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Assessment of Acidic Saline Groundwater Hazard in the Western Australian Wheatbelt: Yarra Yarra, Blackwood and South Coast

Brad Degens and Paul Shand (Editors)

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EXECUTIVE SUMMARY

While secondary salinisation has long been recognised to be caused by rising water-tables in the Wheatbelt region of south-west of Western Australia (WA), it has only been recently recognised that there are additional risks coupled with the acidity of some rising groundwaters. Assessment of the distribution, characteristics and hazards of saline groundwaters containing acidity in the Avon Basin indicated that this was risk was extensive. The area of the Wheatbelt affected by shallow groundwater is predicted to continue expanding over the next 40 to 100 years and some landholders in broad valley floors may increasingly resort to groundwater drainage to control saline water-tables. Such practices carry the risk of increasing the interaction of saline acidic groundwater with surface environments. Over 5000 km of deep drains (>2 m depth) are already estimated to exist in the Wheatbelt and there is a need to fully characterise the scale of threat posed by the natural hazard posed by acidic groundwaters and how this might be modified by practices such as groundwater drainage.

This report provides an expanded regional assessment of the distribution, characteristics and interactions of saline groundwater-containing acidity in the WA Wheatbelt beyond that reported for the Avon (Shand and Degens, 2008). The area includes the agricultural zones of the Yarra Yarra and Ninghan Basins, Upper Blackwood and selected South Coast catchments. The assessment was coupled with investigations focused on improving understanding of the fate of metals and pH when acidic groundwater mixes with surface waters or discharges to lakes using geochemical mixing models and case-study investigations of lakes acidified by drainage waters.

Saline groundwaters with low pH (containing acidity) in the WA Wheatbelt have been confirmed to occur within an area broadly defined as south of a line from Perenjori to Three Springs, east of a line from Three Springs to Katanning and north of a line from near Cranbrook through Ravensthorpe to just north of Esperance. Acidic groundwater mostly occurs within broad valley floors in these areas although has been noted to occur beneath sandplains and upland areas.

The distribution of pH occurring in drain waters across the same area was generally similar to that of groundwaters, although skewed slightly downwards at pH <3.5 and upwards at pH >7. For 82 drain systems, including data collected previously in the Avon, 45% of drains had a pH of less than 4.5, although 41% had a pH of >7. Similarly, over 45% of drains and 75% of groundwater sites had water with net acidity exceeding 40 mg $CaCO_3$/L with up to 10% being very acidic, where net acidity exceeds 1000 mg $CaCO_3$/L. This indicates that a number of drains and groundwaters across the Wheatbelt contained the potential to acidify surface environments on discharge. The extent to which this will occur, however, will depend on discharge volumes, neutralising processes in receiving environments and the relative timing of each. Areas of the central and eastern Wheatbelt and northern South Coast are likely to contain groundwater with high acidity (>700 mg $CaCO_3$/L).

Detailed sampling and analysis of water chemistry in a sub-catchment of the Upper Blackwood Basin indicates that groundwater acidification might have occurred by sequential iron mineral dissolution, carbonate alkalinity mobilisation and iron hydrolysis. This process originates and is postulated to be mediated in part by organic decomposition and accumulation of CO_2 within groundwater systems. Further work is required to refine this hypothesis, particularly in understanding unsaturated zone processes and interactions between infiltrating water, groundwater and the regolith.

Acidic groundwaters are characterised by typically containing high concentrations (commonly > 10 mg/L) of metals such as aluminium, iron and manganese and high concentrations (up to 1000s µg/L) of trace elements such as lead, copper, nickel, zinc, uranium, lanthanum and cerium. The concentrations of lead, copper and zinc, in particular, pose risks to many aquatic species in inland ecosystems, although the risks may be slightly lessened due to the high salinity of the water and ephemeral nature of aquatic ecosystems (possibly decreasing likely exposure to the metals).

Surveys of lakes and surface waters in most basins indicated that the majority were alkaline. However, acidic waters occurred in some lakes in the southern Yarra Yarra and Ninghan and Upper Blackwood Basins. Acidity was found in the headwaters of the Dalyup River catchment on the South Coast and attributed to a combination of regional groundwater discharge and discharge from drains. This was complimented by alkaline surface waters in the lower part of the catchment; however, on mixing of the waters, metals such as aluminium appeared to remain in concentrations that may pose a risk for down-stream aquatic environments.

On-going discharge of groundwater to valley floors driven by rising water-tables, particularly where the groundwater is acidic, may result in acidification of floodplains and smaller lakes. The extent to which this will occur will depend on sub-surface and surface sediment neutralisation processes (by carbonates or microbial sulfate reduction) and rates of groundwater discharge.

Bench-top mixing of acidic water from groundwater drains and alkaline surface waters from the Wheatbelt confirmed that at least 20 times the volume of surface water was required to neutralise (raise to pH > 7) acidic drainage waters, although the pH of some could be raised above 6 with lesser volumes. The concentrations of trace elements such as Co, Ni, Cu and Pb in final mixed waters were also dependent on the pH. These results confirmed earlier modelled predictions of the behaviour of pH when acidic water from groundwater drains were mixed with alkaline surface waters. Furthermore, the investigations confirmed that the acidification potential of these waters can be estimated from concentrations of major metals and arbitrary mixing determined on comparison of this with measurements of water alkalinity.

Investigation of lakes acidified by drain waters indicate that conditions form that enable the soils to be classified as inland acid sulfate soils (ASS), in that the chemistry and behaviour is strongly similar to those of coastal ASS, although the source of acidity may not be due to sulfide oxidation. The capacity to neutralise waters can remain in the central basin sediments of the acidified lakes although the soils on the margins of the lakes show the strongest signs of acidification and may require active neutralisation to reduce the risk of surrounding environments being acidified. Sediments in the central basins of some lakes (if initially sulfidic) may contribute slowly to neutralisation of waters or, at the least, provide a refuge for aquatic life from acidification (between flood filling events). Sampling also indicated large variation in geochemical reactions in space and over time greatly increases the uncertainties in assessing the behaviour of acidic waters in Wheatbelt lakes.

Acidic groundwater is a natural hazard extending across the Wheatbelt with some regional variations in the magnitude of the hazard. Risks associated with the acidic groundwaters are largely dependent on whether groundwater discharge occurs to surface environments by either land management (deep drainage) or driven by on-going hydrological imbalance in landscapes and whether the discharge is managed to treat or contain acidity. While the origins of groundwater acidity in the Wheatbelt remain unclear, which limits predicting and therefore accurate mapping where the hazard occurs, there are clear indications that the water poses widespread threats to surface environments. This threat can be addressed by limiting the uncontrolled discharge of the acidic water to surface environments and managing (by treatment or containment) the acidity wherever the discharge is planned.

1. INTRODUCTION

Brad Degens
Salinity and Water Resource Recovery Branch, Water Resource Management
Division Department of Water, P.O. Box K822 Perth WA 6892

Salinised land in the Wheatbelt of Western Australia (WA) is likely to increase to more than 3 million hectares in future decades, representing a tripling of the area currently affected (Macfarlane et al. 2004). Recent evidence of falling trends in groundwater levels in a number of areas in the northern and central Wheatbelt since 2000 (George et al. 2008a) may indicate that the rate of increase in salinisation is slowing and may be less than initially expected due to climate variability. However, this conflicts with annual trends in rainfall (1970-2008) for most of the WA Wheatbelt which have been generally increasing up to 10 mm/decade (Bureau of Meteorology 2009). Most of this increase has been in summer rainfall, offsetting a decreasing trend occurring in winter and spring rainfall (Bureau of Meteorology 2009). The change in seasonal rainfall patterns may result in less groundwater recharge, due to greater evaporation rates in summer, although could equally result in future rising groundwater trends in some areas since summer rainfall events can occur in larger events (thunderstorm and cyclonic).

The limited range of options available for farmers to manage rising water-tables in many of the broad valley floors of the WA Wheatbelt has led to increasing farmer interest in using deep (up to 3m) open drains to lower and control shallow saline watertables (Dogramaci & Degens 2003; Kingwell & Cook 2007). Over 11000 km of drains (>1 m depth) have been constructed across the Wheatbelt (ABS 2002), of which at least 5000 km are estimated to be deep (>2 m) open groundwater drains. These occur as largely disconnected systems discharging to floodways and lakes (Dogramaci & Degens 2003; Shand & Degens 2008).

There is increasing interest amongst some valley farmers in the WA Wheatbelt to increase the use and scale of drains to deal with salinity threats along valley floors (Ruprecht et al. 2004). However, widespread implementation of deep open drains is widely acknowledged as requiring careful planning and management of the water discharged from these drains, in order to address the risks of increased flooding, water quality and environmental impacts (Ruprecht et al. 2004; Ali & Coles 2002; Stewart et al. 2009). Acidity and elevated trace elements in drainage waters have been identified as major issues of concern associated with planning and managing the discharge from drains. These concerns have been addressed in WA by the Engineering Evaluation Initiative (EEI) and the Wheatbelt Drainage Evaluation Project, both commissioned as part of the National Action Plan for Salinity and Water Quality (NAPSWQ).

The broad spatial extent and geochemical characteristics of acidic groundwaters in the southern part of WA is broadly known from earlier investigations (Mann 1983; McArthur et al. 1991, Gray 2001, Lee & Gilkes 2005) and has been refined in the Wheatbelt through more recent work in the Avon basin (Shand & Degens 2008; Figure 1.1). These studies have highlighted that acidity and high concentrations of trace elements were present in shallow saline groundwater across much of the Avon basin, and that deep drains could intercept these waters and export acidity and trace elements to waterways and lakes (Shand & Degens 2008). The potential risks were identified as primarily being acidity associated with saline groundwater in valley floors (Shand & Degens 2008), which when discharged to the land surface, could lead to the formation of conditions similar to inland ASS in lakes and waterways (Degens et al. 2008). The extent of acidic saline groundwater and the risks posed to waterways and lakes in other catchments in the Wheatbelt was largely unknown and required further investigation, similar to that previously undertaken in the Avon Basin.

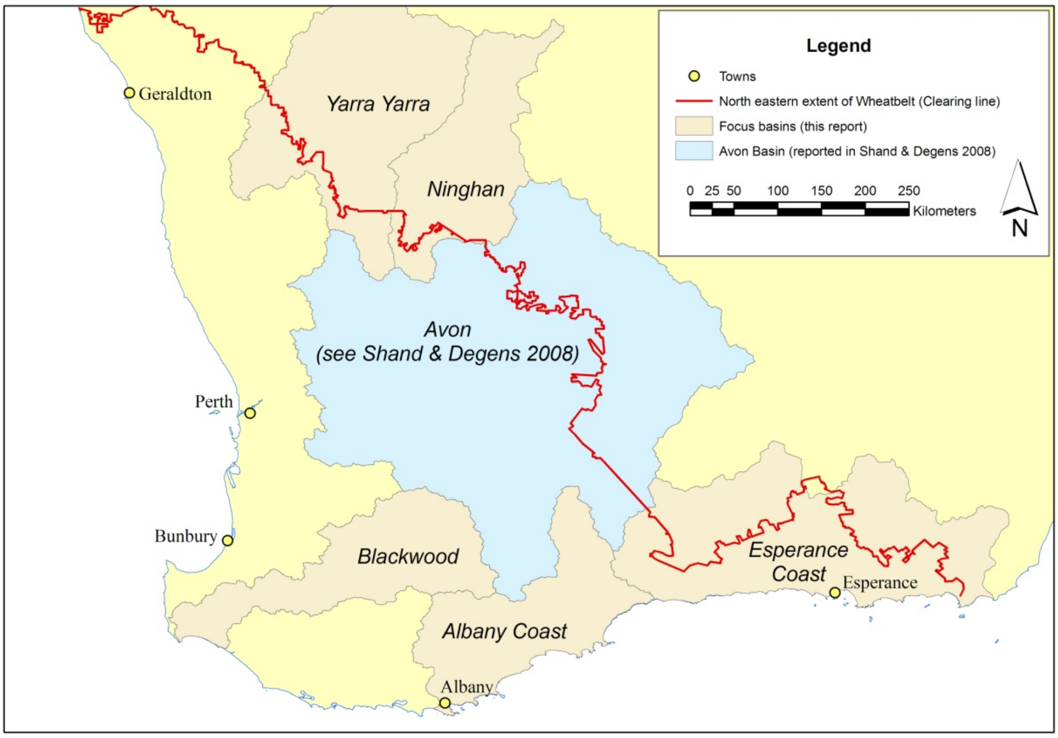


Figure 1-1 WA Wheatbelt showing location of focus drainage basins for investigations of acidic saline groundwater risks.

With investigations in the Avon Basin indicating extensive risk posed by acidic saline groundwater (Shand & Degens 2008), a second multi-agency research project was launched in 2006 to assess whether similar geochemical hazards and risks occurred in association with saline groundwaters in other catchments in the Wheatbelt. This work focused on catchments where there was farmer interest in employing deep drains to manage rising saline water-tables in valley floors, including the agricultural zones of the Yarra Yarra and Ninghan basins, upper Blackwood basin and catchments along the South Coast (Figure 1.1). The project was jointly funded and developed by CRC LEME and the WA Engineering Evaluation Initiative (EEI) and carried out in partnership with CSIRO Land and Water, the Department of Water (DoW) and the Department of Agriculture and Food-WA (DAFWA). The objectives of the overall project were to:

1. assess geochemical hazards and risks associated with acidic saline groundwaters at regional scales in the Yarra Yarra basin, upper Blackwood basin and in selected south coast catchments,
2. support catchment scale drainage evaluation projects (commissioned by the Department of Water) by providing support in assessing geochemical risks,
3. assess geochemical risks of trace element-rich discharge to receiving environments, and
4. support active management of acidic trace element rich drainage waters.

This report details the outcomes of the objectives 1 and 3, detailing the regional assessment of acidic saline groundwater risks and the behaviour of these in receiving environments (also partly reported on in Shand & Degens 2008). Objective 2 was undertaken in partnership with consultants undertaking projects for the Department of Water, and objective 3 was carried out by assisting with development of projects to conduct pilot trials of acidic drainage water management (reported in draft Department of Water guidelines: Degens 2009a).

2. REGIONAL GROUNDWATER GEOCHEMISTRY RISKS (OVERVIEW) - AGRICULTURAL ZONE OF THE YARRA YARRA AND NINGHAN BASINS

Brad Degens[1] and Ian Fordyce[2]
[1] Salinity and Water Resource Recovery Branch, Water Resource Management Division Department of Water, P.O. Box K822 Perth WA 6892
[2] Yarra Yarra Catchment Management Group, P.O. Box 18, Kalannie WA 6468

2.1. Introduction

Dryland salinity has been identified as a significant and expanding problem in parts of the Yarra Yarra and Ninghan basins (Henschke 1989; Clarke 2001) and may be coupled with acidic groundwater issues in some areas. Initial assessment of groundwater data across the agricultural zone (Lillicrap & George 2008) indicated that that the southern part of the Yarra Yarra and Ninghan basins contained a high likelihood of acidic groundwaters (>40% of groundwater monitoring sites with pH<4.5). However, there was limited on-ground data at the time of the analysis to verify this pattern.

This chapter presents the main results of a broad-scale survey to characterise the regional distribution, characteristics and risks of acidic saline groundwaters in the agricultural zones of the Yarra Yarra and Ninghan basins.

2.2. Physiography, hydrology and hydrogeology

The Yarra Yarra and Ninghan Drainage basins (618 and 619 in the Australian Water Resource Council scheme) are adjoining, internally draining catchments located about 200–400 km north-northeast of Perth (Figure 2.1). These basins experience a warm Mediterranean climate in the west, grading to a semi-desert Mediterranean climate in the east. Average annual rainfall decreases with distance inland, from 400 mm in the west to 200–300 mm in the east. The basins are typically low-relief and form part of the Darling Plateau (Commander & McGowan 1991). The western part of these basins has been mostly cleared of native vegetation and is used for broadacre wheat-sheep farming (Shepherd et al. 2002).

2.2.1. Regional geology and hydrogeology

The bedrock underlying most of the Yarra Yarra and all of the Ninghan basins is Archaean granite and gneiss of the Yilgarn Craton (Lipple et al. 1983; Blight et al. 1984; Baxter & Lipple 1985). Granitic/gneissic outcrops are generally uncommon and subdued. They tend to be concentrated along (or near) subcatchment divides, where they form low, rounded hills or rocky pavements. Greenstone belts comprise Archaean sedimentary and volcanic rocks, with characteristically prominent ferruginous units, known as banded iron formations (BIFs). Full-sequence greenstone belts are rare in the wheatbelt – they are more common (or at least more conspicuous) in the pastoral section of the Yarra Yarra/Ninghan, or in the goldfields further east. Inside the clearing line, greenstones are known only in the Koolanooka Hills/Perenjori Hills and extensions to the north-northwest. However, isolated outcrops of sedimentary rock, chert and/or basalt have been identified throughout the region.

