and therefore disposal of drainage waters can pose an environmental risk to receiving water-bodies.

Acidification can impact on aquatic systems in a number of ways. These can be grouped into three broad categories: (i) the direct effects of acidity; (ii) metal toxicity; and (iii) sedimentation. These effects result in reduced species diversity and abundance as well as change in community composition of aquatic plants, invertebrates and waterbirds. Additionally, acidification impacts on fringing vegetation. Acidification also impacts on infrastructure as it corrodes concrete and some metals such as aluminium and iron. Acid saline groundwaters occur under many wheatbelt towns, such as Moora, Merredin, Nyabing and Lake Grace.

With the increased use of engineering options such as drainage or groundwater pumping to manage saline watertables, it is important to understand origins and extent of acid groundwaters so that adverse effects can be managed. This report details a methodology to map the extent of acidity and poses causal mechanisms to explain its distribution.

The study used statistical modelling to build relationships between groundwater and spatial datasets. Using groundwater data from available databases, each bore was assigned a vegetation type, rock type, regolith type, soil landscape and depth class, where available. Logistic regression statistical models were used to determine the significance and relative importance of each of the variables (vegetation, geology, depth and regolith) in explaining the occurrence of acidic groundwater.

Groundwater showed a distinct bi-modal distribution in pH. The main population (1573 bores) had a median pH of 6.6. The smaller population (514 bores) was distinctly acidic, with a median pH of 3.5. There was a regional trend in the occurrence of acidity, with acid groundwater least common in the steeper, higher rainfall areas of the Zone of Rejuvenated Drainage and more common in the drier, inland palaeodrainages of the Zone of Ancient Drainage. Within individual Zones, the distribution was heterogeneous.

The logistic regression models showed that all tested variables—vegetation, geology, depth and regolith - had a statistically significant ($p < 0.05$) relationship with acidic groundwater. Vegetation was the strongest predictor of acidic groundwater occurrence (explaining ~ 30 per cent variability), followed by geology (around 4 per cent).

Acidic groundwater had the highest occurrence under Eucalyptus woodlands and shrublands. Two of the most common species associated with acidic groundwaters were salmon gum (Eucalyptus salmonophloia) and sand mallee (Eucalyptus eremophila). The occurrence of acid groundwater was also strongly correlated with subsoil alkalinity. This correlation was strongest in the Zone of Ancient Drainage ($r^2 = 85$ per cent).

The relationship between acid groundwater and subsoil alkalinity in the Zone of Ancient Drainage was used to develop a predictive map of acid groundwater occurrence for use in planning regional drainage. The probability map suggested that acid groundwaters are far more wide-spread than previously thought, though mainly confined to valley floors of...
Acid Groundwater Origins

palaeodrainages. The most extensive area of acid groundwater occurred in the south-east of the agricultural area. This work provided the basis for the development of acid groundwater probability maps currently in progress.

A number of conceptual models have been proposed for the origins of acid groundwater. They involve processes in the saturated zone, where iron is mobilised and subsequently oxidises to generate acid. Based on the results of this study, an alternate conceptual model has been proposed whereby acid groundwaters are mainly result processes in the unsaturated zone. Evidence presented here suggests the distribution of acid groundwater is locally controlled by vegetation type (mainly Eucalyptus) and regionally by controls on vegetation such as climate, geology and regolith. The biogeochemical reactions in the proposed conceptual model were modelled using PHREEQC to test the plausibility of the conceptual model. The PHREEQC modelling showed that the proposed reaction pathways could potentially result in acid recharge, indicating that the proposed conceptual model is plausible.
1 Introduction

1.1 Background

The main agricultural regions of Western Australia occur in the south-west of the state (Figure 1). Annual and perennial horticulture, dairying and grazing occur in the higher rainfall regions (greater than 600 mm). In the lower rainfall areas, between 600 mm and 300 mm, dryland cropping and sheep grazing are the main forms of agricultural production. This drier region, known as the ‘wheatbelt’, stretches in an arc from Geraldton through to Esperance and usually produces over 10 million tonnes of grain per annum.

![Figure 1 The agricultural region of south-western Australia](image)

The clearing of native vegetation for agriculture in the south-west has altered the natural hydrology. The changes in hydrology include reduced evapotranspiration and increasing recharge to shallow and deep groundwaters, as well as increased surface water runoff. The increase in recharge has resulted in naturally occurring saline watertables to rise. Consequently, over a million hectares of land are affected by secondary salinity (salinity brought about by anthropogenic changes to the landscape). Currently, 4–6 per cent of the agricultural area is affected by secondary salinity (McFarlane et al. 2004), whereas originally less than 0.5 per cent of the land was affected by primary (naturally occurring) salinity.
It is estimated that 15–30 per cent of agricultural land, around 2.8 to 4.5 million hectares, could eventually be affected by shallow watertables and secondary salinity, threatening agricultural production in these valley areas (George et al. 2005). Various estimates for the cost of dryland salinity to farmers have ranged from $60 million up to $1 billion a year (Clarke et al. 2002). George et al. (2005) estimates that the annual losses avoided or additional profits to be gained from salinity management could be $667 million.

The use of deep rooted perennial plants to reduce recharge to the watertable is a common practice recommended for salinity management. However, in the wheatbelt it has been calculated that the area needed to be replanted in order to have a significant impact on watertables and salinity would have to be close to the original vegetation cover (Hatton & Nulsen 1999). In the low rainfall areas, George et al. 1999 estimated that over 80 per cent of the catchments would need to be revegetated, to recover any substantial areas impacted by salinity. This would remove large areas from agricultural production making the practice unfeasible (Clarke et al. 2002). Additionally, though revegetation is an important component in salinity management, there are currently too few economically viable plants available in the low rainfall areas for broadacre recharge control (Clarke et al. 2002).

The lack of plant based solutions, especially in the lower rainfall areas has seen the adoption of engineering solutions to lower watertables for the management of dryland salinity. Engineering solutions such as pumps and deep open drains are expensive to install and are considered uneconomic except when used to protect high value assets or where the lateral impact exceeds 100–200 m (Clarke et al. 2002). Despite these issues, engineering options are preferred to manage salinity by many farmers (Clarke et al. 2002).

There are around 11 000 km of drainage lines, deeper than one metre, for salinity management in Western Australia (ABS 2002). Drains deeper than a metre occur in almost every catchment of the Avon basin. The drainage systems are scattered without extensive regional linkages. They have generally been constructed with limited planning and design and without much quantification of the downstream effects (Ali et al. 2004).

One of the most difficult problems when using engineering options for salinity management is the disposal of drainage waters (Clarke et al. 2002). Disposal problems are further compounded when drains receive discharge from naturally occurring acid saline groundwaters. These acid saline groundwaters were first reported in by Bettenay et al. (1964). Large numbers of acid saline lakes have also been found in the region. Some of the lakes would have been naturally acidic, though some could have become secondarily acidified (acidification brought about by anthropogenic changes to the landscape) through rising watertables as the result of clearing (Degens et al. 2008).

Acid saline groundwaters contain elevated levels of metals such as aluminium, iron, nickel, lead, copper and zinc. (Mann 1983; Shand 2008). When released into the surroundings through drainage, these waters have the potential to pose significant problems to the environment and infrastructure (Degens et al. 2008). Drainage is an important tool to manage salinity therefore it is important develop a better understanding of these acid groundwaters so they can be managed.

1.2 Impacts of acidity

As acid saline waters are natural to the wheatbelt, some species have become acidiohalophiles and adapted to the acid saline conditions. The acid saline lakes are more depauperate of species than neutral to alkaline lakes at similar salinities (Pinder et al. 2004). Pinder et al. (2004) concluded that secondary acidification due to rising water tables or agricultural drainage is a further threat to salt lake diversity. Silberstein et al. (2008) found
that the discharging acid saline drainage waters into ‘streams affected by secondary salinisation may have negative impacts on the biota, especially in those systems that still retain some ecological values.’

Acidification impacts on aquatic systems in a number of interactive ways. These impacts can be grouped into three broad categories; the direct effects of acidity, metal toxicity and sedimentation (Grey 1997). However, the effects of acidification are interrelated and operate in combination. The relative importance of these different types of impacts varies within and between affected systems. This consequently results in multiple stresses, direct and indirect, on both organisms and ecosystems (Grey 1997).

The direct effects of acidity include increasing metabolic malfunction and a decline in species that require particular bicarbonate concentrations in the water for metabolic processes (Grey 1997) such as some species of macroinvertebrates found in naturally saline waters of the south-west WA agricultural areas (Lizamore et al. 2008; Pinder et al. 2005).

The impacts of metal toxicity resulting from acidification can be both direct and indirect. The direct effects include the loss of sensitive plant and animal species and the indirect effects include bioaccumulation and biomagnification of metals (Grey 1997). Acidification can also result in sedimentation, caused by the precipitation of aluminium and iron flocculants particularly as the pH of waters increases. The impacts of sedimentation on aquatic flora and fauna can include: smothering of aquatic flora and sessile fauna, destruction of substrate and the clogging of filters, gills and feeding mechanisms (Grey 1997).

The overall impact of acidification is controlled by the buffering capacity of the receiving waters and the available dilution. Poorly buffered waters, with low alkalinity (bicarbonate) concentrations are more severely affected than well-buffered systems where the major mode of impact is sedimentation (Grey 1997).

Jones et al. (2009) undertook a review of the potential impacts of drainage for salinity management on wetland biota. They identified that the potential impacts of acidification included:

(i) reduced microagal species diversity and change in community composition and potentially a significant decline in biomass depending on the pH of the waters

(ii) change in aquatic vegetation with reduction in species diversity and community composition with dominance by acid tolerant species

(iii) decline in invertebrate species diversity and abundance as well as a change in community composition of invertebrates. Ceratopogs or biting midges increase in abundance in acid waters

(iv) decrease in waterbird species diversity and change in community composition due to the secondary effects of loss of food sources such as submerged vegetation and aquatic invertebrates

(v) impacts on fringing vegetation resulting in species poor communities.

A diagram illustrating the potential impacts of acidification on water-bodies in the wheatbelt is shown in Figure 2.
Figure 2 A conceptual model of the impacts of acidification on water-bodies in the wheatbelt

Acidification can also impact on agricultural production. Where the salinity of waters is low enough to be stock quality (i.e. less than 1800 mS/m) acidity could pose problems to livestock health. Metals such as aluminium, cadmium, iron and nickel become more soluble under acidic conditions. Aluminium can react with phosphorus in the intestine to form a non-absorbable complex producing symptoms of phosphorus deficiency. Excessive cadmium can cause anaemia, still-birth, abortions and reduced growth in stock. Iron in access can
cause slight scouring and loss of condition (ANZECC/ARMCANZ 2000 section 9.3). Any water supplied to livestock for drinking should be tested for acidity and salinity. If the water is acid it should be further tested in the laboratory for suitability for stock consumption.

Some of the greatest economic costs associated with acidification results from damage to infrastructure. Regional councils in eastern Australia have spent millions of dollars to replace urban infrastructure damaged by acidification and sulfate attack. (NWPCASS 2000; DSE 2008). Acid saline groundwaters occur under many rural towns of the wheatbelt such as Moora, Merredin, Nyabing and Lake Grace (Pridham 2010a, Pridham 2010b, DAFWA unpublished data).

The impacts of acid on infrastructure include: the weakening of concrete structures and corrosion of concrete slabs, steel fence posts, foundations of buildings and underground water and sewerage pipes. Metals such as iron and aluminium become soluble under acid conditions, which results in corrosion of metal infrastructure such as pipes and fencing (NWPCASS 2000). Acid attacks and weakens the concrete then the concrete and reinforcing is more susceptible to chloride attack (Guirguis 1989) Figure 3.

![Figure 3 Damage to a road culvert caused by acid saline waters](image)

### 1.3 Acidification processes

Some of the largest areas of acid waters in the world are found across southern Australia, from Western Australia through to western Victoria (Long et al. 2009). The first study that identified acid saline groundwaters in south-west Australia was Bettenay et al. (1964) which found acid saline groundwaters around the Merredin area though the extent of these waters
was unknown. There have been a number of subsequent studies on acid saline groundwaters in the south-west of Australia (Benison & Bowen 2006; Benson et al. 2007; Bowen & Benison 2009; Gray 2001; Mann 1983; Shand & Degens 2008; McArthur et al. 1991). These studies have been localised investigations or regional hydrochemical surveys of groundwaters, salt lakes and sediments.

The origins of the acid saline groundwaters remains poorly understood particularly in the south-west of Australia. There have been a number of different mechanisms proposed for their origin. The oxidation of pyrite in the geologic formations around salt lakes, has been proposed for the origins of acidity at Lake Tyrrell and the South Australian acid saline lakes (Bird et al. 1989; Chivas et al. 1991; Hines et al. 1992; Long et al. 1992a; Long et al. 1992b; Macumber 1992). However, the studies in Western Australia have proposed other mechanisms for the origins of acidity. Bettenay et al. (1964), while acknowledging that oxidation of pyrite was the usual source of acidification, proposed the acidic waters were the result of an exchange mechanism between acid (aluminium) clays of the aquifer and the saline groundwaters. Mann (1983) measured the oxidation—reduction potential and pH of acid saline waters at Yalanbee station near Northam. Mann then measured the Eh and pH of a 1M solution of ferrous sulfate (FeSO4) as it oxidised and found strong correlation between both sets of results. This led Mann to propose that the oxidation of ferrous iron originating from the weathering of basement rocks was the source of acidity. Mann termed this process 'ferrolysis'. McArthur et al. (1991) discounted the oxidation of sulfides as the source of acidity and also proposed 'ferrolysis' was the source of acidity. However McArthur et al. (1991) proposed that the ferrous iron resulted from biogenic reduction of ferric iron minerals. More recently, Bowen and Benison (2009) proposed an alternate mechanism. They suggested that the groundwaters evolved by evaporation past the carbonate divide (consuming alkalinity) and acquired low pH through extreme bed rock weathering, sulfide oxidation and ferrolysis. As can been seen from above there is no consensus as to the origins of the acid saline waters. For more detailed discussion on the origins of acid saline groundwaters see Appendix A.