A small part of the Yarra Yarra basin (the section west of Three Springs) lies outside the Yilgarn Craton, in the Perth basin: a 1,000 km-long half-graben extending along the south–western margin of Australia across the coastal plain and the continental shelf. The boundary between the Yilgarn and the Perth basin is the Darling Fault, a major structure with a complex history, with an eventual westerly downthrow of at least 15 km. Movements along the Darling Fault at various times through the Mesozoic, and possibly into the Cainozoic (Playford et al. 1976), are probably responsible for the pattern of palaeodrainage systems in the region.

The hydrogeology of the Yarra Yarra basin is characterised by predominantly local and intermediate flow systems in the areas with granitic and gneissic bedrock (Commander & McGowan 1991; Henschke 1989; Clarke 2001). These occur mostly within in-situ weathered materials, although aquifers are also present in some alluvial materials in valleys (Commander & McGowan 1991; Henschke 1989). Intermediate groundwater flow systems also occur in mainly Eocene and Pliocene sediments and in overlying, thinner Quaternary sediments in palaeodrainage systems which commonly interact with existing salt lakes (Commander & McGowan 1991; Commander et al. 2002). In the western part of the Yarra Yarra basin, the groundwater occurs mostly within local flow systems within Permian and Proterozoic fractured rocks around Three Springs and Carnamah (Commander & McGowan 1991). Little is known of the hydrogeology of the Ninghan basin, however, it is expected to resemble that of the Yarra Yarra basin where the geology is similar.

2.2.2. Surface hydrology

Both the Yarra Yarra and Ninghan basins are internally draining, and support lake systems that are largely disconnected. The Yarra Yarra basin has an area of 41824 km^2, with a lake system consisting of over 4500 lakes (Boggs et al., 2006) spanning an area of more than 300 km (Figure 2-1, Figure 2-2). There are several large lakes (>100 ha) within the basin and a large number of smaller lakes (<10 ha; Boggs et al. 2006), most of them fringing the larger lakes or aligned along the floodways.

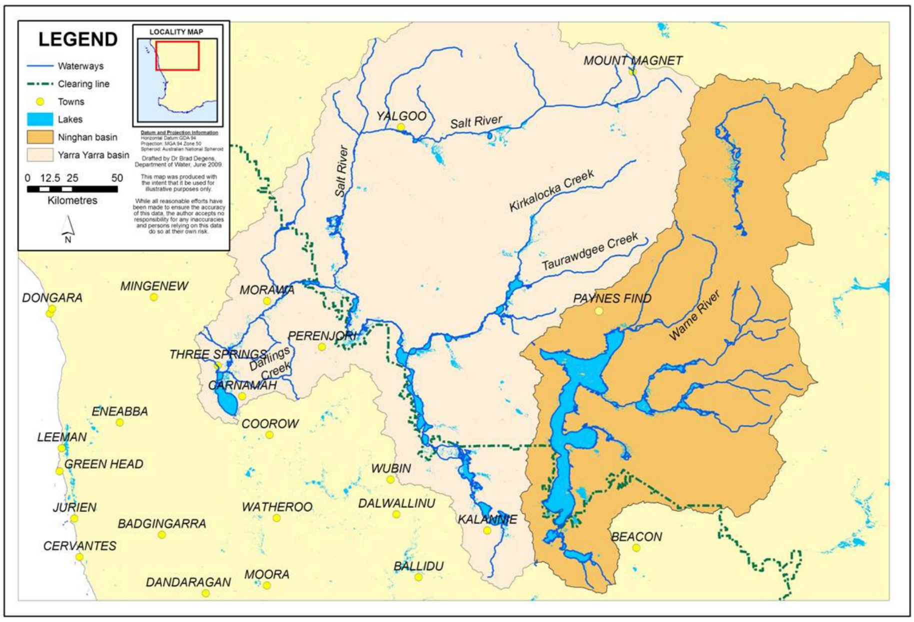


Figure 2-1 Location of Yarra Yarra and Ninghan drainage basins, with the clearing line defining the north-eastern limit of the agricultural zone.

By far the greater part of both basins (approximately 75%) lies in the rangeland zone. A large sub-catchment in the northeastern Yarra Yarra basin, from Yalgoo to near Mt Magnet, drains via the Salt River towards the Canna-Gutha area and Morawa. Kirkalocka Creek rises to the north-east of Paynes Find, and eventually flows into Mongers Lake. There are also a series of catchments, most of them smaller than 450 km^2, in the agricultural zone. It is only this segment inside the 'clearing line' that is of interest here (10062 km^2 and 2557 km^2 in the Yarra Yarra and Ninghan basins respectively; Shepherd et al. 2002); together this forms a substantial proportion of the northern Wheatbelt.

Drainage within the Yarra Yarra basin lake systems, based on analysis of land gradients in floodways and lakes is generally from south to north, from Lake Hillman near Kalannie through to Mongers Lake (Figure 2-2), then towards the south-west from near Lake Nullewa to the Yarra Yarra Lakes near Carnamah (Boggs et al. 2006). However, there is no historical record of continuous flow from end to end along the system. Given that the average gradient is only 20 cm per km, and that several sections are almost flat (Boggs et al. 2006), flows are probably dominated by the timing of lakes filling in relation to each other. It seems probable that the lake system follows a Tertiary palaeochannel, but it is unlikely that a single river was involved. There were probably several connections between the Ninghan and Yarra Yarra basins at various times, and Tertiary rivers would have continued westwards to the sea, across what is now the Moore River basin (Beard 2000).

The Ninghan basin has an area of 24269 km^2 and is dominated by Lake Moore (approximately 120000 ha) in the south-western part of the basin. Lake O’Grady (approximately 3100 ha) and Mollerin Lake (approximately 4000 ha) lie at the southernmost end of the basin. As with the Yarra Yarra basin, there are numerous smaller lakes and claypans on the fringes of larger lakes and along floodways. The majority of the catchment drains from north-east in the rangeland zone near Sandstone (east of Mount Magnet) towards Lake Moore, with several large catchments also draining to the lake from the east (north of Beacon). Only a small part of the basin falls in the agricultural zone (less than 11%) and this consists mainly of catchments in the southern part of the basin (generally smaller than 2000 km^2) draining to the southern end of Lake Moore, Lake O'Grady and Mollerin Lake.

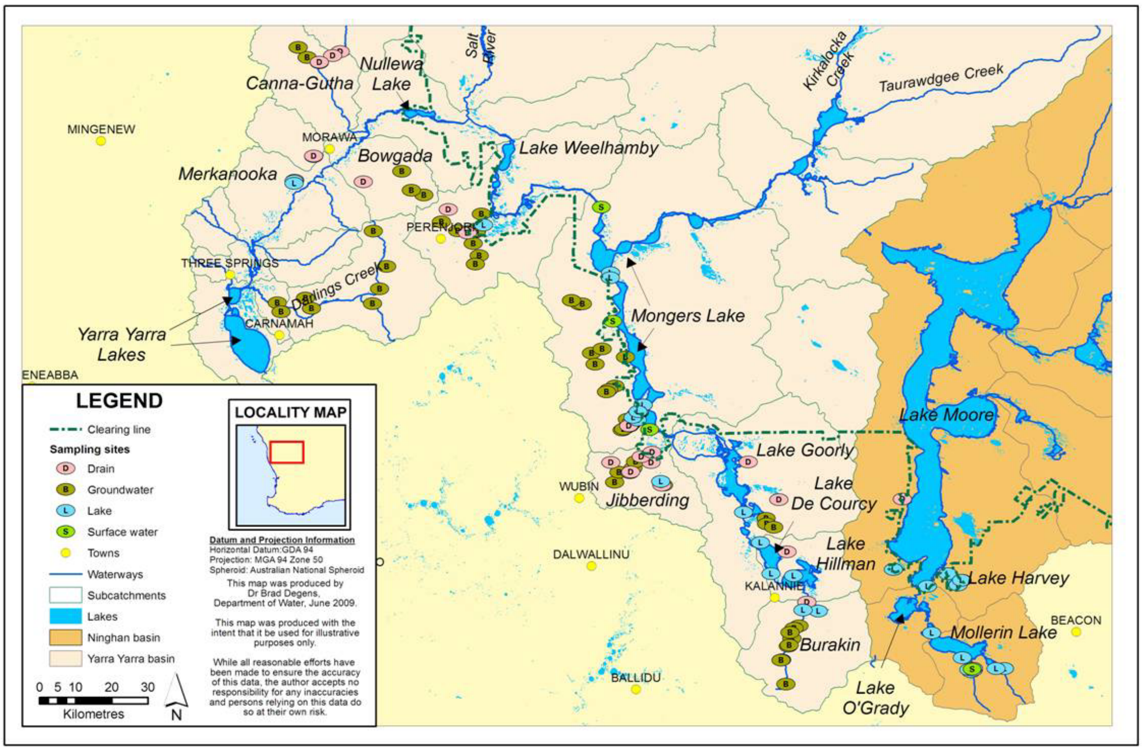


Figure 2-2 Location of groundwater, drain and surface water (lakes and floodways) survey sites in the Yarra Yarra and Ninghan basins.

2.3. Hydrogeochemical characteristics

2.3.1. Survey details

The present survey sampled groundwater bores, drains, lakes and surface waters throughout 2005-2008 to assess the geochemical risks of acidic groundwaters to surface environments in the agricultural zone of the Yarra Yarra and Ninghan basins. Groundwater was sampled at 80 sites, consisting of samples of fresh discharge waters in 27 shallow pits (2-3 m depth) in 2005 and 53 groundwater bores in 2006 and 2007 (see Appendix 2.1 for site details). The majority of groundwater bores were less than 5 m deep, with water-tables less than 3.5 m from ground-level. They were sited in valley floors and selected for sampling on the basis of being in areas where acidic groundwater was expected, guided by previous in-situ pH measurements by the Yarra Yarra Catchment Management Group (YYCMG). This focused groundwater sampling largely in the area south of a line from Carnamah to Perenjori (Figure 2-2). Groundwater samples were obtained using a peristaltic pump (for low–flow bores) or bailed, if supply was poor.

Surface water samples were taken opportunistically from 72 sites consisting of drains, lakes, flowing creek lines and floodways between 2005 and 2008 (Figure 2-2). Drainage waters samples, 32 in all, were obtained from 23 different sites with repeat sampling at several sites. The 36 samples from lakes were obtained from 29 different sites, with repeated samples being obtained from some sites. Ten of the lake sites were identified as receiving waters discharged from deep drains either directly or indirectly (i.e. water flowed into the lakes via floodways or creek lines). Surface water flows in floodways and creeks are rare in the Yarra Yarra – Ninghan basins. Only four surface-water samples were collected, following rare rainfall events in autumn 2008. For all samples, measurements of pH, EC and ORP (when possible) were made on site. Further details on the sampling and analysis methods are available in Shand & Degens (2008). All water quality data collected in this project has been archived with the Department of Water and is available on request from the water information database.

2.3.2. General characteristics

The waters sampled in the agricultural zone of the Ninghan and Yarra Yarra basins ranged widely in salinity and pH Figure 2-3). The median salinity of groundwaters was 29553 mg l^{-1} TDS, but could be at least twice this at some sites. The salinity of drain waters was similar to that of groundwater although the median was 39911 mg l^{-1} TDS, whereas surface waters (mostly being lakes) exhibited a wide range of salinity with the median being mg l^{-1} TDS. The pH of waters sampled in the basins also varied widely across generally similar ranges. However, the median pH values of groundwaters and surface waters were similar (median pH values of 5.7 and 5.5, respectively, whereas this was lower for drain waters (median pH 3.8).

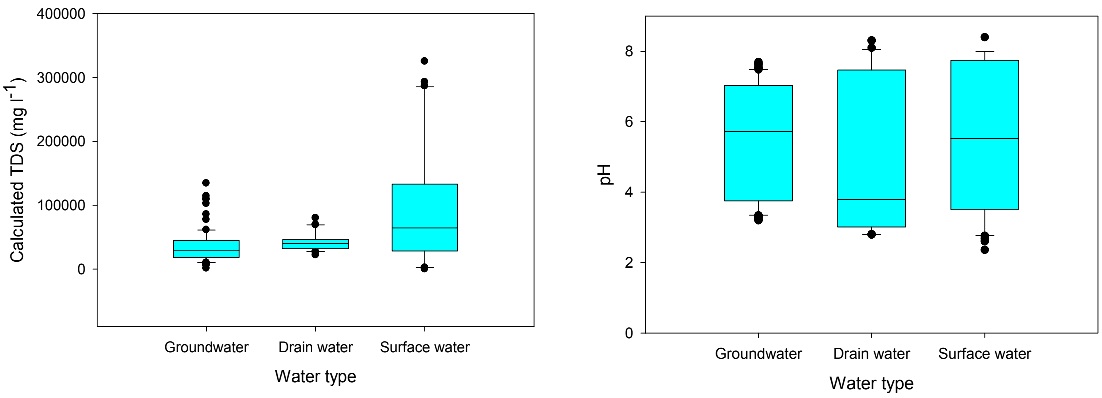


Figure 2-3 Box plots displaying median, interquartile ranges (25% and 75%) and 5% and 95% boundaries of pH and TDS for groundwaters, drain waters and surface waters (lakes, creeks and floodways) in the agricultural zone of the Yarra Yarra and Ninghan basins.

Waters are mainly of the Na-Cl type, but their ionic composition differed substantially from that of seawater (Figure 2-4).

Oxidation-reduction potential was measured *in situ* or with closed flow-through cells (for groundwater) at most sites. These indicated that oxidising conditions prevailed in most groundwaters, with Eh values (hydrogen half cell) being between 275 mV (25th quartile) and 491 mV (75th quartile). Eh values were slightly higher for water in drains or surface water than for bore water.

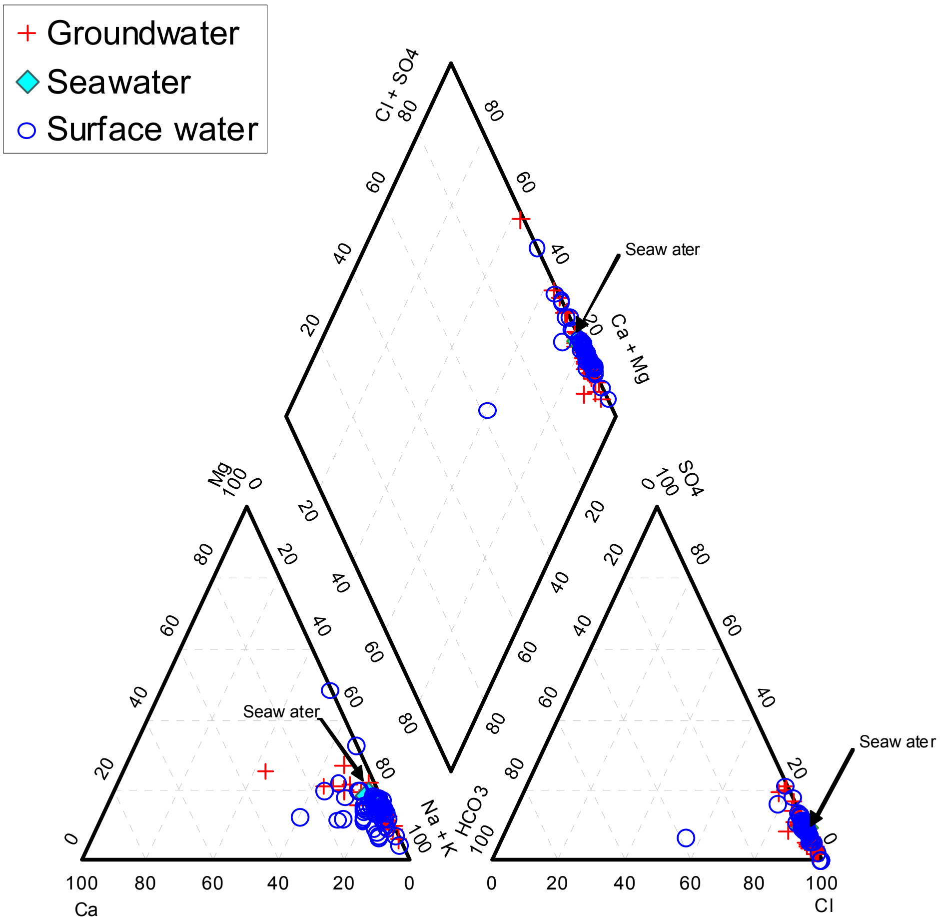


Figure 2-4 PIPER plot for major elements in surface waters and groundwaters in the agricultural zone of the Ninghan and Yarra Yarra basins.

2.3.3. Major element variations

TDS values were high in both surface waters and groundwaters (Figure 2-5). It was generally much higher in surface water due to evaporation and the dissolution of evaporite minerals in lakes. Sodium was well correlated with chloride (r^2=0.95) and, to a lesser extent, with sulfate, potassium and magnesium (r^2>0.88), with the correlations being significantly stronger when groundwaters were considered alone. These results contrast with previous investigations in the Avon, where sulfate, potassium and magnesium were poorly correlated with chloride (Shand & Degens 2008) and often depleted with respect to seawater. Calcium was poorly correlated with chloride (Figure 2-5), which has also been reported in earlier work in the Avon basin (Shand & Degens 2008). These plots indicated few losses or gains of major elements relative to water of seawater origin, despite concentrations varying across an order of magnitude. In the case of calcium, losses appeared to be associated mainly with acidic groundwaters (pH<4.5), whereas circum-neutral pH waters (pH 6.5–8.5) exhibited no consistent pattern of losses and gains with respect to seawater (Figure 2-5). No similar pattern of losses or gains on the basis of water pH was apparent for other major elements (Figure 2-5). In previous studies in the central Yilgarn Craton, acidic waters were generally potassium and sulfate, but not calcium depleted with respect to seawater reference values (Gray 2001).

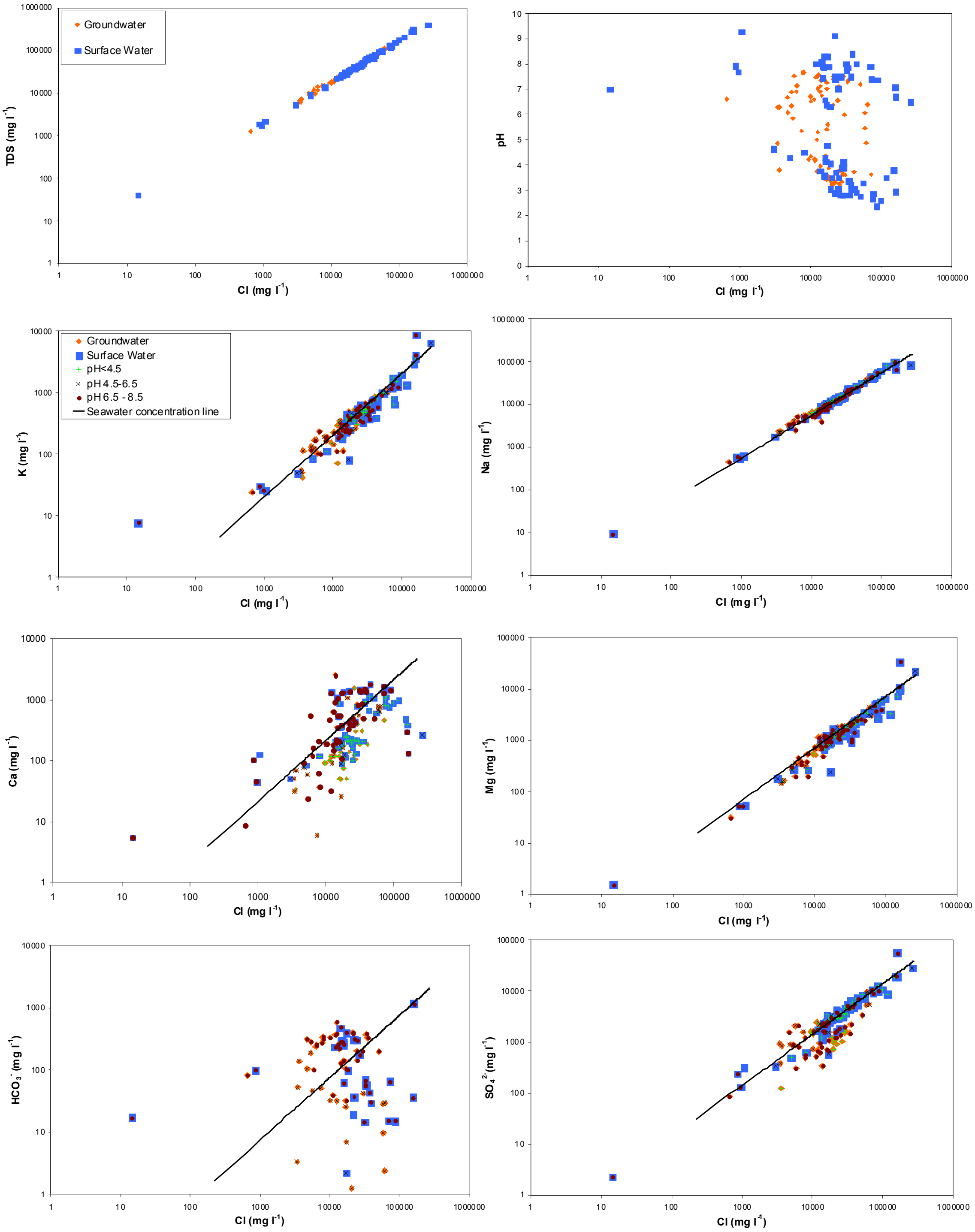


Figure 2-5 Relationship of TDS, pH and major element concentrations to chloride in surface water and groundwater in the agricultural zone of the Yarra Yarra and Ninghan basins.

2.3.4. Minor and trace element variations

Concentrations of minor and trace elements varied over several orders of magnitude in both surface water and groundwater (Figure 2-6; Figure 2-7). Aluminium concentrations were generally greater in acidic waters (pH<4.5) than in waters with higher pH, whereas iron could be present in circum-neutral groundwater at concentrations up to 154 mg L^{-1} (Figure 2-6). This contrasted with redox potentials (Eh) in groundwater, which varied from 100 mV to more than 700 mV, indicating oxidising groundwater conditions. By contrast, manganese and silica concentrations did not vary with pH in any consistent pattern; concentrations were equally high in circum-neutral to alkaline and in acidic groundwater.

Elements such as Ni and Pb could occur in much greater concentrations in waters with low pH ($pH<4.5$), whereas Zn, Cu and U were sometimes present at high concentrations in both alkaline and acidic waters (Figure 2-6). Arsenic was detected in some surface water and groundwater, though generally at levels lower than 5 $\mu g\ L^{-1}$. Selenium was not detected in most waters, but was occasionally found at concentrations exceeding 11 $\mu g\ L^{-1}$ in groundwater ranging in pH from 3.3 to 8.3. Cadmium was below detection level (0.1 $\mu g\ L^{-1}$) in more than 75% of samples. However, Cd was detected in some surface water ($\leq 5\ \mu g\ L^{-1}$) and some groundwater ($\leq 3\ \mu g\ L^{-1}$). One sample (from a circum-neutral non-receiving lake) contained 17 $\mu g\ L^{-1}$ Cd.

Many surface water and groundwater samples contained concentrations of trace elements exceeding guideline limits for low-level species protection in aquatic ecosystems (fresh and marine; ANZECC & ARMCANZ, 2000a). The implications of this for aquatic ecosystems are discussed in later sections. Acidic waters also commonly contained high concentrations of the elements lanthanum (La) and cerium (Ce), which sometimes exceeded 0.3 g L^{-1} as a result of evapo-concentration in drains and receiving lakes (Figure 2-7).

In general, nutrient concentrations were similar for surface water and groundwater (Figure 2-8). Median concentrations of dissolved organic carbon were 14.4 mg L^{-1} and 14.1 mg L^{-1} for surface and groundwater respectively, although concentrations tended to be lower for acidic groundwater ($pH<4.5$; median of 14.7 mg L^{-1}) than for circum-neutral to alkaline groundwater ($pH>6.5$; median of 52.3 mg L^{-1}). This pattern was not repeated for total dissolved nitrogen or other nutrient fractions (NH_4^+, NO_x or PO_4^{3-}), where median concentrations were similar for groundwater (GW) and surface waters (SW), irrespective of pH (GW medians 1.1 mg NH_4^+/L, 0.05 mg NO_x/L and 0.010 mg PO_4^{3-}/L, SW medians 1.4 mg NH_4^+/L, 0.15 mg NO_x/L and 0.014 mg PO_4^{3-}/L). Oxidised nitrogen and phosphate concentrations were frequently below detection limits in many surface waters and groundwaters (0.1 mg L^{-1} and 0.02 mg L^{-1}, respectively).

2.4. Distribution and characteristics of acidic groundwater

Shallow acidic ($pH<4.5$) groundwater is genrally confined to valley floors south of a line from Three Springs to Perenjori. Circum-neutral to alkaline groundwater tends to occur in upper landscape positions in these areas (Figure 2-9). In the northern part of the Yarra Yarra basin circum-neutral to alkaline groundwater generally occurs beneah all landscapes (Figure 2-9). Areas where acidic groundwater is highly likely in valley floors include the Mollerin, Lake O'Grady and Southern Lake Moore catchments, Burakin, Lake Hillman and De Courcy, Lake Goorly, Jibberding and the central and southern parts of the Mongers Lake catchment. There is evidence of acidic groundwater also occurring in valley floors elsewhere, such as parts of the Darling Creek, Merkanooka and Perenjori catchments. Acidic groundwater in these areas is more sparsely distributed and infrequent, and often not associated with pH values lower than 3.5. The distribution of acidic groundwater encountered in the present survey is broadly consistent with a more extensive set of borehole pH measurements (Figure 2-9) collected previously by the Yarra Yarra Catchment Management Group (2002-2006) and by the Geological Survey (1948–1987; available in the Department of Water WIN database). The majority of historical data from the WIN database is for groundwaters at upper-landscape locations, with circum-neutral to alkaline pH (Figure 2-9) and salinity levels generally less than 5000 mg TDS/L. This distribution reflects the focus of sampling on available farm wells and

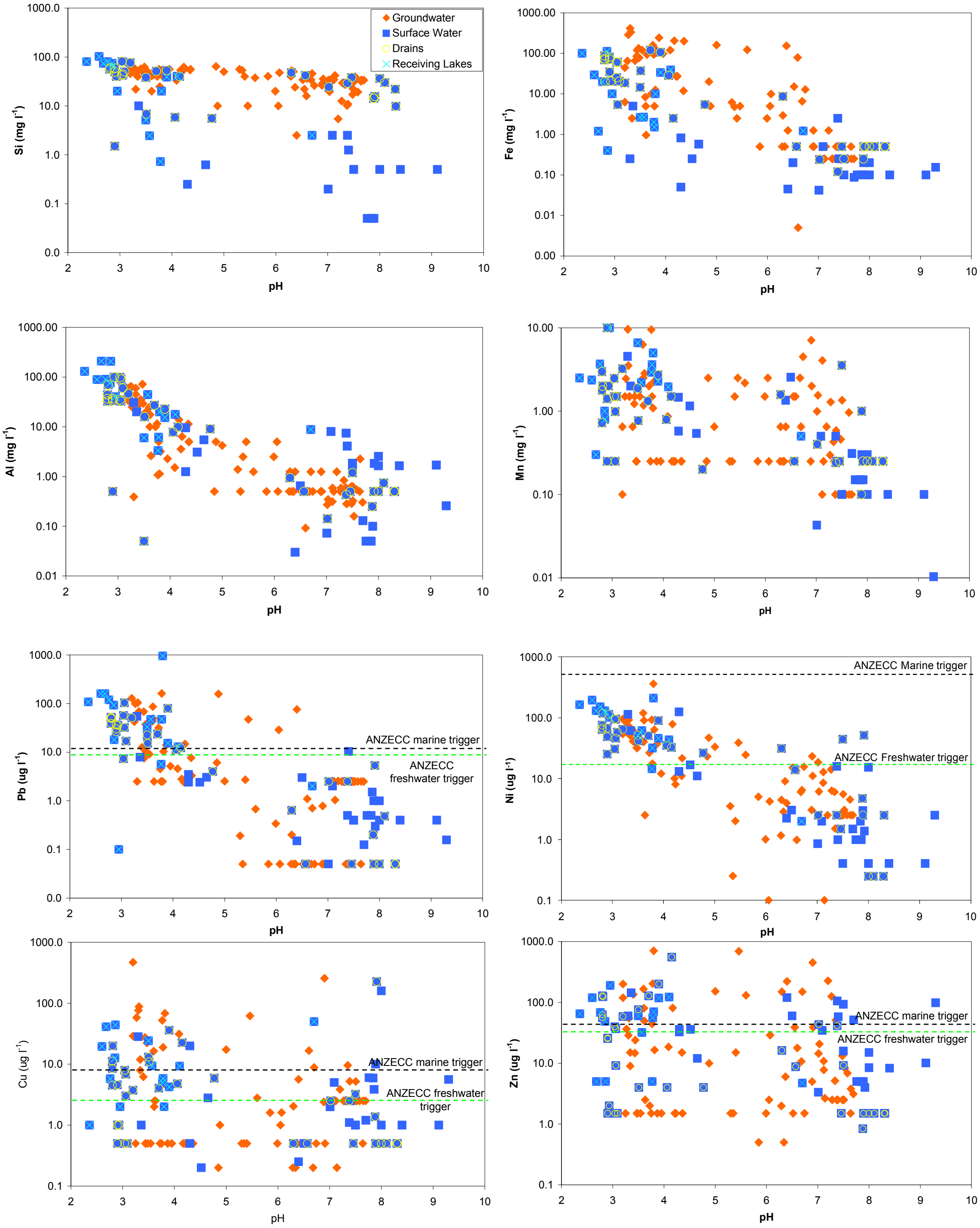


Figure 2-6 Relationship of minor and selected trace element concentrations to pH in surface water and groundwater in the agricultural zone of the Yarra Yarra and Ninghan basins. ANZECC and ARMCANZ (2000a) trigger limits for 80% aquatic species protection are also shown where available.

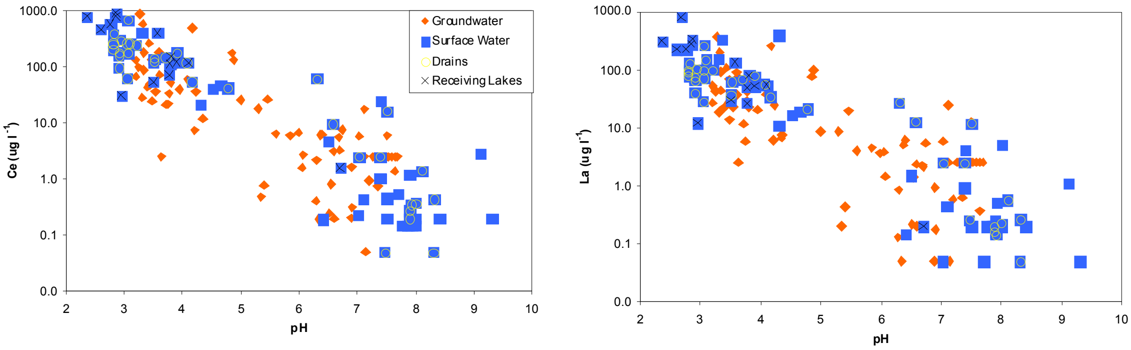


Figure 2-7 Relationship of selected rare earth element concentrations to pH in surface water and groundwaters in the agricultural zone of the Yarra Yarra and Ninghan basins.