In order to manage acid saline groundwaters it is important to establish the extent of their occurrence, however it has not been possible to accurately map the spatial distribution of acid saline waters in south Western Australia. The study will use the statistical modelling of relationships between groundwater and spatial datasets to attempt to determine the extent of acid groundwaters. The statistical relationship developed will be verified through field work. The derived statistical relationships will be attempted to be explained through field work and review of literature. Additionally, existing hypotheses of acid saline origins will be compared with the results of this analysis and consequently an existing hypothesis will be either be confirmed or modified or an alternative hypothesis will be developed to explain the origins of acid saline groundwater.
2 Physical characteristics of the study area

2.1 Climate

The study area covers the agricultural regions in the south-west of WA, and has a temperate to semi arid climate with warm to hot summers and cool winters. The climate is strongly influenced by a band of high pressure known as the subtropical ridge. During the warmer months the ridge is located to the south, creating generally low rainfall conditions. As the ridge moves to the north during the cooler winter months, it allows moisture laden cold fronts from the Southern Ocean, to move into the region, delivering much of the regions annual rainfall (Bureau of Meteorology 2005). Consequently rainfall mostly occurs during the winter months, from May to October, due to passage of these cold fronts and occasionally, cloud bands from the north-west. Summer rainfall is mainly due to thunderstorms which sometimes produce heavy localised falls in short periods. The annual rainfall is the highest in the extreme south-west, with Pemberton receiving around 1200 mm per annum and the rainfall decreases heading north and east as well as inland (Figure 1 and Appendix A) (Bureau of Meteorology 2005).

The annual evaporation and mean summer temperatures increases from the extreme south-west (Pemberton 1200 mm) to north (Geraldton 2460 mm) and east (Merredin 2100 mm) (Appendix B). Evaporation is lowest during the cooler months, and rainfall during this time can exceed evaporation. However, the further north and east, the difference between rainfall and evaporation during the cooler months decreases to the zone where evaporation exceeds rainfall in all months (Bureau of Meteorology 2005). This zone generally marks the limit of the dryland cropping areas.

2.2 Physiography, hydrology, geology and regolith

The main geological units and the rock types of the study area are shown in Figure 4. The area consists of Precambrian metamorphic and igneous rocks (Yilgarn Craton, Albany Fraser Orogen and Pinjarra Orogen) and Mesozoic to Tertiary age sedimentary rocks (Perth Basin, Carnarvon Basin and Eucla Basin)\(^1\).\(^2\)

The Darling Fault forms the boundary between the Perth Basin and the Yilgarn Craton. During the Tertiary, there was movement along this fault line, with the Yilgarn Craton being uplifted (Mulcahy et al. 1972). The uplift of Yilgarn Craton led to a rejuvenation of west and south flowing rivers. The eastern limit for the rejuvenation for west flowing rivers is demarcated by the ‘Meckering Line’ (Mulcahy et al. 1972) see Figure 5. The northern boundary of the south flowing rivers is demarcated by the ‘Jarrahwood Axis’ (Cope 1975). To the east of the Meckering Line the valleys are broad and shallow, with low gradients and deep weathering. These landscapes are known as the ‘Zone of Ancient Drainage’. To the west of the Meckering Line, valleys gradually get deeper towards the coast. These landscapes are known as the ‘Zone of Rejuvenated Drainage’ (Mulcahy et al. 1972).

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\(^1\) The western portion of the Eucla Basin, between Albany and Esperance, was formally known as the Bremer Basin (Clarke et al. 2003) and will be still be referred to as the Bremer Basin in this study to avoid confusion with the eastern portion of the Eucla Basin.

\(^2\) For further details on simplified geology of the area see Appendix C.
In the Zones of Rejuvenated Drainage surface waters drain to the ocean through well connected stream networks. Groundwater flow systems generally share the same divides as the surface water and usually discharge into the valley floors. Due to rejuvenation, much of the old weathered surface has been stripped away to expose fresh rock or saprolite and valley sides carry less weathered soil materials. In the valleys more recent alluvium has been deposited (Beard 1999; Mulcahy et al. 1972). The deeper weathered profiles have been preserved on the on the uplands forming the interfluvies

The Zone of Ancient Drainage has broad valley floors (1–10 km wide) and gently undulating interfluvies with low topographic relief (100 m). The relict surfaces have been preserved on the interfluvies and sandy deposits have levelled out irregularities. These sandy deposits are known as ‘sandplain’ (Bettenay & Hingston 1964).

The broad valley floors are palaeochannels that have infilled as the climate became increasingly arid during the Tertiary. The palaeochannels commonly contain sedimentary sequences over 50 m thick (Salama et al. 1993). Valleys have very low gradients and are often internally drained, with extensive salt lake systems and thick lacustrine deposits. There are two broad palaeodrainage systems in the study area, the Swan-Avon palaeodrainage which previously drained westwards (towards Mundaring) and the Eucla Palaeodrainage which previously drained eastwards towards the Eucla Basin and the Australian Bight.
Erosion occurred on the valley sides of palaeochannels to expose fresh bedrock or saprolite and colluvial deposits have built up on the footslopes of the valleys. The colluvial sand deposits (sandplain) on hillsides can be at least 5 m thick (Bettenay & Hingston 1964). Colluvium as well as alluvium, has infilled the drainage lines of the secondary valleys (Bettenay & Hingston 1964).

Shallow, perched groundwater systems can develop within the sandplain and discharge as permanent seeps in the midslopes (George 1992a). By contrast, deeper groundwater flow systems occur in the weathered basement on the valley sides and discharge at the break of slope with the valley floor (Bettenay et al. 1964; George 1992b). The groundwater systems in the broad valleys have very low gradients, 0.04 to 0.17 m per km, so groundwater in the valley floors have very little lateral movement and discharge is by evaporation. Consequently groundwater in the valley floors has very high salinities. Due to this low lateral movement, groundwater separated by only a few hundred metres can have very different salinities, suggesting the groundwater forms cells (Mazor & George 1992).

2.3 Vegetation

The dominant vegetation types and biogeographic regions of the agricultural area are shown in Figure 6. *Eucalyptus* species are the dominant vegetation type in the southern areas of the agricultural region. Mallees, Eucalypts that have multiple stems coming from a single root
stock or lignotuber, are the main types in the drier areas further east. In the northern areas of the agricultural region Acacias are the dominant vegetation. Butt et al. (1977) defined the ‘Menzies Line’ as the demarcation boundary between the mulga (Acacia species) dominated geomorphologically ‘old’ inland plateau area with hardpan soils to the north and the younger mallee vegetated areas with calcareous soils to the south. Banksia and proteaceous heath species are often the dominant vegetation type on sandplains. For further information of biogeographic regions and vegetation types in the agricultural area see Appendix D.

Figure 6 The IBRA subregions and dominant vegetation types of the agricultural area
3 Methodology

3.1 Sources of data

Groundwater data was collected from different sources. These sources were: Department of Agriculture and Food (AgBores database), Department of Water (WIN database), CSIRO (CSIRO Exploration and Mining—Mount Holland exploration) and Department of Environment and Conservation (Buntine–Marchagee Recovery Catchment). Groundwater data that contained spatial coordinates for bores that had at least one pH reading was used in the study. Any duplicate bores were removed or where a cluster of bores occurred, a representative bore for that cluster was selected. A total of 2088 groundwater records were used in analysis except when depth was included then 1563 more complete records were used.

Spatial datasets were used to determine attributes such as bedrock type, regolith, vegetation and soil units for groundwater bores. These datasets came from the Department of Agriculture and Food – Land and Resource Assessment Group (DAFWA – LRAG) and the Geological Survey of Western Australia (GSWA). The spatial datasets used were:

(i) 1:500 000 Interpreted bedrock geology of Western Australia (GSWA)
(ii) 1:500 000 regolith map of Western Australia (GSWA)
(iii) Soil landscape zones (Version 4) (DAFWA – LRAG)
(iv) Soil landscape systems (Version 4) (DAFWA – LRAG)³
(v) Pre-European vegetation – Western Australia (DAFWA).

3.2 Data limitations

The groundwater data come from five sources and the accuracy of their spatial coordinates is usually reliable however some records could be inaccurate. If the spatial coordinates of a bore were incorrect, it could be assigned the wrong spatial unit such as geology, vegetation or soil which could introduce errors to statistical analysis performed on the data. This would be more likely to occur if the bores are located near the margins of different units or occur in units of small geographic extent.

Additionally, the methods for collecting and sampling pH are not always known. Sampling standards require bores be bailed until at least three times casing storage is removed, or in low permeability areas, until 50 per cent recovery of the original level. Similarly it is not always known whether the data is field or laboratory derived. It cannot be certain if these sampling procedures have been followed, and as a result pH measurements may not always represent the true pH of the groundwater, but rather the interaction between the groundwater and the atmosphere in the bore. However, while these issues are not considered significant, these pH measurements do indicate whether the groundwater will turn acid when it comes in contact with the atmosphere, consequently provides a reliable indicator of the potential acidity of the groundwater. Where pH measurements do not reflect the true pH of the groundwaters it could introduce bias into interpreting results, but this is considered minor.

The coverage of groundwater bores are not uniformly distributed across the study area and can be clustered in particular localities. This could introduce biases into the study, particularly in areas where there are a small number of bores or clustered in particular type of spatial unit

³ See Appendix E for an explanation of soils mapping.
such as geology, regolith or soil unit. To limit these biases, spatial units with low numbers were amalgamated into larger units where possible.

The geological and soils spatial data used were mapped at large scale, 1:250 000 to 1:500 000. Additionally, the GSWA data were taken from 1:100 000 to 1:1 000 000 geological maps, consequently the geological, regolith and soil unit boundaries could be imprecise. This could mean that bores near boundaries could be assigned to the wrong units. However, given the large number of bores used in the study the possible spatial limitations should only have a minor influence on the results.

3.3 Data processing methods

Most bores only had one pH record and where a bore had multiple records, the latest pH value for bores was used in the analysis. Basic statistical and exploratory analysis of the data was performed using the Genstat (VSN International Ltd) statistical program.

The spatial coordinates for the groundwater bores were in different coordinate systems and datums. The coordinates for the bores were converted to a common coordinate system, Universal Transverse Mercator Zone 50, and datum, Geocentric Datum of Australia 1994. Coordinates that used an earlier grid, Australian Grid Datum 1984, were converted using the DatumTran program (version 1.04) which was obtained from the NSW Department of Lands website (www.lands.nsw.gov.au).

Spatial joins in ArcGIS 9.1 and 9.2 (ESRI) were used to link the groundwater datasets to the spatial datasets. In that way each groundwater bore was attributed with geological, regolith, vegetation and soils information.

The groundwater records were assigned the value ‘acid’ or ‘non-acid’ based upon the statistical analysis performed on the pH data. For each of the spatial datasets, the percentage of acid bores was calculated (the number of ‘acid’ bores divided by the total number of bores in a particular spatial unit) for each variable. The groundwater records and the percentage of acid bores within the different Soil Zones were compiled and presented in ArcGIS to show the spatial distribution of acid groundwater within the agricultural regions.

In order to better understand the origins of acidity in groundwaters, four variables that the literature suggested could be important; bedrock type, regolith (landscape position and geomorphic processes), vegetation and depth of groundwater were compared to pH to look for relationships.

Through a spatial join between the groundwater dataset and the 1:500 000 regolith map of Western Australia dataset each bore was assigned one of the following values:

Alluvium—alluvium in drainage channels, floodplains, and deltas

(i) Beach
(ii) Calcrete
(iii) Colluvium—slope deposits; includes colluvium and sheetwash
(iv) Exposed—exposed rock, saprolite and saprock
(v) Lacustrine—lacustrine deposits; includes lakes, playas, and fringing dunes
(vi) Relict—residual or relict material; includes ferruginous, siliceous and calcareous duricrust
(vii) Sandplain—sandplain, mainly aeolian; includes some residual deposits.
Bores that had the values ‘Beach or Calcrete’ were removed from the data set due to low numbers or not being relevant to the study.

Through a spatial join between the groundwater dataset and the 1:500 000 Interpreted bedrock geology of Western Australia dataset geological data was attributed to each bore that included tectonic unit, formation name, rock type and a description. In the context of this study the most important attribute was rock type. In order to improve the statistical robustness of the dataset similar rock types with low numbers of bores were amalgamated if had similar percentages of acid bores and assigned a rock type code based on GSWA standard codes where possible. Not all sedimentary rock units were assigned a rock type, so all bores that occurred in a sedimentary rock unit were assigned the value –s (undifferentiated sedimentary rocks) with the exception of rocks within the Bremer Basin which were assigned the value –sh as it had a higher percentage of acidic bores compared to other sedimentary rock types. There were a low number of bores in many basic rock types such as ultramafics, mafics, amphibolites and gabbro. These rock types were amalgamated and assigned the value –xb (undifferentiated mafic and ultramafics). Granulite and paragneiss rock type were merged and labelled High grade metamorphic rocks. Only a few bores occurred in granodiorite or monzogranite (adamellite), so these bores were amalgamated with granite (g). The values for the rock type were:

(i) Granite (g)
(ii) Gneissic granitoid, orthogneiss (gn)
(iii) Gneiss (n)
(iv) Granitic gneiss (ng)
(v) Sedimentary (s)
(vi) Sedimentary (Bremer Basin) (sh)
(vii) Mafic and ultramafic rocks (xb)
(viii) High grade metamorphic rocks (h+np).

Few bores contained records on the depth at which the groundwater was sampled though a large number of groundwater records (1563 records, DAFWA and DoW) contained data on the depth drilled. An assumption was made that the water sample originated from the bottom of the bore, and drill depth was used as surrogate for the depth of the water sample. The bores were divided into depth classes, based on divisions in Short and McConnell (2001) p23, Deep (> 10 m), Intermediate (< 10 m and > 5 m) and Shallow (< 5 m).