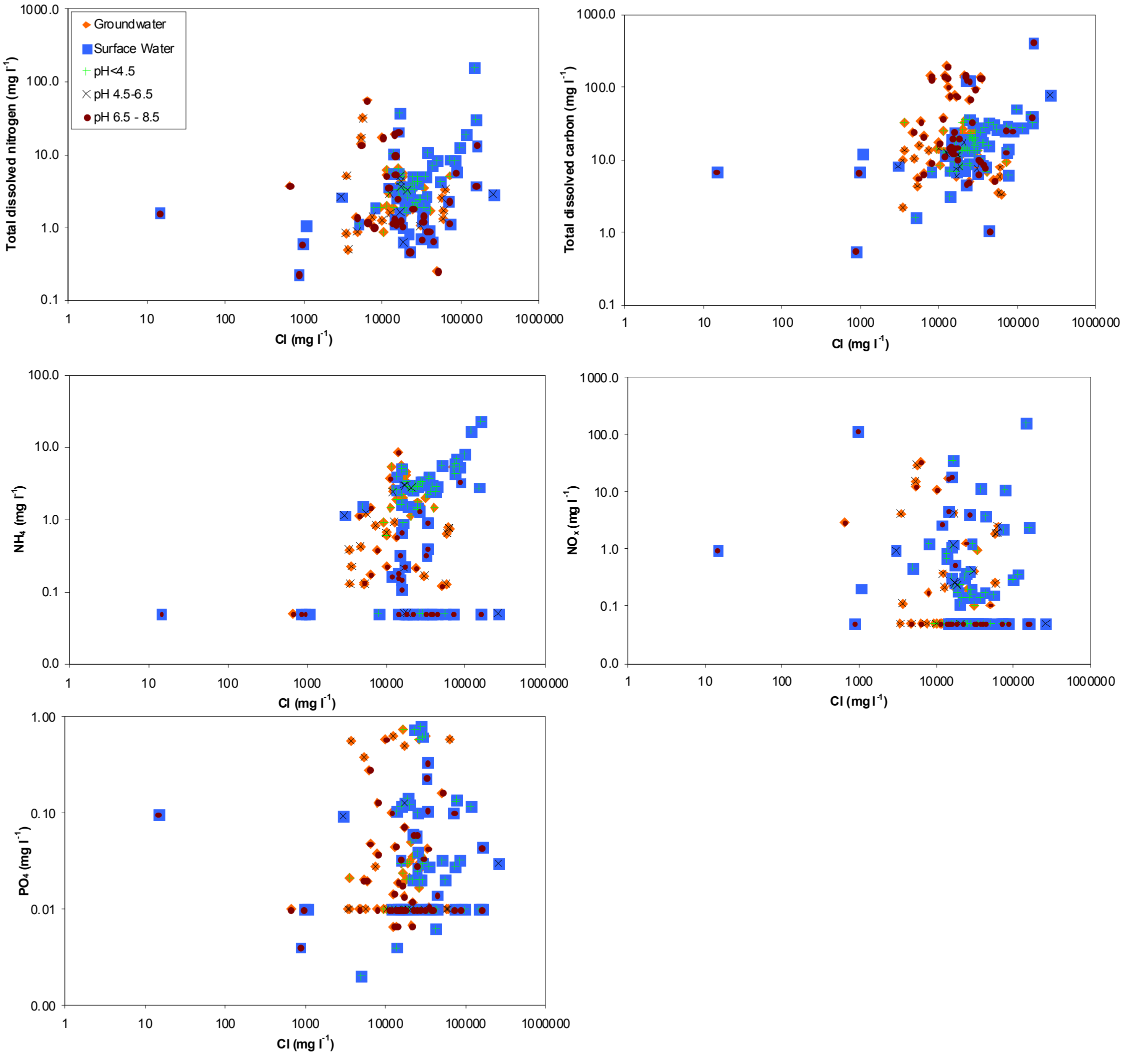
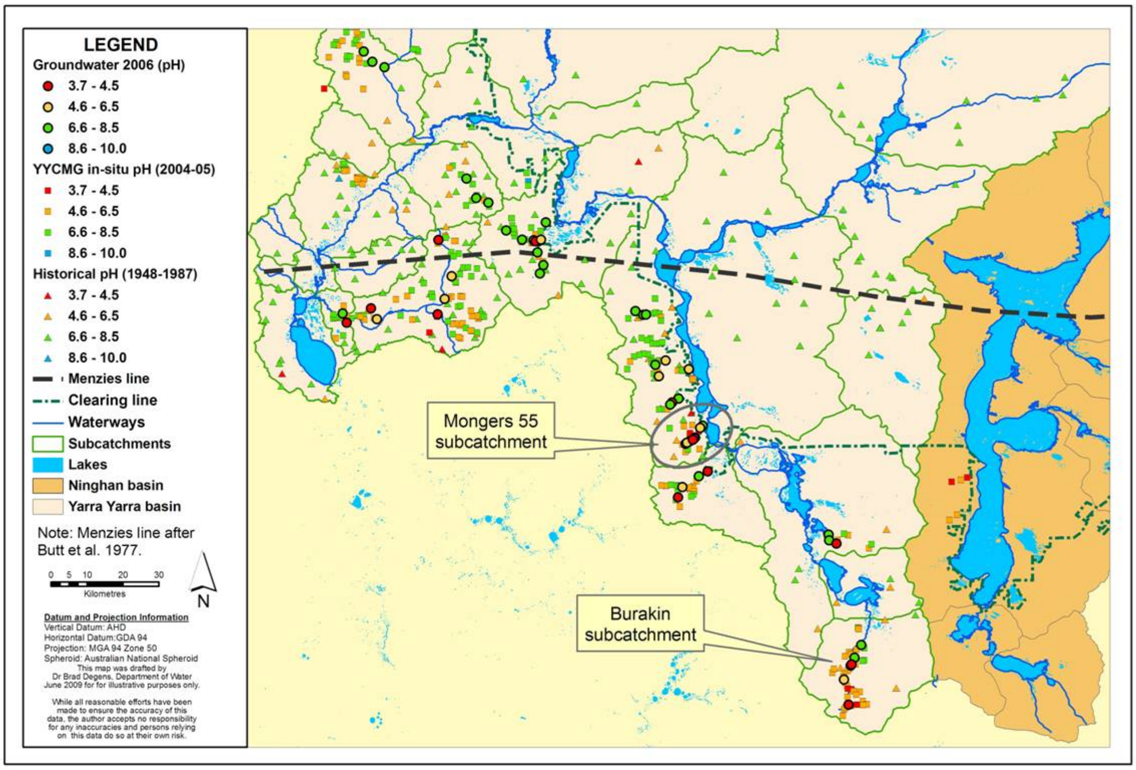


Figure 2-8 Relationship of total dissolved nitrogen, total dissolved organic carbon and nutrients (NH_4^+, NO_x and PO_4^{3-}) to chloride in surface water and groundwater in the agricultural zone of the Yarra Yarra and Ninghan basins.

bores installed for water supply. Although the reliability of pH data in the historical and community datasets is uncertain, given that the sampling methods probably involved air-lifting and pump testing, the broad regional picture of groundwater pH distribution is probably valid.

Acidic and neutral to alkaline groundwater can also be present within the same sub-catchments, and not all groundwater in the southern part of the Yarra Yarra basin is acidic. Neutral to alkaline groundwater can occur in the upper reaches or margins of valleys of some catchments, with acidic groundwater in valley floors and the lower reaches of catchments (near lake outlets, e.g. Burakinand Mongers 55). Some of the Mongers Lake sub-catchments (draining from the west) did not contain any observation sites with acidic groundwater.

Acidic groundwater is encountered more frequently south of a line between Three Springs and Perenjori, coinciding broadly with the Menzies line (after Butt et al. 1977), where marked changes have been noted in vegetation, soils (Butt et al. 1977; Gray & Lillicrap 2008) and regional patterns of groundwater hydrochemistry in the central and eastern parts of the Yilgarn Craton (Gray 2001). This contrasts with earlier investigations suggesting limited low pH groundwater in the southern Yarra Yarra and Ninghan basins based on sampling shallow groundwaters predominantly on the eastern margin of Lake Moore, Mongers Lake and Mollerin Lake (Mann 1983). Notably, groundwater in valley floors with low pH in the present survey was not necessarily more saline than circum-neutral to alkaline groundwater, as has been found to occur in the central part of the Yilgarn Craton (Gray, 2001). However, historical data from the Department of Water WIN database indicates that groundwater beneath upland landscapes is often far less saline (<5000 mg TDS/L) with higher pH (pH>6.5) than in lowland landscapes.



Note: Menzies line after Butt et al. 1977.

Datum and Projection Information
Vertical Datum: AHD
Horizontal Datum:GDA 94
Projection: MGA 94 Zone 50
Spheroid: Australian National Spheroid
This map was drafted by
Dr Brad Degens, Department of Water
June 2009 for for illustrative purposes only.

While all reasonable efforts have been made to ensure the accuracy of this data, the author accepts no responsibility for any inaccuracies and persons relying on this data do so at their own risk.

Figure 2-9 Groundwater pH collected during this survey (2006) in relation to historical pH data collected by the Yarra Yarra Catchment Management Group (YYCMG) and other extensive groundwater pH collected in groundwater surveys (1948-1987).

In the present survey, acidic groundwater (with pH < 5.5) often contained high concentrations of iron and aluminium (although manganese was not necessarily elevated) compared with circum-neutral and alkaline groundwater (Figure 2-6). These elements are considered to pose the most acute risks to aquatic environments because of the inherent acidity associated with the dissolved metals, as well as potential eco-toxic effects on aquatic organisms. The acidifying effects of these metal concentrations is reflected in the net total acidity of the groundwaters – a median of 355 mg $CaCO_3$ L^{-1} for water with pH less than 4.5 and a range of 58 to 831 mg $CaCO_3$ L^{-1} (Figure 2-10). Some groundwater with pH between 5 and 6.5 could contain high concentrations of dissolved iron (up to 154 mg L^{-1}), which can result in potential net total acidities up to 380 mg $CaCO_3$ L^{-1} (Figure 2-10). The high net total acidity associated with some groundwaters indicates their potential to acidify surface waters and sediments should they discharge to surface environments.

High concentrations of other trace metals and metalloids were also present in some acidic groundwaters, though less consistently than iron and aluminium. In general, groundwater with pH < 4.5 contained concentrations of lead, nickel and copper high enough to pose a risk to aquatic organisms if the water were to reach these environments (Figure 2-6). Similar risks are inherent with the sometimes high concentrations of zinc, selenium, cadmium and arsenic in some groundwaters, though these were not confined to acidic waters and the comparatively high concentrations of calcium and magnesium in the waters might mitigate any toxic effects (ANZECC & ARMCANZ 2000a). Rare earths such as lanthanum and cerium were also present in high concentrations in some acidic groundwaters (Figure 2-7), with a site east of Carnamah reporting 250 µg La L^{-1} and 481 µg Ce L^{-1}.

Assessments of the potential hazard that trace elements pose to surface aquatic environments are preliminary and made using the ANZECC guidelines for surface waters (ANZECC & ARMCANZ 2000a). These guidelines present conservative trigger limits for trace metals and metalloids in aquatic environments and are intended for marine and lowland freshwater aquatic ecosystems. Exceeding the guidelines does not mean that aquatic ecosystems will collapse. What these indicate, rather, is that there is a possibility of negative effects on aquatic organisms occurring (short and long-term). It also calls attention to the need for further investigations to determine whether this would be the case (ANZECC and ARMCANZ 2000a). The guidelines primarily concern direct eco-toxic effects on organisms and do not consider the risk of bioaccumulation of trace metals such as lead and cadmium in aquatic ecosystems.

A significant limitation in applying the guidelines to the WA Wheatbelt is that these were developed for fresh-water coastal rivers, while the guidelines for saline waters were developed for marine ecosystems. It is possible that there are fundamental differences between both of these systems and brackish to hypersaline inland ephemeral waterways and lakes. In spite of this limitation, the ANZECC guidelines can still be useful in indicating the relative potential areas of risk for inland waterways posed by different water quality constituents. Locally derived trigger values may be needed given the high concentrations of some trace metals and metalloids in some surface waters in this survey (irrespective of pH).

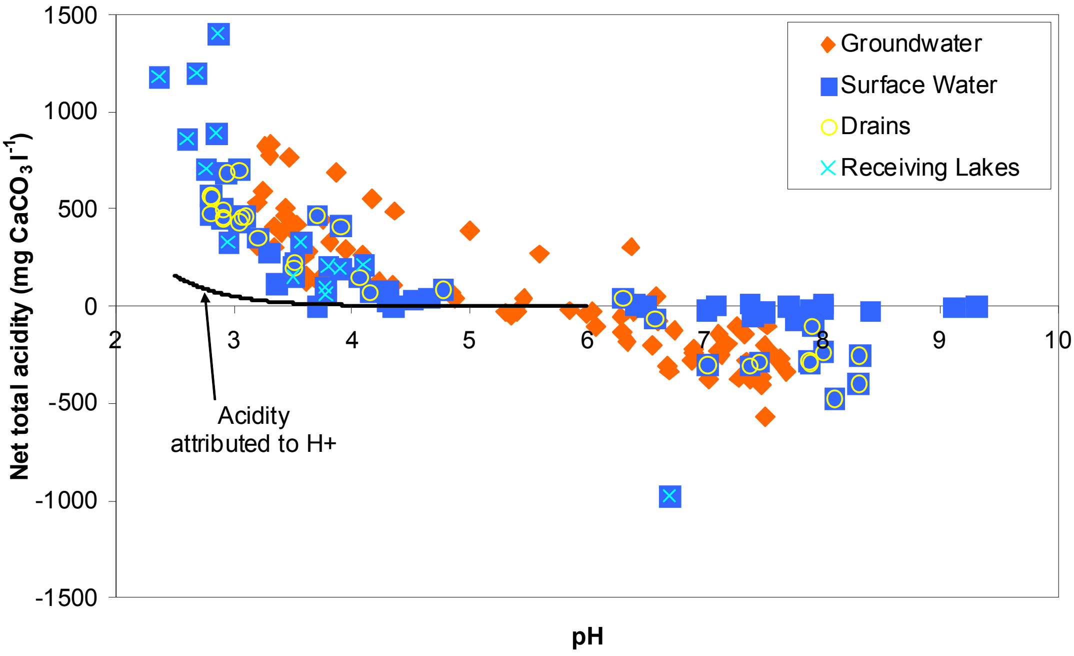


Figure 2-10 The relationship of net total acidity (titratable acidity – alkalinity) to pH in surface water and groundwater in the agricultural zone of the Yarra Yarra and Ninghan basins. The solid line is the net acidity due to H^+ ions.

2.5. Geochemical risk pathways

2.5.1. Discharge of acidic groundwater to surface environments associated with rising groundwater levels

The extent to which acidification could occur by the discharge of regional groundwater to lakes and waterways is probably indicated by the rise in regional groundwater levels and an expansion in the area affected by salinity. The most immediate effects from discharge of groundwater acidity would be expected in areas of primary salinisation (where groundwater levels are rising) and areas of older (pre 1990) secondary salinity.

Salinity monitoring and hazard mapping indicates that salinity in the agricultural zone of the Yarra Yarra basin could double in some sub-catchments, although whether this actually takes place will depend on rainfall patterns and land-use practices (GHD 2006). Since clearing, almost 9% of the basin has become saline, with the proportion in individual Yarra Yarra sub-catchments ranging from 4 to 26% (Clarke 2001; GHD 2006). Modelling indicates that in a worst-case scenario, 28% of the basin (including existing lakes) could develop shallow water-tables and be at risk of salinisation (Clarke 2001). No analysis is available for the agricultural zone of the Ninghan basin, though similar patterns of change for this area are indicated in Land Monitor datasets (Land Monitor 2000). Regional trends in groundwater levels indicate that these have been falling in many areas of the Northern Agricultural Zone since 2000 (George et al. 2008a), although prior to this, they had been rising at rates much greater than other parts of the agricultural zone (Clarke 2001). This probably reflects reduced rainfall over recent years and possibly the recession in groundwater levels following large floods and wet years (George et al. 2008a) that occurred in 1999–2000, 2001 and 2006.

Some of the smaller (< 10 ha) lakes are acidic, even though there is no evidence of drainage discharge. These tend to occur in the southern part of the Yarra Yarra and Ninghan basins (Figure 2-11). Many of the lakes have probably been acidified by the discharge of local acidic groundwater – a process that has increased since landscape clearing, as has also been proposed in the Avon basin (Degens et al. 2008). However, some of these lakes may have been acidic for decades or even centuries, as evidenced by their distinctive flora. The singular samphire species *Tecticornia lylei* is almost entirely confined to the shores of some acidic lakes (Unpublished data, Ian Fordyce 2008). Of the limited number of lakes where it was even possible to obtain water samples, only 4 (from a total of 21 lakes sampled) were acidic (Figure 2-11). This result might partly reflect the dry winters and failure of most lakes to fill during the study period.

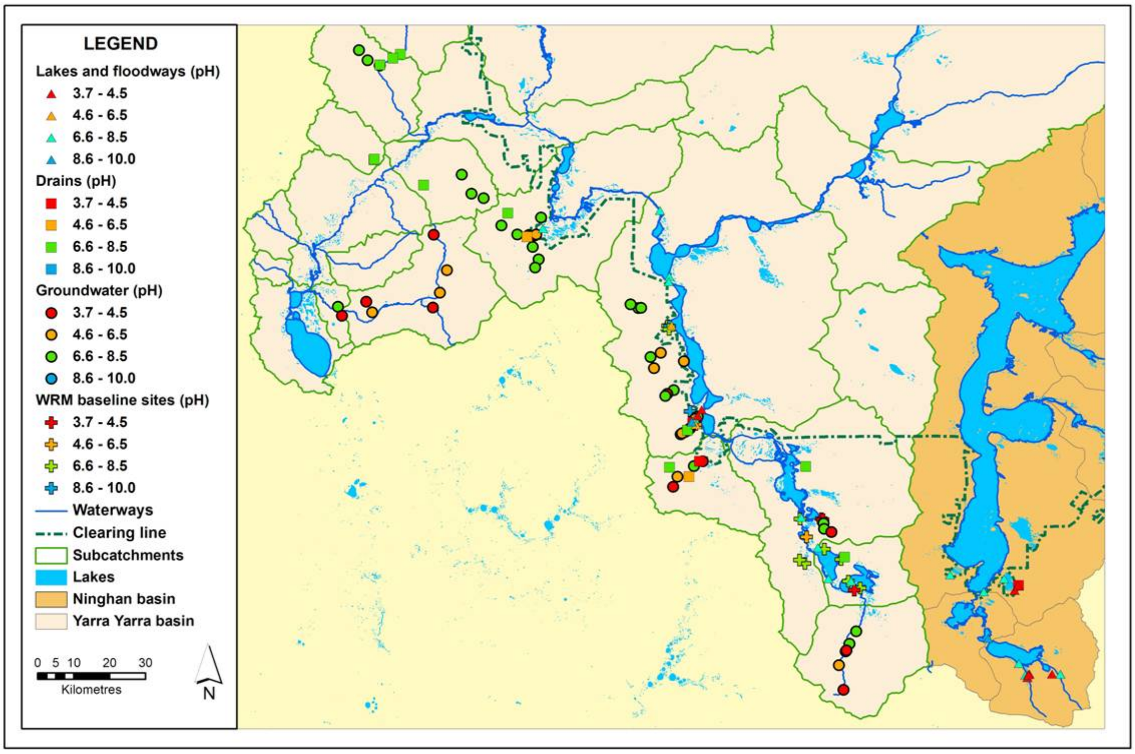


Figure 2-11 Groundwater, drain and surface water (lakes and floodways) in-situ pH in the Yarra Yarra and Ninghan basins.