Through a spatial join between the groundwater dataset and the Pre-European vegetation—Western Australia dataset, vegetation type was attributed to each bore. In order to improve statistical robustness of the dataset, similar vegetation types, based on dominant species, with low numbers of bores were amalgamated where they had similar percentages of acid bores. The values for the vegetation types were:

(i) Wandoo woodland (*Eucalyptus* sp.)
(ii) Scrub-heath (i.e. *Proteaceae*)
(iii) Acacia shrublands
(iv) Shrublands – other
(v) Banksia woodland
(vi) Eucalyptus forest and woodland – other
(vii) Jarrah-marri forest (*Eucalyptus* sp.)
(viii) Marri and wandoo woodland (*Eucalyptus* sp.)
(ix) Succulent steppe
Acid Groundwater Origins

(x) Eucalyptus mallee – other
(xi) York gum dominant woodland
(xii) Wandoo, York gum, salmon gum woodland
(xiii) Jarrah, marri, wandoo (Eucalyptus sp.) dominant
(xiv) Sand mallee and black marlock shrublands (Eucalyptus sp.)
(xv) York gum and salmon gum woodland
(xvii) Salmon gum woodland (grouped).

As the data was categorical, a simplifying assumption was made that the data was bi-modal. This permitted the use of a logistic regression model to statistically analyse the data. The pH values were divided into two groups (acid or non-acid), and a logistic regression model was used to test the hypothesis that there were no relationships between pH class, the dependent variable, and the independent variables; rock type, regolith, vegetation and depth class. For each variable, the number of acid bores and the total number of bores for each value of the variable were calculated in Microsoft Excel using pivot tables and the results were imported into Genstat to run the logistic regression models.

The model was first run assuming that the effect of each variable was additive, that is there are no interactions between the independent variables and the effects of each variable simply adds on top of each other. The model was then run allowing for full interaction between the variables.

When modelling the relationship between pH class, rock type, vegetation and regolith, the full data set was used, due to the larger number of available records (2088). When modelling the relationships between pH class, rock type, vegetation, regolith and depth, 1563 (more complete) records were used.

McArthur et al. (1991) suggested that acidity in groundwaters was caused by the oxidation of ferrous iron and this ferrous iron was the result of microbial reduction of ferric iron minerals. They further suggested that the alkalinity ensuing from these reactions was stored in the soil profile as calcareous deposits. To test this hypothesis, the interpreted soil quality data for soil landscape systems (van Gool et al. 2005) was used. For each soil landscape system, based on the results of soil tests and the proportion of different soils types in that system, Van Gool et al. (2005) estimated the percentages of each system having different soil pH ratings (see Table 2). Different soil pH ratings were assigned at different depths.

Table 1 pH ratings derived for soils based on soil tests (after van Gool et al. 2005)

<table>
<thead>
<tr>
<th>Soil test</th>
<th>Very strongly acid</th>
<th>Strongly acid</th>
<th>Moderately acid</th>
<th>Slightly acid</th>
<th>Neutral</th>
<th>Moderately alkaline</th>
<th>Strongly alkaline</th>
</tr>
</thead>
<tbody>
<tr>
<td>pHw</td>
<td>(&lt; 5.3)</td>
<td>5.3–5.6</td>
<td>5.6–6.0</td>
<td>6.0–6.5</td>
<td>6.5–8.0</td>
<td>8.0–9.0</td>
<td>&gt; 9.0</td>
</tr>
<tr>
<td>pHCa</td>
<td>(&lt; 4.2)</td>
<td>4.2–4.5</td>
<td>4.5–5.0</td>
<td>5.0–5.5</td>
<td>5.5–7.0</td>
<td>7.0–8.0</td>
<td>&gt; 8.0</td>
</tr>
</tbody>
</table>

The total percentage of alkaline soil for each soil landscape system was calculated by adding the moderately alkaline and strongly alkaline percentages together. This was done for different depths, 0–10 cm and 50–80 cm. The total percentage of alkaline soils was compared to the percentage of acid bores for each soil landscape system where data was available. Sensitivity analysis was conducted by selecting soil landscape systems based on the total number of bores in that system. Only soil landscape systems with 12 or more groundwater bores were used in the final analysis. Only the subsoil, 50–80 cm, data was used in the final analysis.
Based on statistical relationships derived in this study which had the strongest correlation with acidic groundwater, maps were developed to estimate the distribution and extent of acid groundwater. These were compared to Mann’s derived pH contours (Mann 1983).

### 3.4 Field investigations

The logistic regression statistical modelling and data analysis indicated a series of statistically significant correlations between the pH class/percentage of acid groundwater bores and independent variables. Field work was undertaken to establish the validity of these correlations and to determine if the determined statistical relationships could be identified in the field. Additionally, field work and review of scientific literature were used to identify possible causal mechanisms that explained the statistical correlations between pH class/percentage of acid groundwater bores and variables.

Field work was undertaken in the Grass Patch area north of Esperance in the south-east of the agricultural area (Figure 7). Extensive soil testing in the area (Burvill 1988) and previous monitoring in the region by the Department of Environment and Conservation provided examples of both acidic and non-acidic salt lakes. This provided the means to compare the statistical correlations.
4 Results

Groundwater pH data showed a bimodal distribution (Figure 8): one population (n = 514) with a median pH of 3.5 (mode = 3.5, mean = 3.6) and a second larger population (n = 1573) with a median pH of 6.6 (mode = 6.6, mean = 6.7). The minima between the two populations occurs around 4.8 to 5. Therefore the groundwaters could be categorised as ‘acid’, pH ≤ 4.8 or ‘non-acid’.

![Frequency Distribution of pH values for groundwater data](image)

The distributions of acid and non-acid bores were mapped in a GIS program (Figures 9 and 10). Bores with acid groundwaters were widespread across the agricultural regions (Figure 9). The occurrence of acid and non-acid bores can occur within hundreds of metres of each other (Figure 10) suggesting acid groundwater can be localised.

The percentage of acid bores for each soil zone and system were calculated. The results for soil zones were displayed in a GIS program (Figure 11) and clear regional trends became evident. The zones in the coastal areas had the lowest percentage of acid bores (< 10 per cent). In the zones of rejuvenated drainage, 10–19 per cent of the bores were acid, whereas the zones of ancient drainage had the highest proportion of acid bores (> 40 per cent). The transition areas between the zones of rejuvenated drainage and the zones of ancient drainage had around 30 per cent of bores that were acid. The highest percentage of acid bores (69 per cent) occurred in the Salmon Gums Mallee Zone in the south-east of the agricultural area. The highest concentration of acid groundwater bores were in the southern areas and acid bores decreased in the more northern zones.
Acid Groundwater Origins

Figure 9 Distribution of acid and non-acid groundwater bores in the agricultural regions

Figure 10 Distribution of acid and non-acid groundwater bores in the Beacon area
(Sources: Satellite imagery provided by the Landgate)
Acid Groundwater Origins

Within the soil landscape zones, the acid bores were not evenly distributed. The acid bores were usually concentrated in the valley floor alluvial soil landscape systems. The soil landscape systems in higher parts of the landscape like sandplains on the interfluves generally had a higher frequency of non-acid bores (Appendix F).

As the distribution of groundwater pH was bi-modal a logistic regression statistical model was used to determine the statistical significance and relative importance of each of the variables (vegetation, geology, depth and regolith) in explaining the occurrence of acidic groundwater. The full model was run that looked at relative importance of each variable individually and at the interaction between variables. Selected results are shown in Table 3 and the results of the full model as shown in Appendix G.

All four variables, vegetation, rock type, depth class and regolith had a relationship with acid groundwater. These were statistically significant (p < 0.05). Vegetation was the strongest predictor of acid groundwater occurrence (explaining about a third of the variability). The other variables were far less reliable predictors, each accounted for less than 5 per cent of the variability. After vegetation, the strongest predictors of acid groundwater were the interactions between vegetation and rock type and vegetation and regolith. They accounted for 12.3 and 11.7 per cent of the variability, respectively (Table 2). The interactions between variables to explain acid groundwater occurrence will not be discussed further as it is too difficult to differentiate between the effects of vegetation and other variables as they are often dependent on each other. Regolith type (for example alluvium versus sandplain) and geology (for example granite versus dolerite) can determine the vegetation type.
Table 2

<table>
<thead>
<tr>
<th>Variable</th>
<th>Degrees of freedom</th>
<th>Deviance</th>
<th>Mean deviance</th>
<th>Approximate chi pr</th>
<th>Per cent deviance</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ Vegetation</td>
<td>16</td>
<td>221</td>
<td>13.8</td>
<td>&lt;.001</td>
<td>31.6</td>
</tr>
<tr>
<td>+ Dominant rock type</td>
<td>7</td>
<td>30.3</td>
<td>4.32</td>
<td>&lt;.001</td>
<td>4.3</td>
</tr>
<tr>
<td>+ Depth class</td>
<td>2</td>
<td>16.9</td>
<td>8.45</td>
<td>&lt;.001</td>
<td>2.4</td>
</tr>
<tr>
<td>+ Regolith type</td>
<td>5</td>
<td>20.8</td>
<td>4.16</td>
<td>&lt;.001</td>
<td>3.0</td>
</tr>
<tr>
<td>+ Vegetation, Dominant rock type</td>
<td>41</td>
<td>86.0</td>
<td>2.10</td>
<td>&lt;.001</td>
<td>12.3</td>
</tr>
<tr>
<td>+ Vegetation, Depth class</td>
<td>30</td>
<td>49.7</td>
<td>1.66</td>
<td>0.01</td>
<td>7.1</td>
</tr>
<tr>
<td>+ Dominant rock type, Depth class</td>
<td>12</td>
<td>23.2</td>
<td>1.93</td>
<td>0.03</td>
<td>3.3</td>
</tr>
<tr>
<td>+ Vegetation, Regolith type</td>
<td>55</td>
<td>81.5</td>
<td>1.48</td>
<td>0.01</td>
<td>11.7</td>
</tr>
<tr>
<td>+ Dominant rock type, Regolith type</td>
<td>26</td>
<td>40.7</td>
<td>1.56</td>
<td>0.03</td>
<td>5.8</td>
</tr>
<tr>
<td>Residual</td>
<td>15</td>
<td>3.25</td>
<td>0.22</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>333</strong></td>
<td><strong>699</strong></td>
<td><strong>2.10</strong></td>
<td></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

The percentage of acid bores in different vegetation types is shown in Figure 12. Acid bores have the highest occurrence in certain Eucalyptus woodlands and shrublands. Two of the most common species associated with acid groundwaters were salmon gum (*Eucalyptus salmonophloia*) and sand mallee (*Eucalyptus eremophila*). Vegetation communities dominated by Acacias and proteaceous species such as Banksia had amongst the lowest incidence of acid groundwaters.

The distribution of acid groundwaters for the other variables is shown in Appendix G. Of the different rock types, acid groundwater most frequently occurred on granite and gneissic granitoid. Acid groundwaters least frequently occurred on mafic and ultramafic rocks and high grade metamorphic rocks (paragneiss and granulite). Amongst the different depth classes, acid groundwaters most frequently occurred at intermediate depth, between 5 and 10 m and least frequently occurred at depths greater than 10 m. For the different types of regolith, acid groundwater most frequently occurred in alluvial landscapes and least frequently occurred in relict duricrusts or exposed rock or saprolite.

The percentage area of subsoil alkalinity was compared to the percentage of bores that are acid in different soil landscape systems (Figure 13). There was a reasonable correlation between area of subsoil alkalinity and percentage of acid groundwater bores ($r^2 = 65$ per cent). The relationship was also statistically significant ($p < 0.05$).

The distribution of groundwater pH was compared for the zones of ancient drainage and rejuvenated drainage (Figure 14a). The zone of ancient drainage had a higher number of groundwater bores that were acidic, whereas the zone of rejuvenated drainage had a greater number of bores that were neutral to alkaline. When comparing the means of the acid groundwater populations, there is statistical difference between the Zone of Ancient Drainage (mean pH = 3.5) and the Zone of Rejuvenated Drainage (mean pH = 3.8), with groundwaters in the Zone of Ancient Drainage being more acidic.

The percentage area of subsoil alkalinity in soil landscape systems was compared for the zones of ancient drainage and rejuvenated drainage (Figure 14b). The Zone of Rejuvenated Drainage has significantly less alkalinity stored in the soil when compared to the Zone of Ancient Drainage. Most soil landscape systems in the Zone of Rejuvenated Drainage had no alkaline subsoils. Whereas over half the soil landscape systems in the Zone of Ancient Drainage had over 60 per cent alkaline subsoils.
Figure 12 The percentage of acid bores in different vegetation types
Acid Groundwater Origins

Figure 13: The percentage of subsoil alkalinity compared to the percentage of bores that are acid in different soil landscape systems.

Figure 14: a) The graph shows the distribution of groundwater pH for the zones of ancient drainage and rejuvenated drainage. b) The graph shows the distribution of percentages of subsoil alkalinity for soil landscape systems in the zones of ancient drainage and rejuvenated drainage.
The relationship established between subsoil alkalinity and acid bores in different soil landscape systems does not hold for the zone of rejuvenated drainage \((r^2 = 0.0082\ \text{per cent})\). However, there was a very strong correlation \((r^2 = 85\ \text{per cent})\) between subsoil alkalinity and the percentage of bores that are acid in different soil landscape systems for the zone of ancient drainage (Figure 15).

![Soil systems in Zone of Ancient Drainage](image)

**Figure 15** The percentage area of subsoil alkalinity compared to the percentage of bores that are acid in different soil landscape systems of the zone of ancient drainage

This relationship was the strongest correlation established in the study. Therefore the development of a distribution map for acid groundwaters was confined to the zone of ancient drainage. Using the parameters established in the relationship, the likely percentage acid bores in each soil landscape system was calculated for the zone of ancient drainage based on the percentage of subsoil alkalinity. The soil landscape systems were divided into three classes: i) low probability; ii) medium probability; and iii) high probability of acid groundwater. The cut off value for the high probability classification boundary was determined by comparing the ratio of acid to non-acidic bores in high probability classification at different cut off values. The final boundary cut-off value was decided by maximising the percentage of acid bores in the category while minimising the total number of non-acid bores. The cut off value for the low probability classification boundary was done in reverse to maximise the percentage of non-acid bores captured while minimising the total number of acid bores in that category. The moderate classification falls between the high probability and low probability cut off values. The results were mapped in a GIS program and compared with pH contours developed Mann (1983) (Figure 16).
Figure 16 The probability of acid groundwater occurrence in the Zone of Ancient Drainage. The pH contours developed by Mann (1983) are shown for comparison.

The number of acid and non-acid bores for each groundwater probability class is shown in Table 3. Around 70 per cent of the all acid bores were captured in the High probability classification (340 from a total of 488). Around 30 per cent of all the non-acid bores (201 from a total of 650) were also captured in the high probability category. The low probability class had 27 per cent of the non-acid bores (177 from 650) and 9 per cent of the acid bores (43 from 488).

Table 4 The number of acid and non-acid bores are for each groundwater probability class

<table>
<thead>
<tr>
<th>Acid groundwater probability classes</th>
<th>Number of bores that are acid</th>
<th>Number of bores that are non-acid</th>
<th>Grand total</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>340</td>
<td>201</td>
<td>541</td>
</tr>
<tr>
<td>Moderate</td>
<td>105</td>
<td>272</td>
<td>377</td>
</tr>
<tr>
<td>Low</td>
<td>43</td>
<td>177</td>
<td>220</td>
</tr>
<tr>
<td>Grand total</td>
<td>488</td>
<td>650</td>
<td>1138</td>
</tr>
</tbody>
</table>

Of the total number of bores captured in the high probability category (n = 541) around 60 per cent were acid (n = 340). Likewise in the low probability classification of the total number of bores (n = 220) 20 per cent of the bores are acid (n = 43).
5 Discussion

The groundwaters in the south-west of Western Australia showed a distinct bi-modal distribution. One population (n = 514) had a median pH of 3.5 and a second larger population (n = 1573) had a median pH of 6.6. The minima between the two populations occurred around 4.8 to 5. Therefore the groundwaters could be categorised as ‘acid’ (pH ≤ 4.8 or ‘non-acid’. Other studies (Brock 1971; Cravotta et al. 1999; Marini et al. 2003; Nordstrom et al. 2009) that examined acidic and non-acidic waters also found bi-modal distributions for pH. The mode or median values for the non-acid populations in most of the other studies (Cravotta et al. 1999; Marini et al. 2003; Nordstrom et al. 2009) were similar to this study around 6 to 7. However the mode or median pH for the ‘non-acid’ population in the Brock (1971) study on thermal springs was 7–9. The other studies, Brock (1971), Cravotta et al. (1999), Marini et al. (2003) and Nordstrom et al. (2009) had similar minima in pH values to this study between 4–4.5 to 5. The mode or median values of pH for the acid populations varied from 0.5–1.5 (Marino et al. 2003), 2.5–3 (Brock 1971), to 2.5–4 (Cravotta et al. 1999; Nordstrom et al. 1999).

The pH values in the non-acid populations were attributed to carbonate buffering (HCO₃⁻ /H₂CO₃ and HCO₃⁻/CaCO₃) (Brock 1971; Cravotta et al. 1999). The non-acid groundwaters in this study had similar distributions in pH values to the Brock and Cravotta studies so carbonate buffering is the most likely buffer of the non-acid population for this study as well. The controls on the acid populations were more complex and depended on the study, though for the most part attributed to oxidation of reduced sulfur species (Brock 1971; Cravotta et al. 1999; Marini et al. 2003; Nordstrom et al. 2009). These studies were associated with volcanic or geothermal terrains (Brock 1971; Marini et al. 2003; Nordstrom et al. 2009) or acid mine drainage (Cravotta et al. 1999). As there are multiple ideas about the origins of acidity in the south-west of WA (for example Bowen and Benison 2009, Gray and Noble 2006, Mann 1983, McArthur et al. 1991), the attribution of acidification to any reaction suite is more problematic and will be discussed in more detail later.

The first attempt to show the distribution of acid waters was by Mann (1983) who constructed pH contours based on sampling of waters at playa lake margins. The distribution of acid and non-acid bores were mapped (Figure 9) and it showed acid groundwaters are widespread across the agricultural regions of Western Australia. When comparing the distribution of acid groundwater bores to the pH contours developed by Mann, acid groundwater occurs over a far larger area than originally estimated by Mann.

Mann (1983) and Gray (2001) showed there were regional trends in the occurrence of acid groundwater. When the proportion of acid groundwater bores were calculated for each soil zone and mapped (Figure 11), a clear regional trend became evident. On the western coastal margins, the proportion of acid bores was less than 10 per cent. The proportion then increased in the Zones of Rejuvenated Drainage (10–25 per cent) to the Zones of Ancient Drainage (> 40 per cent) (Figure 11). There was also a north–south trend with acid bores becoming less frequent in the northern agricultural regions. This north–south trend is similar to the findings of Mann (1983) and Gray (2001).

Within the soil zones there was considerable variability, with acid groundwaters being mostly confined to particular soil landscapes systems, usually in lower landscape positions (Appendix F). In order to estimate the distribution of acid groundwaters more accurately, statistical analysis was conducted on various spatial parameters to determine the best
correlations with acidic groundwater. The proportion of subsoil alkalinity in soil landscape systems was found to have the best correlation with acid groundwater. However, this relationship was only found to be valid for the Zone of Ancient Drainage.

This was considered acceptable as acid groundwater most frequently occurred in the Zone of Ancient Drainage and this was the area that had the greatest pressure for agricultural drainage. A map was developed that estimated the probability of acid groundwater in the Zone of Ancient Drainage based on the percentage of subsoil alkalinity in soil landscape systems (Figure 16). The probability map was compared to the pH contour map developed by Mann (1983). The acid groundwater probability map showed that acid groundwater was far more extensive and that the distribution of acid groundwater not as simple as Mann (1983) indicated. The map showed that acid groundwaters were mainly confined to particular areas, usually the valley floors. The most extensive area of acid groundwater occurred in the south-east of the agricultural area. This area is flat with extensive salt lakes and calcareous soils, so has the characteristics of the palaeovalleys where acid groundwater occurs elsewhere.

The high probability category in the developed map captured around 70 per cent of the total number of acid groundwater bores (340 out of 488 bores, Table 3). However, when comparing the ratio of acid to non-acid bores within the high probability category, only 60 per cent of bores in the high category were acidic (340 out of 541 bores, Table 3). The predictive accuracy of the map developed in this study though useful as a starting point, is too low to be considered for official use. Further work has been undertaken based on the results of this study to enhance the predictive accuracy of acid groundwater probability maps see Holmes and Lillicrap 2010.

McArthur et al. (1991) believed that controls on acidity were local. There is evidence to support this. Though acid groundwaters most frequently occur in valley landscapes, there was considerable heterogeneity in the distribution of acid bores in the palaeovalleys (Figure 10). This implies a degree of local control to acidification processes. Therefore it appears that Gray (2001), Mann (1983) and McArthur et al. (1991) were all correct, the processes leading to acidification of groundwaters appear to be localised though within the confines of regional controls. The results of the statistical modelling and analysis give more insight into the nature of these acidification processes and controls.

A logistic regression statistical model, as the distribution of groundwater was bi-modal, was used to determine the statistical significance and relative importance of each of the variables (vegetation, geology, depth and regolith) in explaining the occurrence of acidic groundwater. The full model was run that looked at relative importance of each variable individually and at the interaction between variables. All four variables, vegetation, rock type, depth class and regolith had a relationship with acid groundwater. These were statistically significant ($p < 0.05$). Vegetation was the strongest predictor of acid groundwater occurrence (explaining about a third of the variability). The other variables were far less reliable predictors, each accounted for less than 5 per cent of the variability.

The results suggest rock type (geology) and regolith are important controls (they are statistically significant) on acidification processes but not the main ones, due their low proportion of deviance (how much variability they account for).

In this study, acid groundwaters most frequently occurred on granite and gneissic granitoid and least frequently on mafic and ultramafic rocks and high grade metamorphic rocks (paragneiss and granulite). These results are similar to other studies. Data presented in McArthur et al. (1989) showed that groundwaters which originated on granitoid rocks were
mainly acid (pH < 4.5), whereas groundwaters that originated in greenstone belts had pHs between 5.8 and 6.6. Gray (2001) found groundwaters in the Kalgoorlie area were commonly acidic (pH 3–5) except where buffered by alkaline materials such as ultramafic rocks.

McArthur et al. (1991) supposed the reason why acidity is seen in Western Australia was due to the poor buffering of the kaolinite rich weathered granitic and gneissic granitoid bedrock. They stated ‘...if other minerals were present, the acidity would be more quickly titrated and therefore less prominent...’. Mafic and ultramafic rocks have greater amounts of orthosilicate (for example olivine), inosilicate (pyroxenes and amphiboles) and phyllosilicate (micas) minerals compared with granitoid rocks. These minerals are more easily weathered (Paton 1978, p. 19–21) and therefore mafic and ultramafic rocks are better able to buffer groundwater against acidity. Consequently, a major control geology or rock type exerts on acid groundwater is the ability of the rock type to buffer against acidity. Acid groundwaters mostly occur on rock types with poor buffering capacity.

In the Zone of Ancient Drainage, McArthur et al. (1989) found weathering of basement rocks had only a minor influence on groundwater chemistry of playa lakes. Studies (i.e. Bird et al. 1989, Chivas, et al. 1991 and McArthur et al. 1989) had concluded that sulfate in Western Australian acid salt lakes are of marine origin and that sulfide weathering in basement rocks has contributed insignificant amounts of sulfur. This effectively ruled out weathering of sulfides as the main source of acidification for groundwaters (McArthur et al. 1991) in the Zone of Ancient Drainage. Although, Bowen and Benison (2009) contend that weathering of basement rocks has contributed to the acidification of groundwaters in the Zone of Ancient Drainage.

In the rejuvenated landscapes, Mann (1983) observed that much of the weathered profile has been stripped away exposing younger unweathered material. Therefore in the zones of rejuvenated drainage, the weathering of basement rocks could provide sources of acidification as Mann (1983) suggested.

McArthur et al. (1991) proposed that acid groundwaters were the result of regolith processes rather the weathering of basement geology. This study found that regolith, like geology, had a statistically significant relationship with acid groundwaters but was only able to explain a small amount of variance—3 per cent. Therefore regolith exerts some (minor) control over acid groundwater. The role of regolith can be evidenced in an area north of Esperance (Figure 21). The region has the same basement geology but different regolith types as indicated by the different soil zones (Figure 17). The presence of acid groundwater has a stronger correlation with regolith type (soil zone) than basement geology. This supports the findings of other studies (i.e. Bird et al. 1989, Chivas et al. 1991 and McArthur et al. 1989) that basement geology is only a minor influence on groundwater chemistry.

In this study, acidic groundwaters were found to most frequently occur in regolith types located in lower landscape positions such as alluvium and least frequently occur in higher landscape positions. Bettenay et al. (1964) had similar findings. They found in the higher landscape positions, the pH of the groundwater ranged from neutral to alkaline, but in lower landscape positions towards the discharge zone or ‘outlet’ at a salt lake, groundwaters were acid with pH around 3. This also supports the idea by McArthur et al. (1991) that acidification results from local processes.

The comparison of groundwater and soil data from the zones of Rejuvenated Drainage and Ancient Drainage could partially explain this relationship between regolith and acid groundwaters. They show major differences in the stores of alkalinity in these environments. The Zone of Ancient Drainage had a higher number of groundwater bores that were acidic, whereas the Zone of Rejuvenated Drainage had a greater number of bores that were neutral
to alkaline (Figure 14a). When comparing soils data, the opposite is true, the soils in the Zones of Ancient Drainage contained a far greater amount of alkalinity compared the Zone of Rejuvenated Drainage (Figure 17b). Broadly speaking, as the rejuvenated zones have steeper hydraulic gradients than the valley floors of the ancient drainage zones, it is likely that in the Zone of Rejuvenated Drainage that much of the alkalinity generated in the soil profile is flushed into the groundwater whereas in the Zone of Ancient Drainage, due to the flatter landscapes, any alkalinity generated remains in the soil profile.

Figure 17 Distribution of acid and non-acid groundwater bores in the south-east of the agricultural region compared with basement geology (top) and soil zones (bottom)
Looking at the different landscapes within the Zone of Ancient Drainage, a similar principle probably holds, in the higher steeper parts of the landscape such as the valley sides any alkalinity is flushed to groundwater whereas lower in the landscape such as the valley floors alkalinity remains in the soil profile. This is consistent with findings of Bettenay et al. 1964.

The logistic regression model showed vegetation had a statistically significant relationship with acid groundwater and was the strongest predictor of acid groundwater occurrence (explaining around a third of the variability). Gray (2001) found fresher neutral groundwaters occurred north of the Menzies Line and acid saline water occurred to south. The ‘Menzies Line’ is the demarcation boundary between the mulga (acacia species) dominated geomorphologically ‘old’ inland plateau area with hardpan soils to the north and the younger mallee vegetated (Eucalyptus species) areas with calcareous soils to the south (Butt et al. 1977 – cited in Gray 2001; Mann 1983). This study also found acid groundwaters were most strongly associated with Eucalyptus vegetation communities.

Another strong statistical relationship established in this study was between subsoil alkalinity and acid groundwaters in different soil landscape systems. Verboom and Pate (2006) found calcareous soils beneath Eucalyptus communities and ferricretes developed beneath proteaceous scrub-heath. Soil tests also showed that the subsoils beneath Eucalyptus communities were alkaline. Figure 18 illustrates their main findings. The main statistical correlations found in this study between acid groundwaters and Eucalyptus communities and acidic groundwaters and subsoil alkalinity were essentially looking at the opposite sides of the same coin.

Verboom and Pate (2006) proposed that soils processes were closely related to and caused by root zone biological processes of different vegetation types. There may also be merit to this hypothesis in the context of acid groundwater formation. Weathering of basement rocks are an unlikely source of acidification for reasons outline above. McArthur et al. (1991) believed acidification of groundwaters was through ferrolysis resulting from regolith processes. They proposed that the source of the ferrous iron was from microbial reduction of iron oxyhydr(oxides) found in the sand dunes around the salt lakes, rather than from weathering of the bedrock. Additionally, the alkalinity that resulted from the microbial reduction of iron was stored in the soil profile. However, they did not explain how the
alkalinity was separated from the groundwater and stored in the soil profile. Soil zone biogeochemical processes could provide the necessary mechanisms that are missing in the McArthur et al. (1991) conceptual model.