In general, acidic lakes tended to be small and were located on the margins of larger lake systems adjoining cleared landscapes (for example Lake Harvey, in the Ninghan basin, and waterways in the Merkanooka sub-catchment of the Yarra Yarra basin). Sampling carried out in May 2008 as part of an investigation of environmental impacts of drains identified five small lakes in the 'reference' or 'control' group in the southern part of the Yarra Yarra basin (WRM 2008). These lakes were also located on the margin of larger lakes, adjoining cleared land (Figure 2-11).

Most reference lake samples were neutral to alkaline, suggesting that acidification of lakes by groundwater discharge may not be a significant threatening process for all smaller lakes (Figure 2-5; Figure 2-11). Seasonal pools in the larger lakes and partial flood filling in the Mongers Lake system sampled during the current survey were neutral to alkaline. This is consistent with previous measurements of pH in the Yarra Yarra lake system (Boggs et al. 2007a, 2007b). A number of smaller fringing lakes have also been found to contain circum-neutral waters (WRM 2008), indicating that impacts of groundwater acidification may be localised.

From the discussion above, it seems likely that some areas affected by dryland salinity may continue to be influenced by groundwater discharge and could lead to acidification in surface soil and sediment in floodplains and lakes. However, the rate at which this might occur is likely to be variable, given the effects of dry seasons and floods on regional groundwater levels. Concurrent neutralisation processes in existing alkaline lakes and waterways such as soil carbonate dissolution, alkalinity inputs in runoff from surrounding catchments and biological processes such as sulfate reduction may mitigate acidification due to discharge from regional groundwater. Sulfidic materials have been found in the sediments of a lake exposed to acidic groundwater discharge (MacPherson’s lake in the Mongers 55 sub-catchment), which probably mitigated the acidification of surface waters, at least in recent years. Based on evidence that some lakes are already acidic, the number of lakes affected by acidic groundwater discharge appears likely to increase in the southern part of the Yarra Yarra and Ninghan basins. Our data suggest that this process of acidification will most likely be confined to fringing lakes and the shorelines of larger lakes abutting agricultural areas.

2.5.2. Drainage and groundwater pumping

Construction of deep drains or groundwater pumping is a potential pathway by which the geochemical hazards in groundwaters of the region are likely to reach surface environments, whereupon the risks associated with this will need to be considered.

There is considerable interest by landholders in the Yarra Yarra catchment in undertaking a regional program of deep drainage to recover and protect land from salinisation, with the discharge of groundwater to salt lakes and saline wetlands (YYCMG 2007). On-ground work has begun, and this has been accompanied by organisational and governance arrangements to implement and manage such schemes (YYCMG 2007, 2008). Unlike the Avon Basin, regional drainage in the Yarra Yarra has been conceived to involve many smaller networks of drainage channels with numerous associated discharge points.

Snapshot hydrological monitoring between 2005 and 2008 identified high flows from drains immediately after construction, and that most drains continue to flow for at least several years. Flows in drains near discharge points were as much as 13 L/s immediately after construction (e.g. at Jibberding and Burakin), though most drains older than several years discharged at rates of 0.5 – 6.5 L/s. These are point estimates and would be subject to large variation between drains as a result of different lengths of drainage feeding to a discharge point and different depths of groundwater intercepted by the drains. Continuous discharge monitoring of several drains by the Yarra Yarra Catchment Management Group has found similar ranges of flows in drains immediately after construction and in following years in the Mongers 55, Canna-Gutha and Merkanooka sub-catchments in the Yarra Yarra basin (Fordyce & Hudson 2007; YYCMG 2008). Flows in some older drains were observed to become intermittent after several years during the present investigation, although this coincided with a series of years where rainfall was well below average (often less than 25th percentile) at many sites in the basins, particularly in the north.

Drains with acidic discharge waters tended to occur in the southern part of the Yarra Yarra basin and the adjoining Ninghan basin, consistent with the regional pattern of acidity in shallow groundwaters (Figure 2-5; Figure 2-9; Figure 2-11). Some drains (e.g. Mongers 55) contained a mix of circum-neutral and acidic waters (Figure 2-12), reflecting the mix of acidic and cirum-neutral groundwater chemistry within the area drained. The spatial distribution of acidic and alkaline groundwater might be taken into account when designing drainage systems to maximise in-drain neutralisation of acidic waters. It might be possible to maximise volumes of alkaline groundwaters drained in the upper reaches of drainage networks, so that these waters neutralise acidic groundwaters discharged to drains in the lower reaches.

The chemistry of drainage discharge would be expected to mirror that of the shallow groundwater intercepted by the drains, though perhaps at a lower pH. For example, in a drain in the Mongers 55 sub-catchment (see Figure 2-9), the median pH of drain waters at the discharge point was lower than that of groundwater in nearby bores, although bore-water and drain-water contained similar levels of total (titratable) acidity, aluminium and iron (Figure 2-12).

Fitzpatrick and colleagues (Fitzpatrick et al. 2008) reported that certain minerals which form in drains can retain metals. However, this process might only become significant in lowering metal concentrations once flows subside (water in slow-flowing drains typically has more opportunity to interact with sediments).

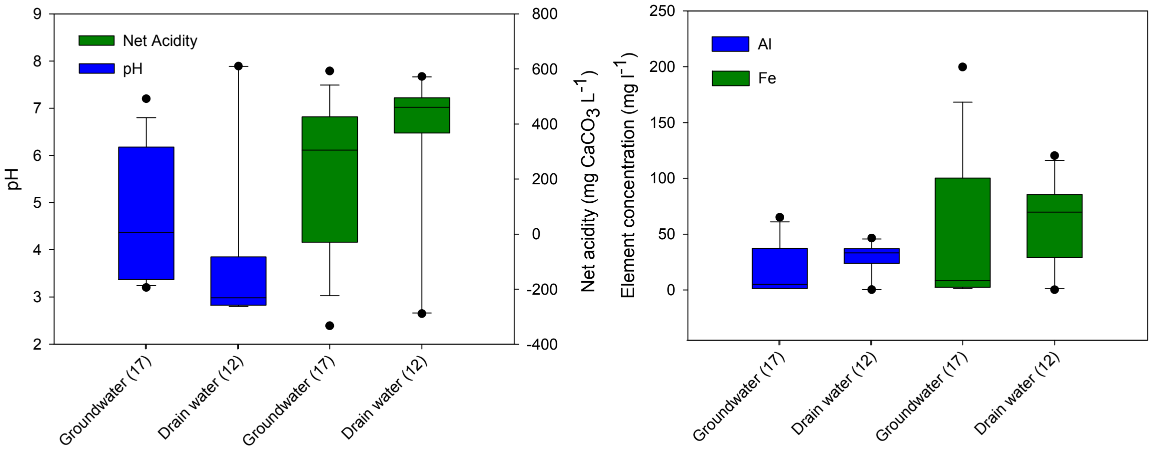


Figure 2-12 pH, net acidity, aluminium and iron concentrations in groundwater adjacent to the Monger 55 drain and within drainage waters (2006–2008).

Groundwater pumping is not used extensively throughout the catchment, although it has shown some promise (Salama et al. 1994) and has been carried out successfully to protect and recover saline agricultural land near Kalannie for several decades (R. S. Nixon pers. comm. 2005). It is not certain whether this approach to managing rising saline groundwaters would be adopted extensively in the Yarra Yarra and Ninghan basins, though some landholders may choose to use pumping to protect high–value infrastructure such as sheds and houses in situations where deep drainage is not possible.

2.6. Potential Impacts

Acidity and trace elements contained within the acidic groundwaters pose greatest risks to riparian vegetation and aquatic organisms that inhabit lakes and floodways. The acidity may also pose a risk to infrastructure within affected floodways.

2.6.1. Lakes and floodways

Emergence of acidity in groundwater discharge zones will result in acidification of surface soils in floodplains and sediments in lakes, to the extent that these eventually resemble inland acid sulfate soils (Degens et al. 2010). This acidification carries risks of on-going acidity impacts to down-stream environments and additional risks of trace metal accumulation and mobilisation.

Construction of deep drains in the Yarra Yara and Ninghan basins is likely to result in accelerated transport of acidity (along with salt) and differential accumulation in the landscape. Where acidic waters are discharged to alkaline lakes, the water and sediments of these sites are likely to become acidified and remain so for at least the duration of discharge, particularly in smaller lake systems. Discharge of acidic waters to lakes can result in storage of acidity in the sediments (Degens et al. 2008; Degens et al. 2010), which is likely to result in recurrent acidification of lake waters during drying phases. This is the most likely scenario, even if the retained waters are neutralised as a result of flood-water inflows. This phenomenon was illustrated in lakes adjoining a floodway near the southern margin of Mollerin Lake. Several lakes contained acidic sediments (pH <4.5) in this area, where, despite overnight filling with circum-neutral floodwaters (pH > 6.5) in April 2008, they became acidic over subsequent months.

Trace elements contained within some drain waters (and also present in shallow groundwater likely to be intercepted by drains), if bioavailable, might cause impacts in addition to those caused by the acidity. These include acute toxic effects of metals such as nickel and copper on aquatic organisms, and the bioaccumulation of elements such as lead and selenium within lake food-chains (Degens et al. 2008). However, these effects are strongly dependent on whether the trace element concentrations persist during the times when organisms might be present in lake environments receiving the waters (Hare 1992). This requires assessment of whether concentrations persist in lake waters or are released from sediments during lake-filling events, which requires further understanding of the behaviour and fate of trace elements at sites receiving acidic drainage.

Organisms within the shallowest sediments of lakes (known as the benthic zone) are sensitive to the formation of a permanent salt crust (Boggs et al. 2007b), and are therefore also likely to be sensitive to acidification. These organisms are frequently important parts of food chains in salt-lake systems that support bird life when lakes are flood-filled (Halse et al. 1998). Boggs et al. 2007b suggested that lake beds in the Yarra Yarra region might contain microbial communities with diversity that is unique to the region. However, in a subsequent study, no unique diatom species were found in crusts or surface waters (Boggs et al. 2008). Aquatic invertebrate monitoring in the southern part of the Yarra Yarra basin also found most species to be ubiquitous (WRM 2008). Species surveys such as these are often constrained, for logistic reasons, to the drier-phase conditions in lakes and wetlands. They probably greatly under-represent the likely aquatic diversity following major filling events (WRM 2008).

2.6.2. Riparian vegetation

The impacts of soil acidification on riparian vegetation in saline areas are not clear, but experience with ecosystem acidification (by acid rain) elsewhere in the world indicate that large changes in diversity can occur when soils and sediments become more acidic (Driscoll et al. 2007). The effects of soil acidification are mostly caused by direct toxic effects of aluminium on roots in acidified soils and impacts on the availability of nutrients, particularly cations such as magnesium, calcium and potassium (Driscoll et al. 2007; Vance 2006). The latter may be less critical in saline environments where concentrations of these ions are not likely to be limiting because of high inputs from saline groundwater.

In the Yarra Yarra basin, impacts of salinisation on vegetation have been noted at catchment inflow points to lakes, and attributed largely to increased waterlogging due to altered flooding and ponding frequencies following landscape clearing (Regeneration Technology 2002). Acidification of soils in floodplains and lake margins may impose an additional stress on vegetation in these environments over the long-term and possibly constrain the opportunistic regrowth of plants after large flooding events. These main effects of acidity, however, are likely to be associated with areas where large acidity loading occurs via either regional groundwater discharge or concentrated discharge from deep drains rather than areas temporarily exposed to acidic waters. Previous investigations have shown that the storage of acidity within sediments of sites receiving concentrated acidic drainage or acidic groundwater discharge over many years is often more than 100 fold greater than the acidity in ponded waters (Degens et al. 2008).

Surveys of riparian vegetation in drain-impacted wetlands carried out by the Yarra Yarra Catchment Management Group (YYCMG) have highlighted that variable responses can occur following drainage. Although there are anecdotal reports of damage to riparian vegetation caused by discharge of poor-quality groundwater via deep drains in the Yarra Yarra basin (e.g. Jibberding Hall drains), there are also reports that wetland vegetation has improved with the increased water-availability (e.g. Youangarra drains). Unfortunately, written or photographic records are inadequate to support either position. The YYCMG has been carrying out before-and-after botanical surveys in the discharge areas of all drains constructed locally over the past four years. Several of these drains are mildly to highly acidic (pH 5.5–2.7; total acidity 250-850 mg $CaCO_3$/L). Apart from some mild discolouration in the samphire *Tecticornia halocnemoides* on the northern shore of the settling lake at Mongers 55, there have been no detectable changes that can be unequivocally attributed to the drain discharge. Certainly, there have been none of the more obvious changes predicted from the understanding of acid rain and acid mine drainage, such as massive plant death, or conspicuous shifts in community boundaries.

2.6.3. Infrastructure

Acidification of floodways by regional groundwater discharge or discharge from drains can potentially accelerate damage of any concrete and steel infrastructure such as culverts, bridge work and water-supply pipes exposed to the waters. While salinity is widely known to threaten the design life of concrete and steel structures, corrosion caused by acidity within the saline waters can accelerate this decline (ABCB 2004). Acidic drainage from acid sulfate soils has been highlighted to corrode concrete in waterways of coastal environments (Sammut 2000; Morgan 2005) and it would be likely that acidic saline drainage would have the same effect on any similar infrastructure exposed to the waters. This risk applies particularly to infrastructure not installed to standards that would resist acid and salt attack (see Standards Australia for standards on concrete and steel infrastructure in saline and/or acidic environments).

In the Yarra Yarra and Ninghan basins, much of the regional road, rail and water infrastructure is not in valley-floor floodplains or on the margins of lakes where surface expression of acidity is likely to be greatest. However, there may be some local road crossings where acid attack could become a problem.

2.7. Main findings

- Acidic groundwater occurs mainly in the valley floors of the agricultural zone of the Yarra Yarra and Ninghan basins south of a line level with Perenjori and Carnamah.
- The acidic groundwater contains high concentrations of trace metals such as copper, nickel, zinc and lead and rare earths such as lanthanum and cerium that can also be found in discharge waters of deep drains intercepting the groundwater.
- Most of the lakes in the region are circum-neutral and likely to acidify rapidly if exposed to drainage discharge.
- Some lakes might be naturally acidic, occurring on the fringes of the larger lake systems, mostly in the southern part of the Yarra Yarra basin. These lakes were probably acidified by groundwater discharge, associated with dryland salinity.
- It is possible that ongoing groundwater discharge (even if hydrological balance has been achieved) might result in further acidification of lakes on the margin of the larger lake systems in the southern part of the Yarra Yarra basin and the agricultural zone of the Ninghan Basin.

2.8. Management implications

- Construction of deep drainage to manage shallow saline water-tables in parts of the Yarra Yarra and Ninghan basins will need to consider whether low pH water will be intercepted and the amount of acidity contained within this water.
- Where discharge of low pH and acidic water is likely, it may be necessary to consider measures to contain or manage the water to reduce the risk of acidifying surface waters and sediments in environments receiving the drain waters.

- Further investigation is required to determine whether aquatic organisms are at risk from concentrations of trace elements likely to occur in both alkaline and acidic waters. This would involve further sampling of surface waters, characterisation of aquatic biota and development of ecotoxicological tests to build a data-set from which locally relevant water-quality trigger limits can be derived.

3. REGIONAL HYDROGEOCHEMISTRY (OVERVIEW): UPPER BLACKWOOD CATCHMENT

Michael S Smith
Department of Agriculture and Food, 10 Dore Street, Katanning WA 6317

3.1. Introduction and location

The distribution, nature, evolution and risks of acidic groundwaters and surface waters in and immediately adjacent to the upper portion of the Blackwood catchment (Figure 3-1) were investigated. For the purpose of this study, the upper Blackwood catchment is differentiated from the lower, higher-rainfall portion by the 600 mm mean annual rainfall isohyet. Groundwaters were sampled mainly in the Fence Road subcatchment (Figure 3-1), rather than more regionally, to more closely match the scale at which hydrochemical evolution takes place.