Field observations conducted as part of this study had found beneath certain Eucalyptus communities that iron oxyhydr(oxides) had been mobilised from the top soil (A Horizon) and accumulated in the subsoil (B horizon) to create a ‘podzol’ profile\(^5\) (Figure 19). Verboom and Pate (2006) found ‘bleached’ ‘A’ horizons beneath Eucalyptus communities indicating the loss of iron oxyhydr(oxides).

Studies (Bernhard-Reversat 1999; Ellis 1971; Hingston 1961; Paton et al. 1976) have shown that extracts from Eucalyptus litter, leaves and bark are highly effective in complexing and dissolving iron oxides. Leachates from Eucalyptus litter, leaves and bark are commonly acidic (pH around 4) and contain organic (carboxylic) acids, phenolic acids, polyphenolic compounds and tannins (Ellis 1971; Hingston 1963; Paton et al. 1976). Ellis 1971 showed that extracts from Eucalyptus litter and leaves can reduce iron as well as complex and mobilise iron under alkaline conditions.

The effectiveness of Eucalyptus leachates in the complexing and mobilising iron oxyhydr(oxides) varies considerably between Eucalyptus species (Ellis 1971; Hingston 1963). Though for a given species, Ellis (1971) found that the complexation and dissolution of iron oxyhydr(oxides) occurred more readily in lower productivity soils. As well Cairney and Ashford, (1989) showed that ectomycorrhizas, a root fungi, of some Eucalyptus species contain reductases, an enzyme that can reduce iron.

The following reaction shows complexation and mobilisation of iron oxyhydr(oxides):

\[
\text{FeOOH} + 3\text{H}^+ + 2\text{C}_2\text{O}_4^{2-} \rightarrow \text{Fe(C}_2\text{O}_4)_2^{2-} + 2\text{H}_2\text{O}
\]

\[
\text{Fe(C}_2\text{O}_4)_2^{2-} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+ + 2\text{C}_2\text{O}_4^{2-}
\]

Figure 19 A soil profile showing evidence of iron oxide depletion in the A horizon and enrichment in the B horizon. Also shown is a simplified chemical reaction showing complexation and mobilisation of iron oxyhydr(oxides).

\(^5\) A ‘podzol’ profile has a highly leached whitish-grey lower ‘A’ horizon and there is accumulation of minerals and/or organic in the ‘B’ horizon as evidenced by stronger colours (Charman & Murphy 2000; Schaetzl & Anderson 2005).
Podzolisation is known to create extremely acidic conditions. The pygmy forests, along the Mendocino coast in northern California, grow in extremely acid soils—the soil pH can be as low as 2.8. The strong acidity is the consequence of podolisation and results in trees being stunted in growth to 1.5 to 3 m (Jenny 1969; Schaetzl & Anderson 2005). Therefore podzolisation processes are a plausible mechanism to generate significant levels of acidity but are not recorded as producing large areas of extremely acid groundwaters. Consequently, there must be other factors involved in the development of acidic groundwaters.

The most cited cause of acid groundwater is the oxidation of ferrous iron (Mann 1983; McArthur et al. 1991; Gray 2001). A possible mechanism that could generate quantities of ferrous iron is the microbial reduction of iron oxyhydr(oxides) that have accumulated in the ‘B’ horizon through podzolisation. However, most of the processes that produce ferrous iron such as microbial reduction of iron oxyhydr(oxides) and weathering of iron rich minerals in basement rocks (Zone of Rejuvenated Drainage) also produce alkalinity. For ferrous iron to generate acidity, the alkalinity produced needs to be removed or separated. In the Zone of Rejuvenated Drainage, the alkalinity could be removed by organic acids in leachates from vegetation such as Eucalypts.

However, in the Zone of Ancient Drainage, the subsoil alkalinity is strongly correlated to the acid groundwater. This suggests that alkalinity and acidity are being separated by some process. The processes leading to the development of calcareous soils could provide a possible explanation.

Calcareous soils and soil calcrites occur in semi-arid regions all around the world (for example south-west United States, Kalahari (Africa), Israel and southern Australia). These calcareous soils can be biogenic in origin caused by soil flora (bacteria and fungi) found in the root zone (Cailleau et al. 2005; Gadd 2007; Schaetzl & Anderson 2005; Verrecchia et al. 2006). Studies have produced biogenic carbonates using fungi under laboratory conditions (Ahmad et al. 2004; Rautaray et al. 2003; Rautaray et al. 2004). There is evidence to suggest that calcrites and calcareous soils in the south-west of WA are biogenic in origin. Carbonate crystals in calcrites showed two distinct micromorphologies: i) needle and microrods; and ii) euhedral rhombohedral. The needle and microrod crystals were the most common and are associated with fungi and bacteria (Anand & Paine 2002).

According to Cailleau et al. (2005), for calcite to form directly by biota it requires three conditions: i) presence of large amounts of oxalate (C$_2$O$_4^{2-}$); ii) the existence of an oxalotrophic flora for oxalate oxidation; and iii) a dry season. Verrecchia et al. (2006) showed biogeochemical reactions for the formation of biogenic calcrite through the oxalate-carbonate pathway. A modified version of their biogeochemical pathways is shown in Figure 20. The main steps in the pathways are firstly plants through photosynthesis covert carbon dioxide to organic carbon which is then converted to oxalic acid by plants and soil fungi. Calcium in the soil is exchanged for hydrogen ions (acidity) to maintain charge balance (Brady & Weil 2008; Gadd 2007) and oxalic acid is converted to calcium oxalate. Calcium oxalate is oxidised by soil bacteria to produce carbon dioxide and calcium carbonate.

The summary chemical reactions are:

\[
\begin{align*}
\text{Ca}^{2+} + \text{H}_2\text{C}_2\text{O}_4 & \rightarrow \text{CaC}_2\text{O}_4 + 2\text{H}^+ \quad (i) \\
2\text{CaC}_2\text{O}_4 + \text{O}_2 & \rightarrow 2\text{CaCO}_3 + 2\text{CO}_2 \quad (ii)
\end{align*}
\]

\[6\quad\text{Anand and Paine (2002) differentiate two different processes producing calcrites: i) pedogenic; and ii) groundwater. This study is only referring to pedogenic processes.}\]
The chemical reactions (i) and (ii) provide the mechanism to separate alkalinity from acidity if they occur in different parts of the soil profile. Burvill (1988) provides evidence to support that the chemical reactions are taking place in different parts of the soil profile. Burvill (1988) in soil surveys of the Salmon Gums region north of Esperance found many soil profiles at depth were depleted of calcium relative to other common cations such as sodium, magnesium and potassium. Burvill (1988) also showed that soils though alkaline in the upper profile could be highly acidic at depth. Northcote et al. (1967) made similar observations for other areas in the south-west of WA. The results of soil pH tests from selected soil profiles (Burvill 1988) are shown in Figure 21.

Figure 20 Biochemical pathways for the conversion of carbon dioxide to biogenic calcrete (After Verrecchia et al. 2006)

Any alkalinity that resulted from microbial reduction of ironoxyhydr(oxides) in the B horizon, could be consumed through acidity resulting from biogenic calcrete formation. Therefore it is possible to develop a mechanism through combining the processes of podzolisation and biogenic calcrete formation that could lead to the development of acidic groundwaters.

Field investigations were conducted around known alkaline and acidic salt lakes to verify statistical correlations found in this study as well identify possible processes to explain these correlations. These field observations found that many acid saline lakes had certain features in common (Figure 22). These features are outlined below:

(i) A calcareous layer and iron oxy(hydroxide) enrichment in the B horizon—around the root zones of eucalypts there were calcareous soils and calcrete nodules and below the root zone there was evidence of enrichment of iron oxyhydr(oxides)—these suggest active podzolisation and biogenic calcrete formation.

(ii) Zone of weathered saprolite, appearing to be mainly kaolinites beneath the calcareous/iron enriched layers.

(iii) Silcretes and ferricretes in the groundwater discharge areas—the silcrete-ferricrete layers in the discharge zones were not always apparent especially when groundwaters discharged directly into lake waters.
A conceptual model has been created to explain the origins of acid groundwater and common features around acid saline lakes (Figure 27). The proposed model couples the soil processes podzolisation and biogenic calcrete formation along with aspects of the conceptual model developed by McArthur et al. 1991.

Figure 21 The results of soil pH tests from selected soil profiles at depth (after Burvill 1988)

Figure 22 Observed common features around many acid saline salt lakes or playas
A closer look at the soil profile around the lower A – upper B horizons shows an abundance of iron in the profile (Figure 23 – upper). Water follows preferential flow paths through soil following the sinker or tap roots (Nulsen et al. 1986). This was observed in the field and creates saturated conditions directly around the sinker roots and the B horizon. Soil flora would quickly deplete the soil water of oxygen and this creates an oxygen free environment. The anoxic conditions with organic matter provided by the roots and abundance of iron oxyhydr(oxides) presents provide ideal conditions for microbial reduction of iron – Figure 23.

For abundant calcretes to form there needs to be a calcium source. There are large stores of salts in the soil profile which can provide a source of cations (George et al. 2008). Additionally, there is gypsum or calcium carbonates present in all the surrounding salt lakes that can be blown in as aerosols. Hingston and Gailitis (1976) found excess calcium, sulfate and bicarbonate in salts precipitated over the south-east agricultural area. It is proposed that the gypsum dissolves along with ions from meteoric sources and move through the soil profile. Gypsum dissolution is suggested as Gray and Noble (2006) have shown that groundwaters can be enriched in sulfate. Hydrogen ions (acid) are exchanged by root biota for the calcium to maintain charge balance. The calcium is used by root biota to form calcium oxalate. The calcium oxalate is then converted into calcium carbonate by the root flora.

The bicarbonate resulting from iron reduction is removed by the acid generated from the exchange of calcium. The soil water solution moving through the profile is enriched in sulfate, ferrous iron and possibly hydrogen ions. As the recharging waters move down the profile, oxidising conditions are again encountered and the ferrous iron oxidises to generate acid (Figure 22 centre). Under these acidic conditions, ferrous iron is stable in oxic environments and ferric iron becomes soluble. The acid generated partially weathers the profile—kaolinite and remaining feldspars weather to produce silica and aluminium in solution. This results in an acid iron-silica enriched recharge solution that mixes with deeper saline, anoxic, iron-rich waters. The iron-silica rich saline acidic waters (Figure 22 bottom) discharge in narrow zones around the salt lakes. In some instances, the dissolved iron precipitates out as various iron oxyhydr(oxides) to form ferricretes and the silica precipitates out to form silcretes.

To test the plausibility of the conceptual model, the key reactions were modelled using PHREEQC (Parkhurst and Appelo 2010) under various scenarios (see Appendix H for further details). If meteoric waters could move quickly through the soil profile, without gaining much alkalinity, the exchange of 20 mg/L (0.5 mmol/L) of calcium would create a soil water pH around 3.8 when ferrous iron was oxidised in contact with oxygen. This is similar to the median pH of acid groundwaters, see Figure 8. Lower pH values than 3.8 could be obtained if more calcium was exchanged by soil biota, but this was not explored in detail due to limitations of the modelling. In the second scenario, if the recharging waters were allowed to equilibrate with the calcium carbonate in the upper soil profile first then move to lower profile, due to the extra alkalinity, 100 mg/L (2.5 mmol/L) of calcium would be have to be exchanged by root flora to obtain a soil water pH around 3.8 when the ferrous iron oxidised. If more than 100 mg/L of calcium are exchanged, then lower pH values with oxidation of ferrous iron are also possible though this was not explored.

Therefore, as recharging waters from rain following preferential flow paths around sinker roots bypassing the calcrite layers, the conceptual model presented, based on the results of PHREEQC modelling, could provide a plausible mechanism to generate acid groundwaters.
Figure 23 A conceptual model of biogeochemical and geochemical processes occurring the unsaturated zone to explain the development of acid groundwaters.
To summarise the conceptual model, in the unsaturated zone, the combination of biogenic calcite formation and iron mobilisation results in an oxygenated acid iron rich recharge solution. The recharging solution infiltrates around the salt lakes and then mixes with deeper saline, anoxic, iron-rich waters while moving towards discharge areas around the salt lakes. As the recharging waters are less dense than the deeper saline waters, there is limited mixing and the saline aquifer is forced to surface at the playa margins, forming narrow discharge zones. These discharge zones are ephemeral, active only after rain (Figure 24).

The conceptual model illustrated in Figures 23 and 24 is similar in some aspects to the conceptual put forward by McArthur et al. (1991). The major differences are: i) where they propose microbial reduction of iron occurs in the regional groundwater we propose that it occurs in the vadose zone; and ii) they propose the recharging solution is less saline and oxygenated we propose the recharge solution is acidic as well as less saline and oxygenated. The conceptual model presented in this study matches up with the findings of Johannesson et al. (1994). They identified two types of brines that correspond to different locations along a transect originating near the shoreline and continuing out into the playa. The brine types identified were a shallow acid groundwater closest to the playa margin and a more neutral entrained brine located furthest out along the transect in the playa.

The limitations of the conceptual model presented in McArthur et al. (1991) are i) they proposed that the source of the ferrous iron was from microbial reduction of iron oxyhydroxides found in the sand dunes around the salt lakes yet they had not explained how the deeper groundwater could come in contact with these iron oxyhydroxides and ii) they proposed that the alkalinity that resulted from the microbial reduction of iron was stored in the soil profile, however, they did not explain how the alkalinity was separated from the groundwater and stored in the soil profile. The conceptual model put forward in this study can account for these.
McArthur et al. (1991) believed their conceptual model was not just confined to playa margins but had wider applicability. The conceptual model presented in this study can explain most occurrences of acid groundwater in the Zone of Ancient Drainage. The proposed conceptual model can also explain the distribution of acid groundwater as well as the regional and local controls. As the distribution of Eucalyptus communities is controlled by factors such as climate, geology and landscape position, this explains the regional variations in acid groundwater. Local factors such as soil type influence vegetation communities so this can explain the local variation. However it is acknowledged there are other processes in operation that also lead to acidification of groundwaters and the developed conceptual model cannot explain all circumstances.

George and Frantom (1990) found in the Wallatin Creek catchment acid saline groundwater discharging as hillside seeps in higher landscape positions. Mann (1983) found acid saline seepages at Yalanbee, near Northam. The conceptual model proposed above is probably not applicable in these circumstances. Ferrous iron is the likely source of acidification but may have originated through microbial reduction of iron (George & Frantom 1990) or weathering (Mann 1983 – Yalanbee is in the Zone of Rejuvenated Drainage) and the subsequent alkalinity may have been removed by organic acids or similar means.

Shand (2008) compared the pH distribution for surface water and groundwater samples taken across the wheatbelt as part of the ‘Avon Catchment acidic groundwater – geochemical risk assessment’—some of the data is reproduced in Figure 29. Surface waters, when compared to groundwaters, showed a bi-modal distribution but the acid population had a lower median pH and the non-acid population had a higher median pH (Figure 25).

![Figure 25 Distribution of pH for groundwaters and surface waters collected during the 'Avon Catchment acidic groundwater – geochemical risk assessment' project (after Shand 2008)](image)

Agricultural drains are often observed to have lower pH than surrounding groundwaters (Degens et al. 2008). Bowen and Benison (2009) found extremely acidic salt lakes (pH < 2) and they noted evapoconcentration plays an important role in controlling the chemistry of surface waters. Evapoconcentration could potentially explain the differences in pH distribution between surface waters and groundwaters. This has been demonstrated by Douglas and Degens (2008) through PHREEQC geochemical modelling.
Additionally, Fitzpatrick et al. (2008) and Degens et al. (2008) have observed sulfides present in agricultural drains and many salt lakes including alkaline ones. Seawater has a chloride-sulfate ratio of 7.1 and ratios higher than the seawater value indicate sulfate depletion and ratios lower than the seawater value indicate sulfate addition. Hydrochemical data from the Fitzgerald River catchment—central south coast of WA—shows chloride-sulfate ratios within the catchment ranging between 4.5 and 9.5 (Lillicrap unpublished data). Additionally there are black sulfidic materials observed in the hyporheic zone of the Fitzgerald River and tributaries and these when exposed over summer oxidise giving a characteristic rust coloured stains to the sediments. These results indicate that sulfur is being cycled within the catchment through oxidation-reduction (redox) reactions.

When sulfate is reduced to sulfide it produces alkalinity and should these sulfides be oxidised when water levels drop over the drier summer months, acid is produced. The waters in the Fitzgerald catchment are neutral to alkaline (Janicke et al. 2009) so there is sufficient buffering in the system to neutralise any acid generated through the oxidation of sulfides. As saline waters in the agricultural regions are usually dominated by the cation sodium, alkalinity generated through sulfide reduction is likely to be coupled to sodium (i.e. sodium bicarbonate/sodium carbonate) which would result in higher pH values than compared with calcium. Alkalinity would also be increased through evaporative concentration. This is shown conceptually in Figure 30a). This conceptual model has applicability in other areas of the agricultural region where sulfur is being cycled through redox reactions.

In receiving waterbodies where there is discharge from acid saline groundwaters (Figure 25b) the final acidity or alkalinity of receiving body will depend on the amount of alkalinity generated or stored in the hyporheic zone or sediments relative to the acid being received through baseflow or sulfide oxidation.

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**Figure 26 a)** Cycling of sulfur in saline waters of the agricultural regions; **b)** cycling of sulfur in environments with acid groundwater baseflow

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7 The hyporheic zone is the saturated sediments lying below and alongside the stream channels and in many rivers links the surface waters to groundwaters (Brooks et al. 2006).

8 Other processes can also be responsible for cycling of sulfate such as gypsum, alunite and jarosite though these have not been observed in the catchment while sulfides have been.

9 Sodium carbonate (Na₂CO₃) and sodium bicarbonate (Na₂HCO₃) have lower Kᵢ values (around 4) than calcium carbonate (CaCO₃) which has a Kᵢ around 5 therefore will have higher pH values.
In larger salt lakes such as Lake Gilmore, significant quantities of alkalinity are produced that buffer against acid groundwater discharge inputs. In some lakes such as Big Ridley (Figure 10) the lake can be net alkaline or acid depending on the relative inputs of acidity or alkalinity. However, in smaller water bodies such as agricultural drains or smaller salt lakes, the acidity produced through acid saline groundwater discharge and sulfide oxidation, can often be sufficient to overwhelm any alkalinity generated through sulfate and other reduction reactions. These smaller water bodies can become extremely acid through the combination of acid saline groundwater baseflow, sulfide oxidation and evapoconcentration (Shand & Degens 2008).

Benison et al. (2007) observed a rough relationship between the size of the salt lake and the pH of surface waters in the salt lake. The smaller salt lakes were acidic while the larger salt lakes tended towards neutral to alkaline. However, there were exceptions to this general trend. The conceptual model presented in Figure 30 can explain this trend. Benison et al. (2007) also observed that some salt lakes can be neutral to alkaline while groundwater around the lake is acidic. Bowen and Benison (2009) suggested possible reasons for neutral or alkaline lakes were: i) higher ratio of meteoric water to acid groundwater; ii) perched aquifer lakes; and iii) localised buffering by subsurface limestones.

Sulfur isotope ratios have been studied in many Western Australian salt lakes (Bird et al. 1989; Bowen & Benison 2009; Chivas et al. 1991; McArthur et al. 1989). On the basis of sulfur isotope analysis, Bird et al. 1989, Chivas et al. 1991 and McArthur et al. 1989 concluded that sulfate in Western Australian salt lakes was of marine origin. However, they found there was some depletion of $^{34}$S compared to seawater. The redox cycling of sulfur could potentially explain this depletion of $^{34}$S. The lighter sulfur isotope, $^{32}$S is preferentially used in biogenic sulfide production, leading to an enrichment in $^{34}$S. However, when the biogenic sulfide is oxidised, $^{32}$S is preferentially oxidised leading to enrichment of $^{32}$S relative to $^{34}$S. Overall, this process leads to an enrichment of $^{32}$S relative to $^{34}$S (i.e. depletion of $^{34}$S relative to $^{32}$S). This process is known as kinetic fractionation (Bird et al. 1989).

Studies (Gray 2001; Lee & Gilkes 2005) have showed that acidity of groundwaters was related to depth, with groundwaters being acid at the surface and tending to more neutral at greater depth. This study found groundwater depth had a statistically significant relationship with acid groundwaters though it only accounted for a small proportion of the variability (around 2 per cent). Acid groundwaters were found in this study to most commonly occur at depths between 5 and 10 metres. Acid groundwaters at shallower depths were probability being buffered by alkalinity in the sub-soil. Groundwaters at depth can be more saline than shallower groundwaters (Gray 2001). So groundwaters at depth could be reflux brines that have been neutralised through processes in the salt lake sediments and sink due to increases in density as a result of evapo concentration (Johannesson et al. 1994). Additionally, groundwaters at depth are better buffered by less weathered basement rocks (Gray 2001).

Even though acid groundwaters are most common in the broad valley floor landscapes, their distribution can be highly localised (Figure 10). The broad valley floors of palaeodrainages have very low hydraulic gradients (0.04 to 0.17 m per km; Beard 1999). The low hydraulic gradient provides for very little lateral flow of groundwater systems in the valleys, which prevents mixing of waters. As a result the groundwater systems in palaeodrainages, Mazor and George (1992) hypothesised, could have become compartmentalised into ‘cells’ which are driven by localised processes.

In other words, the groundwaters in palaeodrainages may not represent continuous groundwater systems, but consist of a series of groundwaters systems or cells with little flow between the cells. Some mixing may occur between the cells by diffusion. Each cell is driven
by local recharge and discharge and its effective length may be of order of 3–10 km. Within the cell, if the recharge areas are under the Eucalyptus communities the shallow groundwaters discharging to the local playa are likely to be acid. Conversely, if the recharge areas of another cell are under a scrub-heath community the groundwaters discharging to the playa are likely to be neutral. A conceptual model (Figure 27) has been developed to possibly explain this.

![Figure 27 A conceptual model to explain the variability in acid groundwater occurrence in the broad palaeovalleys](image)

Acid groundwaters are naturally occurring phenomena (Mann 1983; Turner et al. 1991) though have the potential to impact on biota and infrastructure. Bowen and Benison (2009) have suggested clearing of native vegetation for agriculture has resulted in a rise in water-tables bringing acid saline waters from the deeper subsurface to surface environments. Degens et al. (2008) suggested that rising water tables has resulted in previously alkaline lakes becoming acidic.

Agricultural drainage for salinity management could also result in secondary acidification of water bodies if not carefully managed leading to land degradation and environmental harm (Degens et al. 2008). Consequently, acid groundwaters need to be considered as part of any assessment of drainage, before approvals are given.

Depending on the physical characteristics and biology of a receiving area, acidity and excess metals may present problems for safe disposal of these waters. In the zones of ancient drainage, acid groundwaters may be able to be deposited in ‘terminal sacrificial’ playas that have low biodiversity or environmental values or specifically engineered disposal basins. Alternatively, acid waters can be treated by the addition of neutralising agents or passively by bioremediation techniques10.

In the zones of rejuvenated drainage disposal of acid groundwaters would most likely be to externally drained water courses rather than terminal salt lakes. Consequently, there would need to be full risk assessments conducted before acid groundwaters could be safely disposed of to the local stream. There would also be limited opportunities to use disposal basins. However other engineering options such as passive treatment systems could be utilised to treat the water before it is discharged into final receiving environment. The environmental impacts of the disposal of acid groundwaters is not well known or understood—therefore more work is required on how to safely dispose of and manage acid groundwaters.

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Appendix A Naturally occurring acidic waters and acidification processes

There is extensive literature on the impacts and causes of acidification resulting from anthropogenic practices. The best known examples are: acid rain (caused by the burning of fossil fuels releasing nitrogenous and sulfurous gases), acid sulfate soils (caused by the disturbance and exposure to air of sediments and soils containing sulfidic materials) and acid mine drainage or acid rock drainage (caused by exposure of mining wastes and ore bodies containing sulfidic minerals to oxidising conditions). In more recent years, low pH environments unaffected by human activities have become increasingly recognised (Long et al. 2009), and will be the focus of this review.

Some of the largest areas of acid waters in the world are found across southern Australia, from Western Australia through to western Victoria (Long et al. 2009). Acid saline groundwaters in south-west were first identified by Bettenay et al. (1964) although the extent was unknown.

Bettenay et al. (1964), in a study of the hydrologic cycle and salinity in the Belka Valley near Merredin, identified two groundwater systems; a shallow, perched system and a deeper confined, continuous, system. Bettenay et al. (1964) noted that the pH of the shallow, perched systems which discharged as surface seeps varied from acid to neutral, but those associated with lateritic pallid zones ranged from 3.3 to 4.5. In a later review of sandplain aquifers across the wheatbelt, George (1992a) agreed that sandplain seeps tended to be neutral to slightly acid but that acid seeps were not as common as Bettenay et al. (1964) first identified.

Bettenay et al. (1964) found that the pH of the deeper groundwater systems varied. In the higher landscape positions, the pH of the groundwater ranged from neutral to alkaline, but in lower landscape positions towards the discharge zone or ‘outlet’ at a salt lake, the pH decreased to about 3. Bettenay et al. (1964), though acknowledging acidification usually resulted from the oxidation of pyrite, attributed the acidity in the deeper groundwater system to an exchange mechanism between acid (aluminium) clays in the aquifer and highly saline groundwaters.

\[
\begin{align*}
\text{Al}-\text{X}^+ + 3\text{Na}^{+} + 6\text{H}_2\text{O} & \rightarrow \text{Na}_3\text{X} + \text{Al(}\text{H}_2\text{O)}_6^{3+} \\
\text{Al(}\text{H}_2\text{O)}_6^{3+} & \leftrightarrow \text{Al(}\text{H}_2\text{O)}_6^{(OH)}^{2+} + \text{H}^+ 
\end{align*}
\] (A-i) (A-ii)

This mechanism however is unlikely to result in acidification as aluminium is not readily exchangeable under neutral conditions as it forms hydroxyl complexes which are strongly absorbed onto clay surfaces (Brady and Weil 2008).

The first study of acid saline groundwaters was by Mann (1983) as part of a broader study of the differences in hydrogeochemistry of groundwaters entering salt lakes across the Yilgarn Block (or Craton as it is known today). He found the groundwaters that entered the salt lakes in the more arid north-eastern portion of the Yilgarn Craton were neutral or alkaline, whereas in the south-west, the groundwaters that entered the salt lakes were acidic. As well, the zone of low pH was confined to the part of the Yilgarn Craton, where there was: a) good winter rainfall; b) a period of several months when the soil profile was saturated; and c) groundwater systems were well developed at a zone in the weathering profile close to bedrock. Mann (1983) believed this zonation was due to differences in soil moisture and its consequent influence on hydrogeochemical processes. The first map of acid groundwater distribution was

* X represents binding sites on the surface of clay minerals.
attempted by Mann (1983), who created pH contours for the Yilgarn Craton based on data collected from 48 salt lakes (Figure A1).

![Figure A1 Map showing pH contours developed by Mann (1983)](image)

Though acid saline waters mostly occurred in the areas cleared for agriculture, acidity was not totally related to clearing as acid saline waters occurred in uncleared areas (Mann 1983).