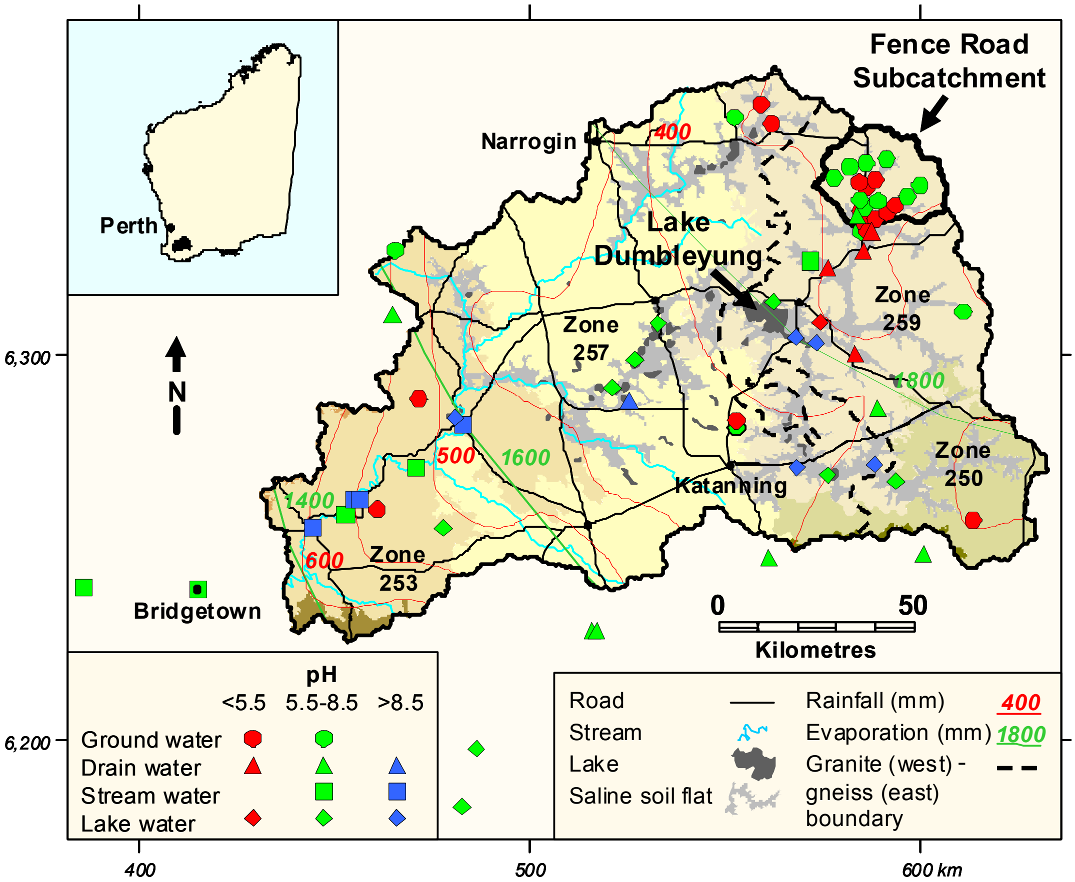


Figure 3-1 Water sampling sites, in the upper (<600 mm mean annual rainfall) Blackwood catchment and Fence Road subcatchment, classified by field pH. Major soil-landscape zones (Zones 250, 253, 257 and 259; Table 3.1) are labelled. Co-ordinates, in km, are for GDA94, AMG Zone 50.

The upper Blackwood catchment has a Mediterranean climate with warm, dry summers and mild, wet winters. From west-southwest to east-northeast (e.g. toward the Fence Road subcatchment; Figure 3-1), the mean annual rainfall decreases from 600 mm to <350 mm (Bureau of Meteorology rainfall data for the period 1976-2005), and the mean annual Class A pan evaporation increases from 1,400 mm to almost 2,000 mm (Luke et al. 2003). The region is underlain by the Western Gneiss Terrain, which in the sampling area comprises 2.7-2.6 Ga granite (including adamellite) of the

Darling Range Batholith (cf. Boddington Terrain of Wilde et al. 1996) in the west and 2.7-2.9 Ga gneiss, intruded by adamellite, in the east (Chin & Brakel 1986; Geological Survey of Western Australia 1990; Wilde et al. 1996). The gneiss coincides with the South-West Seismic Zone (a linear zone of seismic activity; Chin & Brakel 1986) and has been interpreted to be an east-dipping thrust (shear zone), which separates the Boddington Terrain from slightly younger granitoid rocks in the eastern Lake Grace Terrain (Wilde et al. 1996; Dentith & Featherstone 2003). The boundary between the Darling Range Batholith and the western margin of the thrust zone roughly coincides with the Meckering line (Mulcahy 1967), which is the boundary between soil-landscape zones of rejuvenated (external; zone 257) and internal (zone 259) surface drainage (Figure 3-1; Table 3-1). Dolerite and diorite dykes occur throughout the region and sequences of variably metamorphosed mafic to ultramafic volcanic rocks and associated sedimentary rocks (colloquially termed greenstone belts) exist sporadically within the thrust-zone gneiss (e.g. Chin & Brakel 1986) and may locally influence hydrogeology and hydrochemistry.

Seventy ground-, drain-, stream- and lake-waters were sampled in 2005-2008 at the sites listed in Appendix 3.1. Groundwaters were sampled using a QED® Micro Purge bladder pump and following the low-purge sampling procedure of ASTM (2002) to acquire representative samples and accurate field measurements of electrical conductivity (EC), pH, redox potential (Eh), dissolved oxygen (DO; corrected for salinity; Lewis 2006), temperature, alkalinity (by titration) and depth to water; groundwater temperature measurements, though, were strongly influenced by surface conditions due to the low pumping rates. Field probes were checked and calibrated at least each morning, and evening measurements of pH 4.01 and 7.00 buffers were consistently within 0.02±0.01 and 0.03±0.00 units, respectively. The charge balance of all samples was <5%, apart from those of samples 98FR106D and TL7, which were <7% and ~11%, respectively.

Water acidity (meq.L^{-1}) was calculated as:

1) net potential non-CO_2 acidity, $Acy_{net} = Acy_{calculated} - Alk_{measured}$, where $Acy_{calculated} = 10^{(3-pH)} + [Fe_{total}] + [Mn] + [Al]$ and $Alk_{measured}$ is the field-measured alkalinity (Kirby et al. 2009), assuming the dissolved metals were present as Fe^{2+}, Mn^{2+} and Al^{3+} and ignoring element speciation and the presence of acids such as HSO_4^-; and,
2) CO_2 acidity, $Acy_{CO_2} = [H_2CO_3^*] + [H^+] - ½[CO_3^{2-}] - [OH^-]$, where $[H_2CO_3^*] = [HCO_3^-] \times 10^{(6.38-pH)}$ at 20° C (Stumm & Morgan 1996).

The inclusion of $[B(OH)_4^-]$ and $[Al(OH)_4^-]$ has no notable impact on the calculated RA_{CO_3} or Acy_{net} results. The alkalinity (essentially $[HCO_3^-]$ at pH <7) required for the treatment of net-acidic waters equals Acy_{net}.

3.2. Hydrogeochemistry

The basic hydrochemistry and the distribution of acidic waters in the upper Blackwood catchment are described. Results are then presented for the Fence Road subcatchment, where groundwater sampling was focused to better understand the distribution, nature and evolution of acidic waters.

3.2.1. Upper Blackwood catchment

The sampled waters have all been evapoconcentrated to saline levels (total dissolved solids, TDS, >3 g/L) and range in measured pH from 2.5 in a drain to 10.0 in a lake (ignoring ionic strength effects on solution pH measurements; e.g. Dickson 1993; Millero et al. 1993; Figure 3-2a). Groundwaters and lake waters, respectively, attain salinities of almost two and ten times that of seawater (Figure 3-2a). Aside from the few most extremely saline lake waters, the groundwaters commonly have higher TDS than the natural surface waters (i.e. stream and lake waters) as the latter are subjected to dilution with rain water. Water pH (Figure 3-2a) has a trimodal distribution with values commonly of pH 4.3, 6.3 and 8.3-8.4 (Figure 3-3). In comparison, waters from the Avon catchment to the north have a bimodal pH distribution (Shand & Degens 2008).

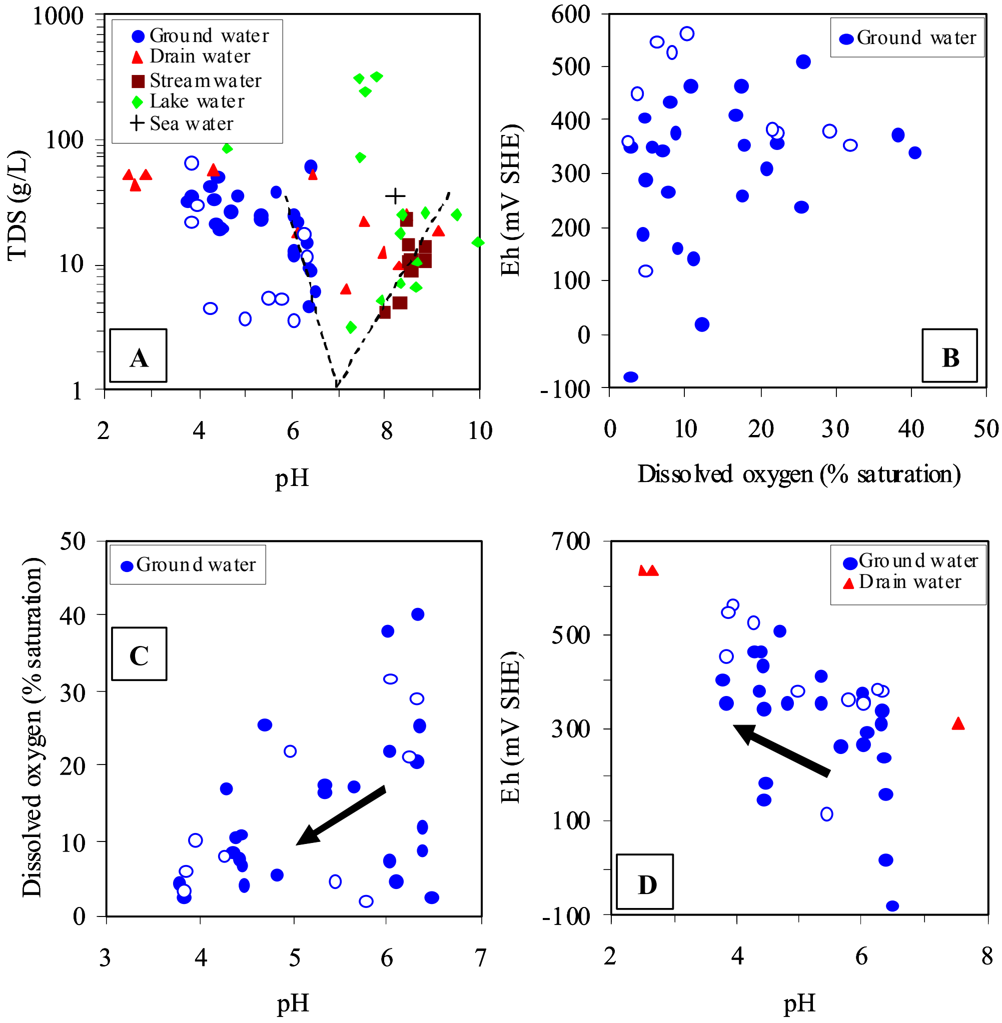


Figure 3-2 Water (A) pH and total dissolved solids (TDS), with a chemical divide suggested by the dashed trend lines; (B) dissolved oxygen and Eh; (C) pH and dissolved oxygen; and, (D) pH and Eh. General trends with decreasing pH are shown with an arrow in (C) and (D). Open symbols represent groundwaters outside the Fence Road subcatchment.

Table 3-1 Description and hydrology of soil-landscape zones in the Avon Province (after Tille et al. 2001; Percy 2000, 2003; Stuart-Street 2003).

Code	Name	Description
250	South-eastern zone of ancient drainage	An ancient, flat to gently undulating plain with palaeo-drainage systems defined by salt-lake chains on Cenozoic alluvial and lacustrine flats in very broad, ill-defined valleys with very low gradients and bound by wide divides and long, gentle slopes; typically shallow texture-contrast soils with sodic, alkaline and calcareous clayey subsoil, and calcareous loamy earths and salt-affected, wet soils on the valley flats. About 7% native vegetation. Local relief <40 m; slope gradients <5%; valley floor gradients <1:500; saprolite thickness 20-60 m; annual surface runoff 20 mm and 4% of rainfall. Groundwater recharges throughout the landscape at rates of 10-50 mm/year (cleared land) into variably confined, intermediate-scale (5-10 km) saprock, pallid-saprolite and sedimentary aquifers with lateral hydraulic conductivities generally 0.01-2.0 mm/year, and at higher rates into local-scale (<5 km) sandy deposits of the sandplains; discharge is generally via capillarity on valley flats, and at the break of slope or as sandplain seeps from local flow systems.
253	Eastern Darling Range zone	A moderately to strongly dissected, ferruginous plateau on granite with minor surficial Eocene sediment; undulating to rolling terrain with perennial streams in relatively narrow, yet broad and shallow, valleys that contain Cenozoic alluvium and become narrower downstream toward major valleys of 30-120 m depth; sandy to loamy ferruginous gravels on plateau remnants, and loamy to sandy ferruginous gravels and loamy texture-contrast soils elsewhere. About 27% native vegetation. Local relief 10-100 m; slope gradients 3-30%; highly variable saprolite thickness; annual surface runoff 60 mm and 10% of rainfall. Groundwater recharges throughout the landscape at rates of 10-150 mm/year into variably confined, intermediate-scale Cenozoic-sedimentary aquifers and fault zones and local-scale saprock and pallid-saprolite aquifers, the saprock having lateral hydraulic conductivities generally 0.5-5.0 mm/year; discharge occurs generally from upslope of dolerite dykes and bedrock highs on hillslopes and in valley floors, and from shear zones, and on slopes from deep ferruginous gravel and Palaeogene sediments, and at the break of slope and as capillary rise on the broader valley flats. Bedrock is more extensively faulted and intruded by dolerite dykes than in the south-western and south-eastern zones of ancient drainage.
257	Southern zone of rejuvenated drainage	Gently undulating rises and low hills with stream channels, which flow at least during winter toward the coast via the Darling Range zone and Swan Province, in broad valleys; active colluviation; sandy to loamy ferruginous gravels on rises and low hills bound by breakaways; deep sandy texture-contrast soils with typically mottled, sodic, neutral to slightly acidic subsoils on slopes and valley flats; grey, salt-affected soils on broad alluvial plains. About 13% native vegetation. Local relief 40-60 m; slope gradients <10%; valley floor gradients <1:250; saprolite thickness <40 m; annual surface runoff 40 mm and 8% of rainfall. Groundwater recharges throughout the landscape at rates of 10-100 mm/year into intermediate-scale sedimentary and local-scale saprock and pallid-saprolite aquifers, the saprock having lateral hydraulic conductivities generally 0.02-2.2 mm/year; discharge is generally

Code	Name	Description
		via capillarity on valley flats, and from local flow systems usually at the break of slope or upslope from dolerite dykes or bedrock highs. Bedrock is more extensively faulted and intruded by dolerite dykes than in the south-western and south-eastern zones of ancient drainage.
259	South-western zone of ancient drainage	An ancient, flat to gently undulating plain on weathered granite and with sluggish, ephemeral drainage systems and lake chains in palaeochannels infilled with Cenozoic alluvial and lacustrine sediments, and uplands dominated by sandy, ferruginous gravels; typically shallow texture-contrast soils with sodic, neutral to alkaline and calcareous clayey subsoils, and salt-affected soils on the broad valley flats. About 9% native vegetation. Hydrological characteristics are as for the South-eastern zone of ancient drainage.

All of the groundwaters are acidic (pH<6.5) whereas the natural surface waters, apart from one low pH lake, are neutral to highly alkaline (Figure 3-2a) and therefore environmentally vulnerable to groundwater incursion. Groundwater pH values as low as four are attained within two distinct ranges in TDS, the lower range in TDS being represented by waters from outside the Fence Road subcatchment. As TDS increases, the pH of groundwaters of intermediate salinity very slightly decreases along a trend line that extends from circum-neutrality. Conversely, the pH of the natural surface waters that are less saline than seawater generally increases with increasing TDS. This divergent trend in pH with water salinisation suggests the existence of a chemical divide between the ground and surface waters, even though all waters have a negative residual carbonate alkalinity ($RA_{CO_3} = Alk_{CO_3} - Ca^{2+} - Mg^{2+}$, in $meq.L^{-1}$, where Alk_{CO_3} = carbonate alkalinity = $HCO_3^- + CO_3^{2-} + OH^- - H^+$, in $meq.L^{-1}$; Figure 3-4a). The presence of a chemical divide is supported by the general divergence of the ground and naturally surficial waters from a pH of ~6.3 with increasing RA_{CO_3} (Figure 3-4a). The groundwaters were strongly effervescent during sampling, but contained low to moderate concentrations of dissolved oxygen (<3.5 mg/L DO; 40 % saturation) and ranged in Eh from slightly negative to highly positive (Figure 3-2b).

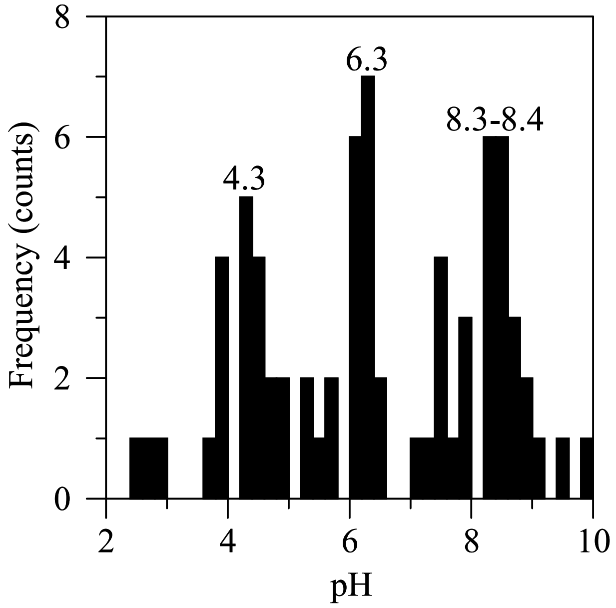


Figure 3-3 Distribution of ground- and surface-water pH values.

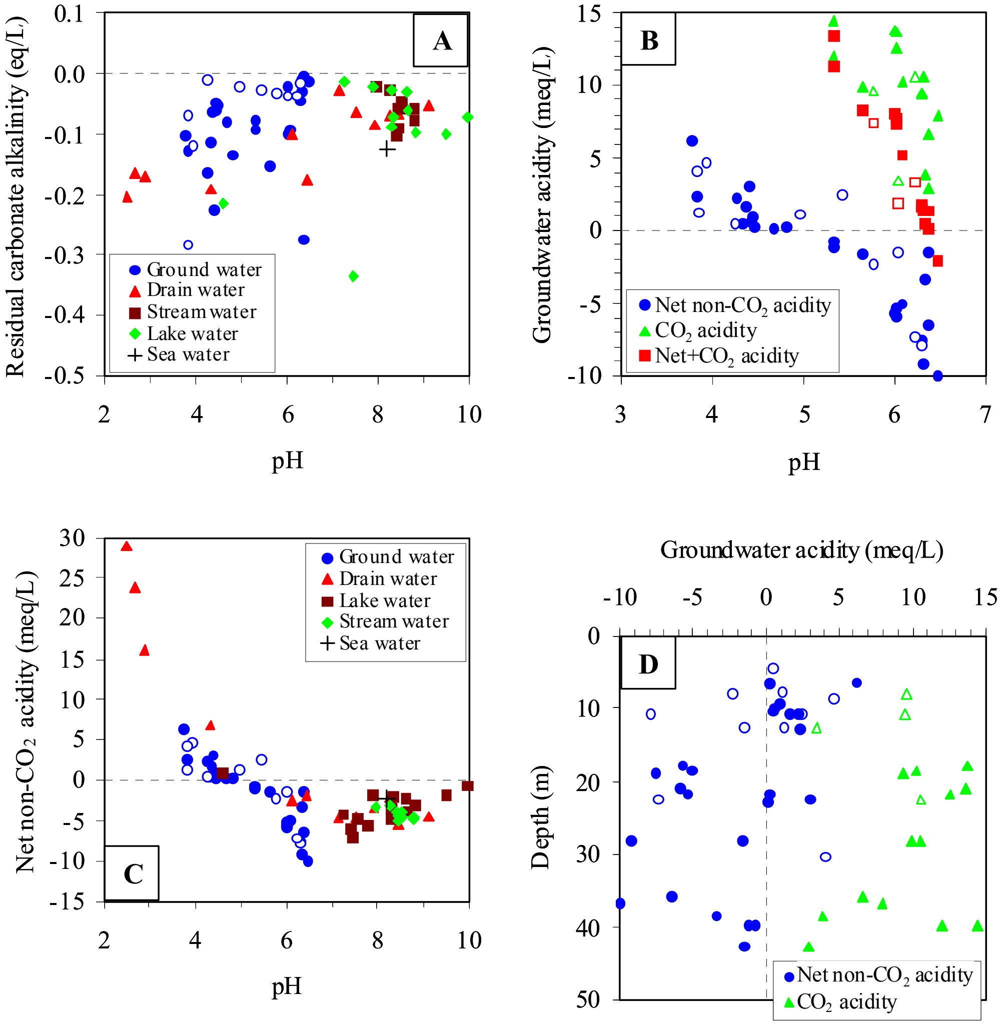


Figure 3-4 Water residual alkalinity and acidity. (A) Variability in $RACO_3$ with pH. (B) Variability in groundwater Acynet and $AcyCO_2$ with pH; the sum of Acynet and AcyCO2 are also shown. (C) Comparison between surface and groundwater Acynet with pH. (D) Acynet and $AcyCO_2$ variability with groundwater depth. Open symbols represent groundwaters outside the Fence Road subcatchment.

The sampled waters are of Na-Cl- or Na-Mg-Cl-type chemistry (Figure 3-5) and, according to element-Cl ratios, their solutes are supplied primarily by cyclic and rock-weathering sources; all waters west of Easting 520 km (GDA, AMG Zone 50) are of Na-Mg-Cl type. The Cl/TDS of all waters (Figure 3-6a) closely matches that of seawater, suggesting that Cl can be used as a conservative reference, whereas Br/TDS is commonly slightly or, in lake waters, much lower (Figure 3-6b) likely due to Br adsorption (cf. Davis et al. 1998). The ratios of dissolved Na, Mg, SO_4^{2-} and Br with respect to Cl are of the same order of magnitude as those in seawater (Figure 3-7 and Figure 3-8), from which these elements are primarily derived (cf. Salama et al. 1993), and suggest that much of the salts, other than gaseous oceanic Cl (Keywood et al. 1997), has accumulated through the intensive evapoconcentration of deposited rainfall. Conversely, aqueous Si/Cl, Al/Cl, Fe/Cl, Mn/Cl, and, at lower salinities and where detectable, HCO_3^-/Cl are substantially larger than those of seawater due to the supply of the metals by secondary-oxide dissolution and of silica, additional Al and Alk_{CO_3} by primary- and/or secondary-silicate hydrolysis. The mean (and median) HCO_3^-/Cl of all groundwaters corresponds with that of seawater (Figure 3-8), but only coincidentally, since the groundwaters include acidic waters with essentially zero alkalinity and relatively dilute (TDS <seawater) waters typically with HCO_3^-/Cl an order of magnitude greater than that in seawater. Groundwater Ca/Cl is typically smaller than that of seawater, suggesting that there has been no major contribution of Ca and Alk_{CO_3} from calcareous dust (cf. Hingston & Gailitis 1976) or that Ca has been immobilized by forward cation exchange or Ca-bearing-mineral precipitation. In comparison, stream and, typically, lake waters have slightly larger Ca/Cl and larger HCO_3^-/Cl ratios than those of seawater, and are saturated with respect to calcite (Figure 3-9a), suggesting a minor contribution of dissolved Ca and HCO_3^- from regolith carbonate minerals in addition to HCO_3^- from silicate hydrolysis. The comparable SO_4^{2-}/Cl of the sampled waters and seawater (Figure 3-7 and Figure 3-8) and the undersaturation of virtually all of the waters with gypsum (Figure 3-9b) indicate that dissolved Ca concentrations in the groundwaters had not been notably depleted by gypsum precipitation.

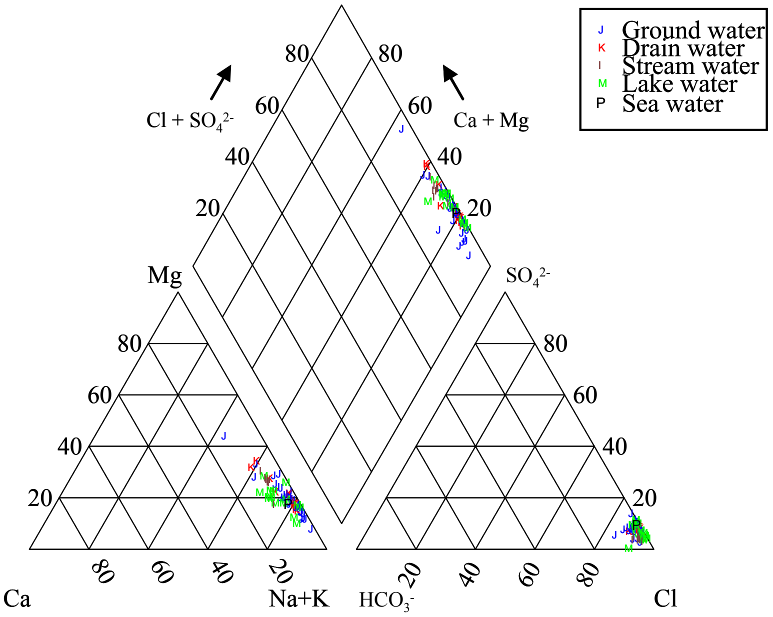


Figure 3-5 Relative major-element composition of waters.

The groundwaters contain dissolved Si at concentrations in the range 5-51 mg/L and, through acidification and consequent silicate-mineral hydrolysis, evolve from the boundary of the feldspar predominance field and into the kaolinite field, and from slight undersaturation into saturation with amorphous silica (Figure 3-10 a and c; note that silica activities were calculated with uncertainty for saline solutions using the Debye-Hückel method). Only two groundwaters sampled from the western part of the catchment are highly undersaturated with amorphous silica. The groundwaters typically also lie in the predominance field of smectite (Figure 3-10b), which is at least a minor constituent (2-10 wt. %) of the aquifer sediments sampled during drilling at bore site 07FR04 and at a depth of 49-50 m at bore 07FR03 (Appendix 3.2; bore locations are given in Appendix 3.1). Conversely, the natural surface waters lie in the predominance field of the primary minerals feldspar or muscovite (Figure 3-10a), and hence secondary illite (Figure 3-10b), and are all distinctly undersaturated with amorphous silica.

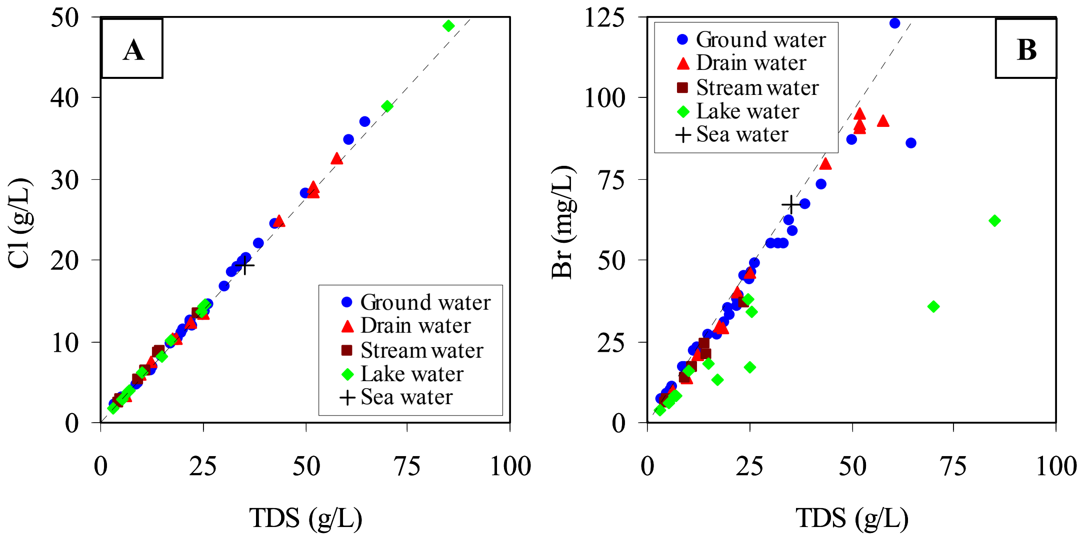


Figure 3-6 TDS versus (A) Cl and (B) Br concentration; the three most saline lake waters (samples SW1-SW3) are not shown.

Groundwater NO_3^-/Cl is substantially larger than that of seawater Figure 3-7g) probably due to an input of NO_3^- from soil biotic activity (e.g. Barnes et al. 1992; Harrington 1999) or, for recently recharged groundwaters, anthropogenic fertilizer (cf. Leys & McTainsh 1999; LWRRDC 1999; Cattle & Elias 2003). The NO_3^- concentration of virtually all samples, though, is typical of background values in groundwaters across Australia (i.e. <2 mg/L; LWRRDC 1999) and groundwater redox-pH relationships (Figure 3-11c) suggest that nitrate reduction (denitrification) takes place in the regolith (Equation 3.1); ammonium nitrification ($NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$) is therefore not a contributor to groundwater acidity. Ammonium concentrations average ~1 mg/L and are <2 mg/L, except for a single groundwater at 19 mg/L, and three acidic drain waters each at about 3 mg/L; stream waters have NH_4^+ concentrations below the detection limit (<0.1 mg/L).

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \qquad (3.1)$$

Groundwater PO_4^{3-}/Cl is variable and K/Cl and typically B/Cl are lower with respect to those of seawater. The relatively low groundwater K/Cl is perhaps due to the depletion of dissolved K via adsorption onto clay minerals (Salama et al. 1999). Groundwater K concentrations could not have been ubiquitously depleted by the precipitation of alunite ($KAl_3(SO_4)_2(OH)_6$; cf. McArthur et al. 1989, 1991) because dissolved SO_4^{2-} concentrations have not undergone a notable loss (Figure 3-7f; cf. Gray 2001). Apart from one groundwater sample with a PO_4^{3-} concentration of 1 mg/L, all waters contain about 0.1 mg/L or less of PO_4^{3-}. Non-purgeable organic carbon (NPOC; ~DOC) is concentrated up to almost 400 mg/L in lake waters whereas ground, drain and stream waters contain typically <25 mg/L NPOC. Most water samples were not analysed for dissolved F concentrations. However, previous analyses of groundwaters in the central wheat belt have shown that F concentrations very commonly exceed the World Health Organization drinking water guideline value of 1.5 mg/L (Shand & Degens 2008).

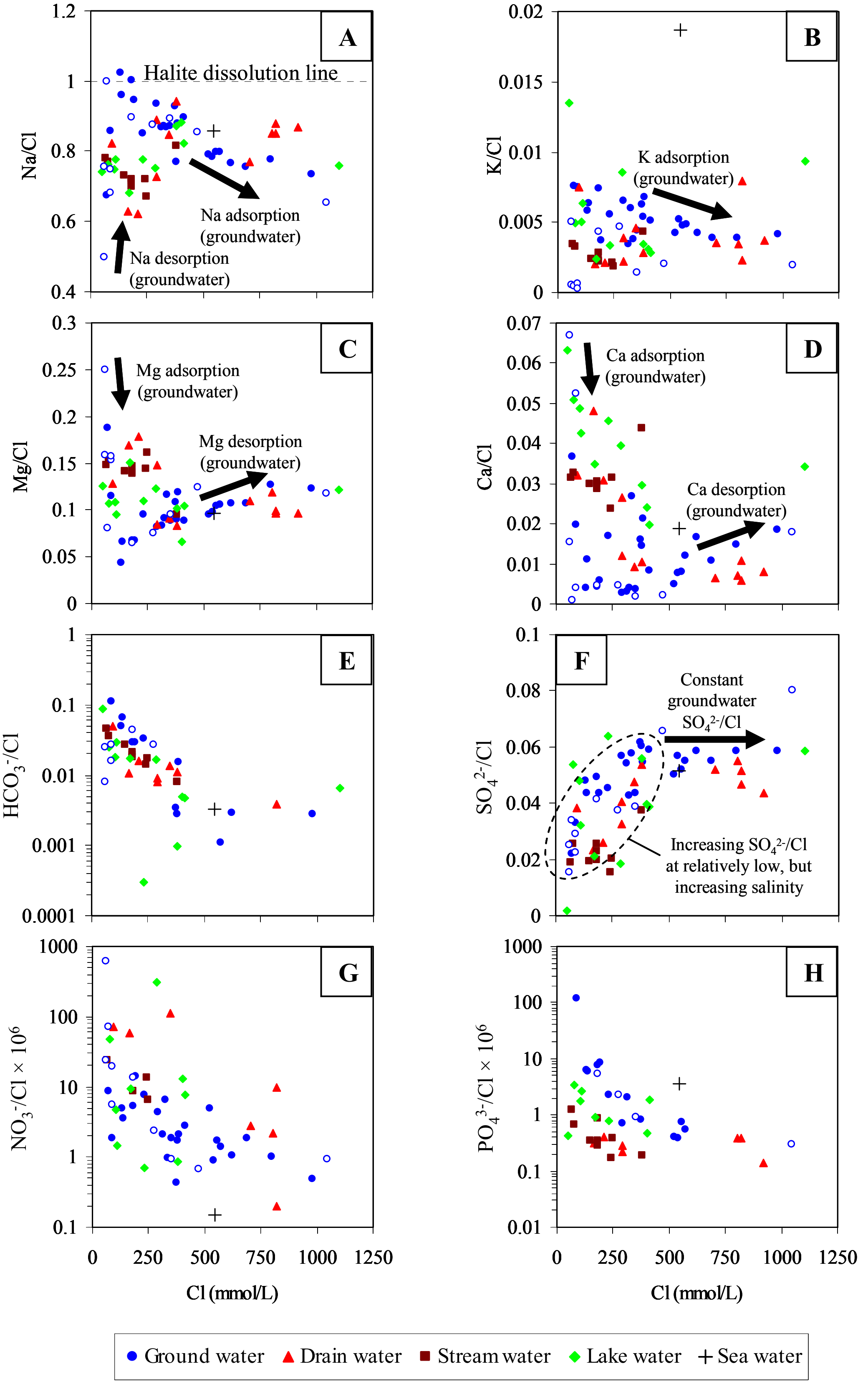


Figure 3-7 Variation in element-Cl molar ratios with increasing Cl concentration. Open symbols represent groundwaters outside the Fence Road subcatchment.