Mann (1983) measured in-situ pH and Eh (reduction-oxidation potential) values of an acid saline seep at different depths, at Yalanbee field station near Northam. He also measured the changes in Eh and pH of a 1M solution of FeSO₄ oxidised by air. The laboratory Eh/pH trends correlated strongly with the field measurements. This led Mann to propose that the acidification of groundwater was the result of *ferrolysis*¹¹, the oxidation of reduced iron, then hydrolysis, in the groundwater. The simplified reaction for ‘ferrolysis’ (Mann 1983) is:

$$4\text{Fe}^{2+} + 6\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{FeOOH} + 8\text{H}^+$$  \hspace{1cm} (A-iii)

¹¹ The term ‘ferrolysis’ was coined by Brinkman (1970) to describe a ‘hydromorphic soil forming process’ involving the seasonally alternating cycles of oxidation and reduction of iron due to waterlogging and drying of the soil profile.
Mann (1983) proposed a conceptual model to explain the origins of groundwater acidity (Figure A2). In the conceptual model, reduced iron (Fe\(^{2+}\)) was released to the groundwater from weathering of bedrock at the base of the regolith. The Fe\(^{2+}\) had a higher rate of diffusion than alkalinity that also results from the weathering reactions. Along the flowpath, through lateral groundwater flow and diffusion, Fe\(^{2+}\) separates from alkalinity and reaches the surface where it oxidises and produces acidity (Figure A2).

The purpose of McArthur et al. (1991) was to develop a model to explain the generation of acidity in Western Australian groundwaters that did involve sulfide oxidation. The study looked at four different potential sources that could produce acidity:

(i) oxidation of diagenetic (changes to sediment after deposition) hydrogen sulfide  
(ii) oxidation of diagenetic pyrite  
(iii) oxidation of sulfide mineralisation in the basement:  
(iv) ferrolysis.

McArthur et al. (1991) found no evidence of hydrogen sulfide generation so it was discounted as possible source of acidification. The oxidation of diagenetic pyrite was also discounted as a potential source of acidification due to the perceived lack of a mechanism that allowed oxygen to salt lake sediments. The reasoning was groundwaters in salt lakes and palaeochannels are hypersaline, so fresh oxygenated waters, being less dense will perch on the more dense brines, not allowing oxygen to reach the sediments. Oxidation of sulfide mineralisation in the basement was also rejected by McArthur et al. (1991) as a potential source of acidification due to: i) the bedrock being deeply weathered and the sulfides being preferentially removed; and ii) the findings of McArthur et al. (1989). The study by McArthur et al. (1989) looked at salt sources for Western Australian brines concluded that sulfide weathering, based on isotopic data, was not a significant source of S. Therefore McArthur et al. (1991) concluded that sulfide weathering in basement rocks is not a significant contributor to acidification of groundwater.

Ferrolysis was concluded to be the most likely explanation for the generation of acid groundwaters (McArthur et al. 1991). Though they accepted some tenets of Mann (1983), they proposed an alternate model to explain the origin of acidic groundwater. They proposed that oxygen rich meteoric (atmospheric origin) recharging waters infiltrate sand dunes around the salt lakes and then mix with deeper saline, anoxic, iron-rich waters while moving towards discharge areas around the salt lakes (Figure A3). As the recharging waters are less dense than the deeper saline waters, there is limited mixing and saline aquifer is forced to surface.
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at the playa margins, forming narrow discharge zones. These discharge zones are ephemeral, active only after rain.

McArthur et al. (1991) believed acidification of groundwaters resulted from regolith processes. They proposed that the source of the ferrous iron was from microbial reduction of iron oxyhydr(oxides) found in the sand dunes around the salt lakes, rather than from weathering of the bedrock. Additionally, the alkalinity that resulted from the microbial reduction of iron was stored in the soil profile. However, they did not explain how the alkalinity was separated from the groundwater and stored in the soil profile.

McArthur et al. (1991) tested their hypothesis through the use of a geochemical models (PHREEQE and PHRQPITZ). The results of the modelling found through hydrolysis of iron, the pH could get as low as 3.0. However, in the field, the minimum pH they found was 2.8. They explained the difference between modelled and measured values due to inaccurate initial boundary conditions being set for the model or that the model itself had limitations due to the high salinities of the waters being modelled.

McArthur et al. (1991) disagreed with Mann (1983) that there were regional controls on groundwater acidity; instead suggesting local controls on groundwater acidity. They further supposed that the oxidation and hydrolysis of iron was common and the reason why acidity is seen in Western Australia is due to the poor buffering of the kaolinite rich weathered bedrock. They stated ‘...if other minerals were present, the acidity would be more quickly titrated and therefore less prominent...’. Data presented in McArthur et al. (1989) support this hypothesis. Groundwaters that originated on granitoid rocks were mainly acid (pH < 4.5), whereas groundwaters that originated in greenstone belts had pH values between 5.8 and 6.6. The greenstone belts contain basic and ultrabasic rocks. Mafic and ultramafic rocks have greater amounts of orthosilicate (for example olivine), inosilicate (pyroxenes and amphiboles) and phyllosilicate (micas) minerals compared with granitoid rocks. These minerals are more easily weathered (Paton 1978, pp. 19–21) and therefore mafic and ultramafic rocks are better able to buffer groundwater against acidity.
A study by Edmunds and Kinniburgh (1986), in the United Kingdom found that areas with granite and acid igneous rocks were more susceptible to acid deposition than areas with basic or ultrabasic rocks (for example basalts, komatiites) due to the minerals in acid igneous rocks being more resistant to weathering.

A study by Johannesson et al. (1994) used the same sampling sites as McArthur et al. (1991) at Lake Gilmore. They identified two types of brines that correspond to different locations along a transect originating near the shoreline and continuing out into the playa. The brine types were identified as: i) a shallow acid groundwater closest to the playa margin; and ii) a more neutral entrained brine located furthest out along the transect in the playa. The shallow groundwaters had the lowest pH and salinity values, and pH and salinity increased out into the playa reaching maximum values in the entrained brine. The shallow less saline groundwaters result from infiltration of meteoric waters into the region around Lake Gilmore, and move into the lake along the playa margins. The entrained brines, Johannesson et al. (1994) suggest, are the result of evaporative concentration of the acid shallow groundwaters which later sink due to the increase in density. They also suggest that the neutralisation of the acid groundwater could have resulted from clay weathering reactions or neutralisation and/or dilution by more neutral brines that are characteristic of the centre of Lake Gilmore (Johannesson et al. 1994).

In a study of the hydrogeochemistry of groundwaters of the Yilgarn Craton, that excluded the agricultural south-west, Gray (2001) observed regional trends to the groundwater. He divided the groundwaters into four zones: Northern, Central, Kalgoorlie and Eastern based on differences in salinity, pH and oxidation potential (Table A1). Gray noted that separations between these zones coincided with the ‘Menzies Line’. Both Mann (1983) and Gray (2001) have discussed the ‘Menzies Line’ as defined by Butt et al. (1977) (cited in Gray 2001; Mann 1983) as the demarcation boundary between the mulga (acacia species) dominated geomorphologically ‘old’ inland plateau area with hardpan soils to the north and the younger mallee vegetated (Eucalyptus species) areas with calcareous soils to the south (Figure 6).

Table A1 Groundwater zones of the Yilgarn Craton (after Gray 2001)

<table>
<thead>
<tr>
<th>Groundwater zone</th>
<th>Groundwater characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Northern</strong> (North Yilgarn and margins)</td>
<td>Fresh and neutral, trending towards higher salinities in valleys</td>
</tr>
<tr>
<td><strong>Central</strong></td>
<td>Neutral and brackish, trending towards hypersaline at salt lakes and commonly increasing in salinity at depth</td>
</tr>
<tr>
<td><strong>Kalgoorlie</strong></td>
<td>Commonly acid (pH 3–5), except where buffered by alkaline materials such as ultramafic rocks, and saline in the upper part of the aquifer. The groundwater tended to become more neutral (pH 5–7) and hypersaline at depth and within a few kilometres of salt lakes</td>
</tr>
<tr>
<td><strong>Eastern</strong> (Eastern Yilgarn and Officer Basin)</td>
<td>Saline to hypersaline, neutral to acid and reducing</td>
</tr>
</tbody>
</table>

While Gray (2001) agreed that ‘ferrolysis’ was the likely cause for the acid groundwaters he observed, he proposed an alternative mechanism for the origin of the Fe$^{2+}$. Gray (2001) found that deep groundwaters in contact with mineralisation commonly had high concentrations of Fe$^{2+}$ and other ions. He proposed that this resulted from the first stage of oxidation of sulfide minerals such as pyrite:

$$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (A-iv)$$

At depth, the acidity was buffered by minerals such as feldspars and carbonates. Nearer to the surface due to the greater availability of oxygen, Fe$^{2+}$, which is soluble, oxidises and generates acidity:

$$2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 (s) + 4\text{H}^+ \quad (A-v)$$
As the upper profile is deeply-weathered, it has a poor buffering capacity so acid groundwaters result, unlike at depth. Gray noted that under most weathering conditions the pH of groundwater has lower minimum of 3, due to buffering by the dissolution of aluminosilicates such as kaolinite.

Gray and Noble in 2006 developed an alternative hypothesis for the generation of acid groundwaters. He proposed that wind-blown gypsum was altered to calcite in soils by sequence of transformations probably biologically mediated.

$$\text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} (A-vi)

In recent years, a multi-disciplinary team from the United States have published numerous articles on acidic groundwaters in southern Australia, particularly the south-west of Western Australia (i.e. Benison & Bowen 2006; Benson et al. 2007; Bowen & Benison 2009).

Bowen and Benison (2009) suggest that acid groundwaters are regional and quite ancient. The groundwaters evolved by evaporation past the carbonate divide\(^{12}\) (consuming alkalinity) and acquired low pH through extreme bed rock weathering, sulfide oxidation and ferrolysis. The acidity may be partially locally sustained by Fe cycling and redox reactions that generate $\text{H}^+$ (acidity). Bowen and Benison (2009) have shown that some acid salt lakes in the south-west represent a mix of meteoric waters and acid groundwater inputs.

Benison et al. (2007) observed that some salt lakes can be neutral to alkaline while groundwater around the lake is acidic. They also observed a rough relationship between the size of the salt lake and the pH of the surface waters of the salt lakes. The smaller salt lakes were acidic while the larger salt lakes tended towards neutral to alkaline. However, there were exceptions to this general trend.

Acid salt lakes and groundwaters have also been found in other areas of southern Australia, from South Australia through to western Victoria. The best studied example is Lake Tyrrell located in the Murray Basin, Western Victoria (Fee et al. 1992; Fegan et al. 1992; Giblin et al. 1992; Herczeg et al. 1992; Hines et al. 1992; Long et al. 1992a; Long et al. 1992b; Lyons et al. 1992; Macumber 1992). The proposed model for acidification at Lake Tyrrell is in some respects similar to the conceptual model presented by McArthur et al. (1991). The groundwaters around Lake Tyrrell consist of two systems—a less saline regional acid groundwater and deeper more saline neutral reflux brines. The proposed mechanism for acidification is recharging meteoric waters oxidise pyrite present in the formation (Parilla Sand) around Lake Tyrrell, generating acid. The shallower acid regional groundwater is forced to the surface mainly at the western margins of Lake Tyrrell as springs by denser reflux brine (Macumber 1992).

Long et al. (2009) suggested that acidification at Lake Tyrrell was caused by sulfide oxidation (pyrite), ferrolysis and nitrogen oxidation (as evidenced by high nitrate concentrations). Acidity was then further enhanced through evapo-concentration. The acid regional groundwater mixed with neutral anoxic reflux brines in the discharge zones at Lake Tyrrell. The reducing neutral nature of the reflux brine was due to sulfate reduction (Hines et al. 1992). Sulfides, resulting from biogenic sulfate reduction are also a common feature in many Western Australian salt lakes and agricultural drains including acidic ones (Degens 2008; Fitzpatrick et al. 2008).

\(^{12}\) Where calcium and magnesium are in excess of carbonate species, under strong evaporation conditions like salt lakes, carbonates precipitate to leave waters depleted of alkalinity (Drever 1997).
In South Australia, at least 22 acid groundwater playa lake systems have been identified (Long et al. 2009). In the Narlaby and Yaninee Palaeochannels on the Eyre Peninsula, acidification is thought to result from the weathering of biogenic pyrites found in the palaeovalley sediments or from the weathering of basement rocks (Bird et al. 1989; Chivas 1991). Acidification of groundwaters near Lake Dey-Dey on the south-eastern margin of the Officer Basin, South Australia is thought to be caused by oxidation of pyrite in unconsolidated sediments or oxidation of Fe$^{2+}$ in reduced groundwaters as it comes in contact with air (Dickson & Giblin 2009). McArthur et al. (1991) suggested that some of the South Australian acid groundwater playa lake systems could have formed due to ferrolysis as conceptualised by them.

Acid saline groundwaters have also been reported in the eastern Dundas Tablelands, Victoria. (Gardner et al. 2004a; Gardner et al. 2004b). The proposed origins of the acidity in this region are through chemical reduction. It is suggested that reduction of sulfate to form pyrite along the groundwater flowpath leads to highly reduced waters which in the discharge zone reduce iron. This reduced iron on exposure to air generates acid (Gardner et al. 2004a). Further acidity could also be generated through sulfate reduction in the discharge zone over winter (the wet period) which then oxidises over summer (the dry period) to generate further acid (Gardner et al. 2004b).

Internationally, there are many recorded examples of natural low pH waters, commonly due to sulfur or sulfide oxidation associated with volcanic activity (i.e. Nordstrom et al. 2009; Risacher et al. 2002; Tassi et al. 2009; Varekamp et al. 2009). Acid-causing sulfides can also originate from mineralisation (i.e. Verplanck et al. 2009) or biogenic sulfide rich sediments (i.e. Graham & Kelley 2009; Kwong et al. 2009).

The naturally acid Colour Lake on Axel Heiberg Island in the High Arctic is unusual as acidification of the lake has been attributed to ferrolysis. The proposed mechanism for acidification is: each winter, the lake becomes stratified where an anoxic iron rich layer develops at the base of the lake, and then with the summer turnover, the ferrous iron oxidises to generate acidity (Johannesson & Lyons 1995).

The deep basin brines of the Palo Duro Basin Texas are another international example of waters that are naturally acidic. The acidity has been attributed to oxidation of ferrous iron in the groundwater when exposed to air during sampling (Fisher & Kreitler 1987). Permian age redbed evaporites in the mid-continent of North America are thought to have formed in acid-saline conditions and it is suggested that the Australian acid systems could be modern day analogues (Benison et al. 1998; Long et al. 2009).

The Australian acid saline systems are also thought to be analogues for acid saline systems in the Meridiani Planum region on Mars (Benison & Bowen 2006; Long et al. 2009). This however is disputed by Dickson and Giblin (2009) amongst others.
Appendix B  Climate statistics for the agricultural region

Geraldton Airport

Perth Airport

Kojonup

Merredin

Pemberton

Albany Airport

Mean monthly rainfall - mm
Mean monthly evaporation - mm
Mean daily maximum temperature - deg C
Mean daily minimum temperature - deg C
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![Graphs showing monthly temperature, rainfall, and evaporation for Esperance and Salmon Gums Research Station.](image)

- **Esperance**
  - Monthly rainfall
  - Monthly evaporation
  - Mean daily maximum temperature
  - Mean daily minimum temperature

- **Salmon Gums Research Station**
  - Monthly rainfall
  - Monthly evaporation
  - Mean daily maximum temperature
  - Mean daily minimum temperature

Legend:
- Yellow: Mean monthly rainfall - mm
- Cyan: Mean monthly evaporation - mm
- Pink: Mean daily maximum temperature - deg C
- Blue: Mean daily minimum temperature - deg C
Appendix C  Simplified geology of south-west Australia

The main geological units and the rock types of the study area are shown in Figure 7. The area consists of Precambrian metamorphic and igneous rocks (Yilgarn Craton, Albany Fraser Orogen and Pinjarra Orogen) and Mesozoic to Tertiary age sedimentary rocks (Perth Basin, Carnarvon Basin and Eucla Basin). The western portion of the Eucla Basin, between Albany and Esperance, was formally known as the Bremer Basin (Clarke et al. 2003) and will be still be referred to as the Bremer Basin in this study to avoid confusion with the eastern portion of the Eucla Basin.

The Perth Basin is bounded by the Darling Fault to the east and consists of sandstones, siltstones and shales with some outcroppings of volcanics. Much of the Perth Basin is now covered by Pleistocene to Quaternary sands. Some coastal areas contain calcrete and limestone (Cockbain 1990).

The Pinjarra Orogen underlies the Perth Basin and outcrops in three localities. The Pinjarra Orogen can be broadly divided into two groups: igneous and metamorphic rocks (granites, migmatites, gneisses and granulites), and metasedimentary rocks (sandstones, siltstones and volcanics such as basalt and tuff) (Myers 1990a).

The Carnarvon Basin is in the north-west of the study area and consists of sandstones, limestones and shales (Hocking 1990a). To the south-east of the study area is the Eucla Basin, that consists of sandstones and limestones (Hocking 1990b). The Bremer Basin, to the south of the study area, forms a discontinuous veneer over Precambrian rocks and consists of siltstones, clays and sandstone (Hocking 1990b).

The Albany Fraser Orogen occurs in the south and south-east of the study area and comprises of granites that have intruded older rocks, orthogneiss (formed from igneous rocks), paragneiss (formed from sedimentary rocks) and metasedimentary rocks (quartzite, slates, schists and phyllite) (Myers 1990b).

The Yilgarn Craton represents most of the study area and consists mainly of granite, granitoid rocks (monzogranite, tonalite, foliated, gneissic or migmatic granite) and gneiss (orthogneiss and paragneiss). There are large areas of greenstones belts that contain mafic, ultramafic (for example tholeiitic basalts) and sedimentary rocks (for example banded iron formation). The greenstone belts are areas of mineralisation that have economic resources such as gold, nickel, lead and zinc (Griffon 1990; Trendell 1990; Myers 1990; Watkins 1990).

Much of the south-west of Western Australia has been deeply weathered during the Tertiary producing a ‘laterite’ profile (Tille et al. 2001; Tille et al. 2004). This deep kaolinised weathered profile can be tens of metres thick (Hocking & Cockbain 1990).
Appendix D  Bioregions and vegetation of south-west Australia

Bioregions are large geographically distinct areas of similar climate, geology, landform, vegetation and animal communities. Australia was divided into 85 bioregions as part of the Interim Biogeographic Regionalisation for Australia (IBRA). Bioregions have been further divided into subregions (Cofinas & Creighton 2001). The IBRA subregions and dominant vegetation types of the agricultural area are shown in Figure 9.

The Geraldton Sandplain bioregion encompasses the Geraldton Hills and Laseur Sanplain subregions. Proteaceous heaths and scrub heaths with emergent mallees\(^\text{13}\) and Banksia occur on sandplains that are most extensive in the north and south-east. York gums and acacia woodlands occur on alluvial outwash plains associated with drainage and valleys in the hill country (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Yalgoo bioregion consists of the Edel and Tallering subregions. Proteaceous heaths and acacia-casuarina thickets occur on the sandplains in the north-east. Eucalyptus (gimlet), callitris (cypress pine) and acacia (mulga and bowgada) open woodlands occur on the earth to sandy earth plains to the south-east (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Coolgardie region incorporates the Mardabilla, Southern Cross and Eastern Goldfields subregions. Eucalypt woodlands occur on greenstone hills, alluvial soils, around salt lakes and the broad plains with calcareous earths. On granite outcrops, ‘granite grass’, wattile (acacia) shrublands and york gums occur. In the playas, shrublands of samphire are common. Sandplain occurring on relict duricrust is dominated by proteaceous scrub in the east and acacia scrub in the west. (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Eastern Mallee and Western Mallee subregions form the Mallee bioregion. Mallee grows on a variety of soil types but usually calcareous sands, clays and loams that often have calcite hardpans or nodules. Eucalyptus woodlands usually occur on fine textured soils. Scrub-heath occurs on sands, sandstones and iron duricrusts. Samphire is common around the numerous playas (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Fitzgerald and Recherche subregions make up the Esperance bioregion. Heath, scrub-heath, mallee heath and mallee occur on the extensive sandplains that cover the region. Yate and York gum woodlands occur on alluvial soils and jarrah-marri woodlands occur in the west (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Avon Wheatbelt has two subregions: the Eastern which correspond roughly to the Zone of Ancient Drainage; and the Western that matches up approximately to the Zone of Rejuvenated Drainage. The sandplains that have formed on residual lateritic uplands are covered by proteaceous scrub-heaths. The erosional slopes and valley floors support woodlands of Eucalyptus (i.e. Wandoo, York gum) acacia (jam) and casuarina (sheoak) (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

\(^\text{13}\) Mallees are Eucalyptus species that have multiple stems coming from a single root stock or lignotuber. Some Eucalyptus species can occur as a single stemmed tree or as a mallee.
The Jarrah Forest bioregion is characterised by jarrah-marri forest, on ironstone gravels and ferruginous duricrust, and in the eastern part by marri-wandoo woodlands on clayey soils. The bioregion has two subregions, Northern Jarrah Forest and Southern Jarrah Forest. The Southern Jarrah Forest broadens and slopes gently to the south coast. The south-east of the bioregion is capped by sands and is flat with numerous wetlands and poor drainage. The wetlands are dominated by paperbarks and swamp yate (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Warren bioregion covers some of the wettest areas of the agricultural region. Tall open forests (greater than 30 m in height) of karri occur on loamy soils, and open forests of jarrah-marri occur on the relict duricrusts. Sandy soils in depressions and on coastal plains support low jarrah woodlands and paperbark-sedge swamps. Coastal dunes in the region support peppermint (Agonis) thickets, Banksia woodlands and heaths (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).

The Perth Coastal Plain and Dandaragan Plateau are subregions of the Swan Coastal Plain bioregion. The coastal plain consists of a sequence of coastal dunes. The younger sandier areas and limestones are dominated by tuart woodlands and heath. The older dune systems are dominated by Banksia and Banksia–jarrah woodlands. The fine-textured outwash plains at the base of Darling escarpment to the south are dominated by casuarina–marri woodlands and Melaleuca shrublands in wetter areas. The higher areas in the north-east are covered by jarrah, jarrah-marri and marri woodlands with areas of Banksia and scrub–heath, particularly on sandplains (Cofinas & Creighton 2001; May & McKenzie 2003; McKenzie et al. 2003).
Appendix E  Hierarchy of soils mapping

The Department of Agriculture and Food, Western Australia uses a hierarchical system for soils mapping which was first developed by CSIRO in 1983. The mapping unit hierarchy provides a consistent approach for dealing with different mapping scales and varying levels of complexity in both landscapes and soil patterns.

The broadest scale of mapping is Region, and the agricultural areas fall into the hierarchy’s Western Region (2). Within a region are Provinces that are used to provide a broad overview of the whole state and are suitable for maps at scales of about 1:5 000 000. Examples of provinces are the Swan Province (21), Stirling Province (24) and Avon Province (25).

Zones within these Provinces are defined using geomorphological and geological criteria and are suitable for mapping at regional level of 1:1 000 000. An example of a zone is the Western Darling Range Zone (255). Areas in Zones with recurring patterns of landforms, soils and vegetation are grouped into Systems. Systems are suitable for regional mapping at scales of 1:250 000. An example of a system is Coalfields System (255Cf) (Schoknecht et al. 2004, pp. 23–25).
## Appendix F  Groundwater bore counts for soil landscape systems

<table>
<thead>
<tr>
<th>Mapping unit</th>
<th>Unit name</th>
<th>Landform pattern</th>
<th>Acid</th>
<th>Non-acid</th>
<th>Grand total</th>
<th>Percent acidic</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>211Qu</td>
<td>Quindalup South System</td>
<td>Parabolic dunefield</td>
<td>0</td>
<td>10</td>
<td>10</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>211Sp</td>
<td>Spearwood System</td>
<td>Low hills</td>
<td>0</td>
<td>10</td>
<td>10</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>212Bs</td>
<td>Bassendean System</td>
<td>Dunefield</td>
<td>1</td>
<td>25</td>
<td>26</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>221Cy</td>
<td>Correy System</td>
<td>Alluvial plain</td>
<td>0</td>
<td>3</td>
<td>3</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>221En</td>
<td>Eneabba Plain System</td>
<td>Plain</td>
<td>0</td>
<td>5</td>
<td>5</td>
<td>0%</td>
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Appendix G  Additional results

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Percentage of bores that are acidic by dominant rock type

![Percentage of bores that are acidic by dominant rock type](image)
Acid Groundwater Origins

**Percentage of bores that are acidic by regolith**

- Alluvium
- Colluvium
- Lacustrine
- Relict or residual duricrust
- Sandplain
- Exposed rock or saprolite

**Percentage of bores that are acidic by depth class**

- Deep
- Intermediate
- Shallow

---

66
Appendix H  PHREEQC modelling of conceptual model

The intended purpose of the PHREEQC model is to test the plausibility of a conceptual model that is based on observed, but not measured phenomena, in soil profiles as outlined in the discussion. Therefore this model has limitations due the simplified assumptions made.

An initial solution representing rainfall was used in the model. The initial conditions were based on average values for major ions shown in Hingston and Gailitis (1976) that were adjusted to balance charge by removing alkalinity. The initial values used were: Ca (0.15 mg/kgw), SO4 (1.3 mg/kgw), Cl (7.1 mg/kgw), Na (3.9 mg/kgw), K (0.3 mg/kgw), Mg (0.47 mg/kgw) and organic carbon – C (1 mg/kgw). The initial solution was subject to a number of scenarios.

**SCENARIO 1** to represent rapid recharge by macropores and around tap root channels to the lower soil profile.

**Initial reactions:**
\[ \text{Ca}^{2+} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 + 2\text{H}^+ \]
\[ \text{Fe(OH)}_3(\text{s}) + 0.25 \text{CH}_2\text{O} + 1.75\text{H}^+ \rightarrow \text{Fe}^{2+} (\text{aq}) + 0.25\text{HCO}_3^- + 2.5\text{H}_2\text{O} \]
**Solid phases** were CaC2O4, Amorphous Fe(OH)3

**Final reaction:**
\[ 2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 (\text{s}) + 4\text{H}^+ \]
**Solid phases** were: Kaolinite, Goethite Hematite, Amorphous Fe(OH)3

Charge was allowed to balance by adjusting pH.

Various concentrations of oxalate, organic carbon and amorphous Fe(OH)3 were modelled to see which had the greatest effect on the pH of the final solution. The initial concentration of oxalate had the greatest influence over the pH of the final solution. 0.5 mmol/L of Oxalate added in the initial reactions, representing about 20 mg/L of Ca being exchanged by root biota lowered the pH of the final solution to around 3.8 which was similar to the median pH of acid groundwater (Figure 8). The addition of oxalate greater than 0.5 mmol/L produced lower pH values in the final solution. However, this was not explored further due to the limitations of the model.

**SCENARIO 2**, the initial solution was allowed to equilibrate with calcite in the upper soil profile.

**Initial reaction:**
\[ \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \]
**Solid phases** were: Calcite, CO2 with a partial pressure of 1 per cent

**Second reactions:**
\[ \text{Ca}^{2+} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 + 2\text{H}^+ \]
\[ \text{Fe(OH)}_3(\text{s}) + 0.25 \text{CH}_2\text{O} + 1.75\text{H}^+ \rightarrow \text{Fe}^{2+} (\text{aq}) + 0.25\text{HCO}_3^- + 2.5\text{H}_2\text{O} \]
**Solid phases** were: CaC2O4, Amorphous Fe(OH)3

**Final reaction:**
\[ 2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 (\text{s}) + 4\text{H}^+ \]
**Solid phases** were: Kaolinite, Goethite, Hematite, Amorphous Fe(OH)3

Charge was balanced by adjusting pH.

2.5 mmol/L of Oxalate, representing about 100 mg/L of Ca being exchanged by root biota added in the second reactions was needed to lower the pH of the final solution to around 3.8. Addition of oxalate greater than 2.5 mmol/L yielded lower pH values in the final solution but was not explored further.
Appendix I  Earlier published results

The percentage of bores that are acid in soil zones
### Logistic regression model results from earlier report

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