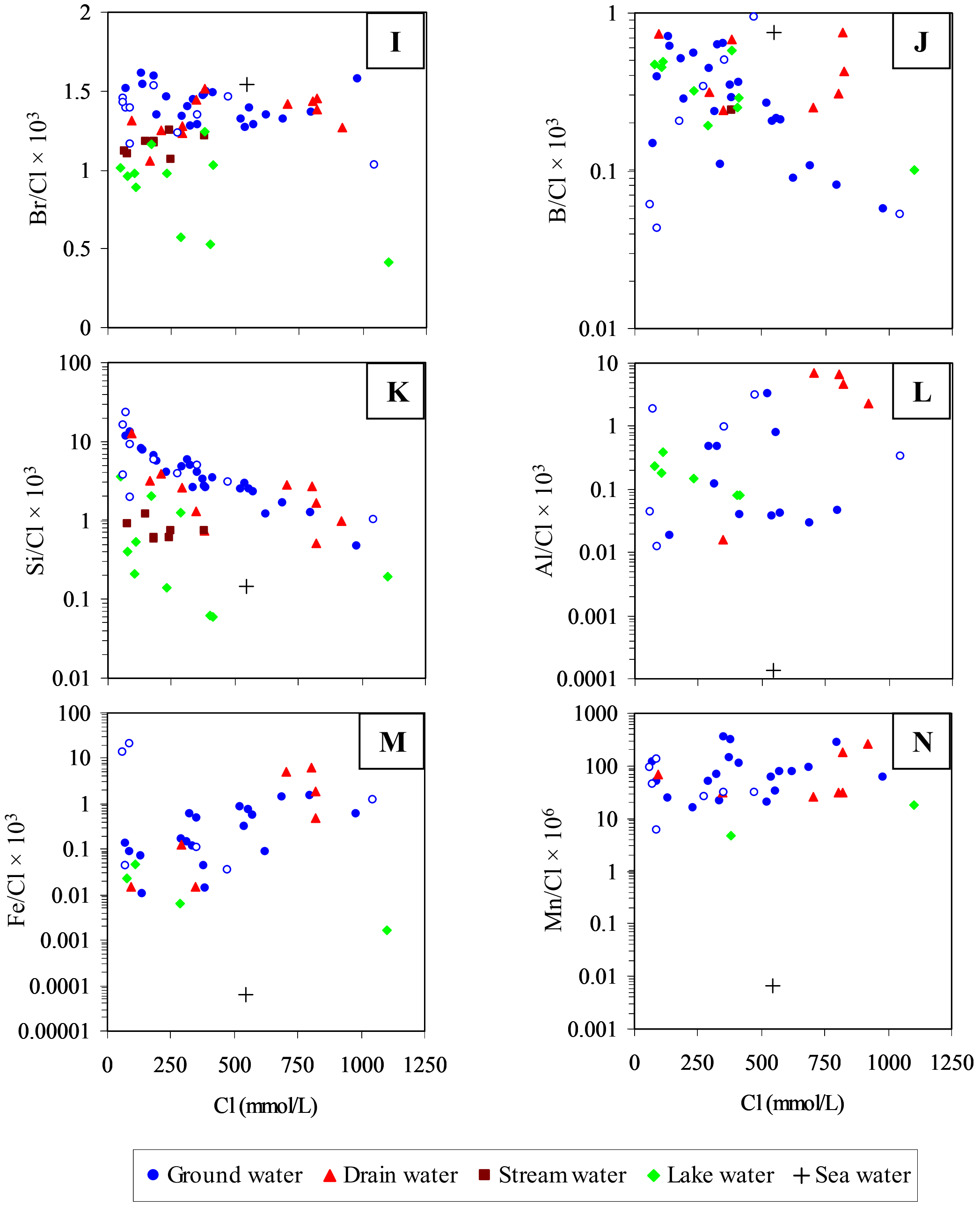


Figure 3.7, continued. Variation in element-Cl molar ratios with increasing Cl concentration. Open symbols represent groundwaters outside the Fence Road subcatchment.

Groundwater chemistry evolves with increasing salinity through cation exchange and, under extreme evapoconcentration, mineral precipitation. The forward exchange of adsorbed Na and K with dissolved Mg and Ca occurs up to a groundwater Cl concentration of about 5 g/L (~0.14 mol/L; TDS ~10 g/L;) beyond which these cations undergo reverse exchange (Figure 3-7) with an increase in ionic strength (cf. Stumm & Morgan 1996). The forward cation exchange at relatively low groundwater salinities indicates that silicate-mineral hydrolysis has not significantly contributed to the total dissolved Na concentration. The ratios Fe/Cl and SO_4^{2-}/Cl increase, and HCO_3^-/Cl, NO_3^-/Cl, PO_4^{3-}/Cl, B/Cl and Si/Cl decrease, with increasing salinity (Figure 3-7) at least partly due to a concurrent decrease in pH and, for Si/Cl, the decrease and increase respectively in the chemical activity of water and silicic acid. The groundwaters are undersaturated with respect to the evaporite minerals calcite, gypsum and halite (Figure 3-9a-c), apart from a single gypsum-saturated sample (TL7). Halite and gypsum had precipitated, at the time of sampling, only in the most saline lakes and these minerals were observed in abundance in the Fence Road drain waters. The other surface waters are undersaturated with respect to these minerals, although the constant stream-water molar Ca^{2+}/SO_4^{2-} of near unity (Figure 3-9b) and the increase in degree of undersaturation toward the west suggest that these waters are influenced by gypsum dissolution in the eastern part of the catchment. Virtually all of the surface waters, including those in drains, are at or above calcite saturation and tend toward a saturation index of about +1 by an influence other than low-Mg calcite. Comparable with gypsum saturation, the stream waters decrease in their degree of calcite supersaturation toward the west.

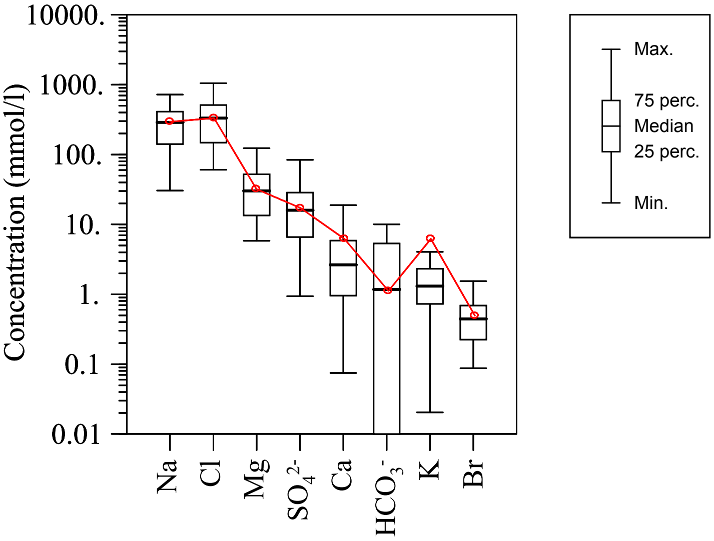


Figure 3-8 Box plot of groundwater major-element molar concentrations, including their quartiles, range and median. The ion concentrations in seawater, normalized to the median Cl concentration in the groundwaters, are shown in red.

A progression through the pH range of 2.5-10 encountered in the sampled waters coincides with a systematic change in the concentration of many elements. The ratios of dissolved Be, Fe, Co, Ni, Zn, Pb, Y and the lanthanides (rare-earth elements) with respect to Cl (and TDS) generally increase by two or more orders of magnitude with decreasing water pH (Figure 3-12). Conversely, groundwater Si, Ni, Se, Br, HCO_3^-, PO_4^{3-} and, in the Fence Road subcatchment, K, Ca, Mg and SO_4^{2-} ratios with Cl (and TDS) decrease with decreasing pH. Groundwater SO_4^{2-}/Cl increases with increasing salinity as the pH of many waters remains essentially constant at about pH 6.0-6.5, but this ratio remains steady in the more saline waters as they decrease in pH toward a value of ~4. The Mn/Cl and Al/Cl of all waters peak and trough, respectively, at a pH of about 5.5 and Si/Cl, HCO_3^-/Cl, Br/Cl and PO_4^{3-}/Cl peak at a pH of about 6-6.5. The lower ratios on the high-pH side of the peak in dissolved Si/Cl suggest the occurrence of Si adsorption or, as is consistent with the mineral-predominance diagram in Figure 3-10a, lesser or no silicate-mineral hydrolysis. The maximum adsorption of silica onto goethite (and similar minerals) occurs at pH 9 (e.g. Hiemstra et al. 2007) and apparently outweighs the increase in silica solubility at pH >8 caused by the dissociation of silicic acid.

The chemistry of the waters changes with distance from the coast in response to systematic variations in climate, landscape relief, regolith thickness, cyclic-salt accumulation, land clearing and the mobilization of stored salts (cf. Morrissy 1974;

Tille et al. 2001). The TDS of flowing stream and drain waters decreases from the east-northeast and toward the coast (Figure 3-13a, and b) where rainfall and runoff are greater and evaporation rates are lower. The westerly decrease in TDS, at the time of sampling, occurred at twice the rate and from twice the magnitude as that calculated using the February 1974 electrical conductivity values and conversion factor (i.e. $TDS_{g/L} = 0.62 \times EC_{dS/m}$) of Morrissy (1974; cf. Mayer et al. 2005); the stream-water TDS and EC of the present study are also related by a factor of 0.62.

The molar ratios Na/Cl, K/Cl and SO_4^{2-}/Cl are generally lower, and Mg/Cl and Ca/Cl higher, in surface and ground waters in the western portion of the sampling area (Figure 3-13); the sodium adsorption ratio is therefore also lower in the west. This geographic variability in water composition indicates that the chemical evolution of groundwaters, and thus perhaps the processes and rates of groundwater acidification, differ significantly across the region. The distribution of sampled groundwaters is insufficient to confirm any spatial trends in TDS and pH, but suggests a decrease in TDS and, perhaps, an increase in the minimum pH toward the west (Figure 3-13and c). However, groundwaters of low pH (<5.5) exist across the sampled region (Figure 3-1).

3.2.2. Fence Road subcatchment

Spatial trends in the field-measured chemistry of groundwaters in the Fence Road catchment highlight the relatively shallow depths at which acidification takes place and the existence of a halocline (vertical salinity gradient). In profile, the groundwater pH decreases toward the land surface (Figure 3-14b; cf. general increase in acidity in Figure 3-4d) as Eh increases (Fig. 3.14C; note that samples 98FR112I and 98FR112S are from broken piezometers that contained backfilled topsoil bearing organic matter) and DO concentrations decrease and then commonly increase (Figure 3-14d). Low-pH (pH <5.5) groundwaters are generally restricted to depths <25 m, although they have been found at a depth of 40 m, whereas groundwaters of pH 6-6.5 are common, yet restricted to depths >18 m. The TDS also decreases toward the profile surface (Figure 3-14a), forming a density gradient. From the divide to the outlet of the catchment, though, salinity increases (EC in **Figure 3-15**d, which closely correlates with TDS; Figure 3-14a Figure 3-16a) as pH decreases (Figure 3-14b, Figure 3-15e and Figure 3-16b) and groundwater levels generally decrease in depth (**Figure 3-15**c).

Preferential recharge into Cenozoic alluvium, comprising primarily quartz sand and clay minerals, has resulted in groundwater mounding and strongly influences the flow and chemistry of groundwaters within the Fence Road catchment. The impact of preferential recharge is evident in a down-valley transect along Kukerin Gully, parallel to Springhurst Road, in which a groundwater mound's peak coincides with the uppermost occurrence of sediments that occupy the central to lower portions of the valley (Figure 3-17a; see Figure 3-15a for Springhurst Road location; existing piezometers are inadequately positioned for a study transect parallel to Fence Road). The sediments have higher saturated hydraulic conductivities (HC_{sat} = 0.21±0.06 m/day, n = 3) than the very highly weathered saprolite (HC_{sat} = 0.02±0.01 m/day, n = 3; cf. saprolite grit HC_{sat} = 0.08±0.02 m/day, n = 5; Whitfield 1999) and define an intermediate-scale groundwater flow system of <20 km in length. Recharge must be either very localized on the valley floor or restricted to the adjacent hillslopes as suggested by automated groundwater-level monitoring in a transect that extends from the groundwater mound at piezometer 07FR02 to the northern valley-floor margin. The sedimentary aquifer at this site has a barometric cumulative response that increases toward a short lag time (Figure 3-18), which is indicative of confined

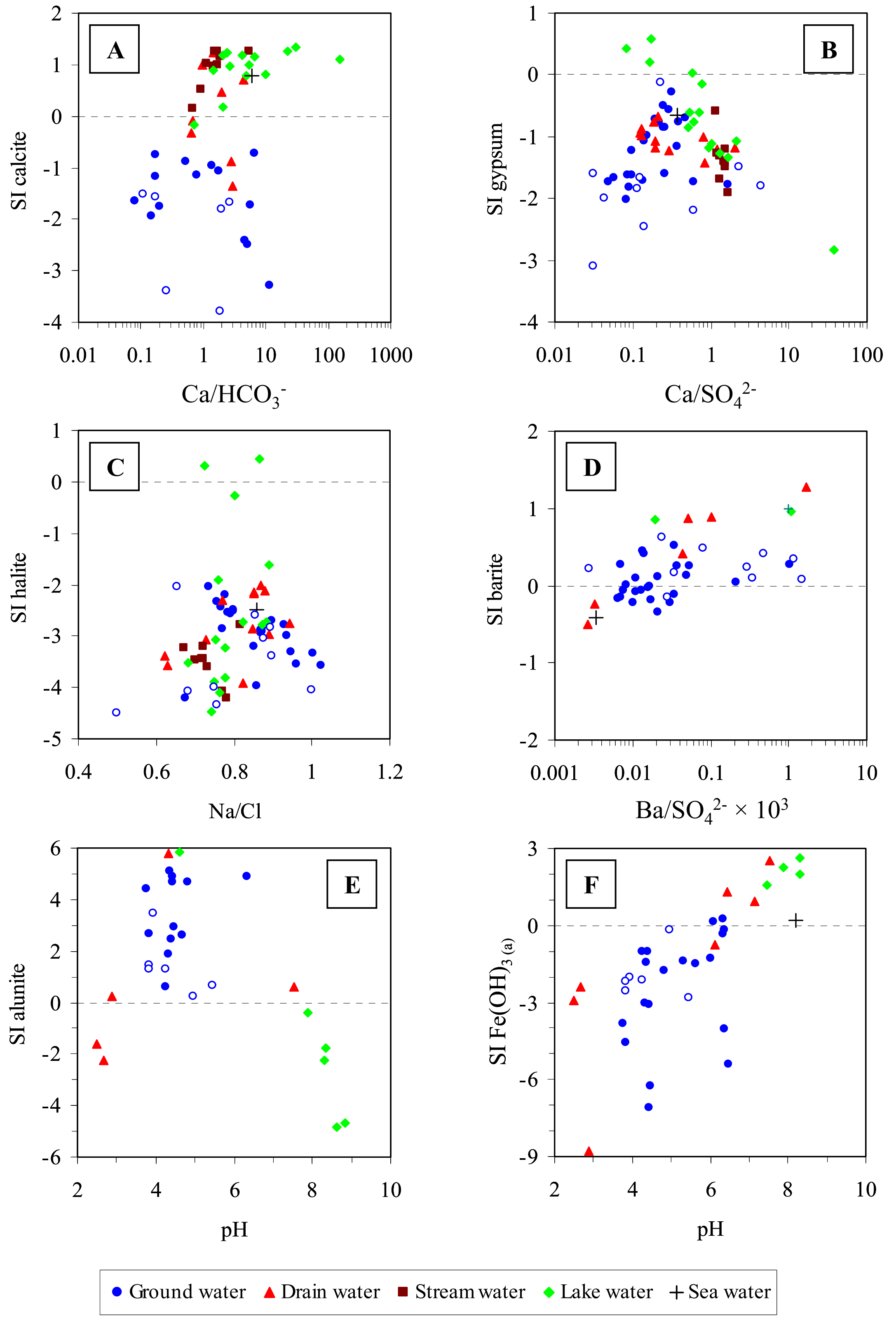


Figure 3-9 Saturation indices of (A) calcite, (B) gypsum, (C) halite, (D) barite, (E) alunite, and (F) $Fe(OH)_{3\ (a)}$, calculated using PHREEQC, and its accompanying pitzer database for (A) to (C) and phreeqc database for (D) to (F), and plotted against molar-ion ratios or pH. Open symbols represent groundwaters outside the Fence Road subcatchment.

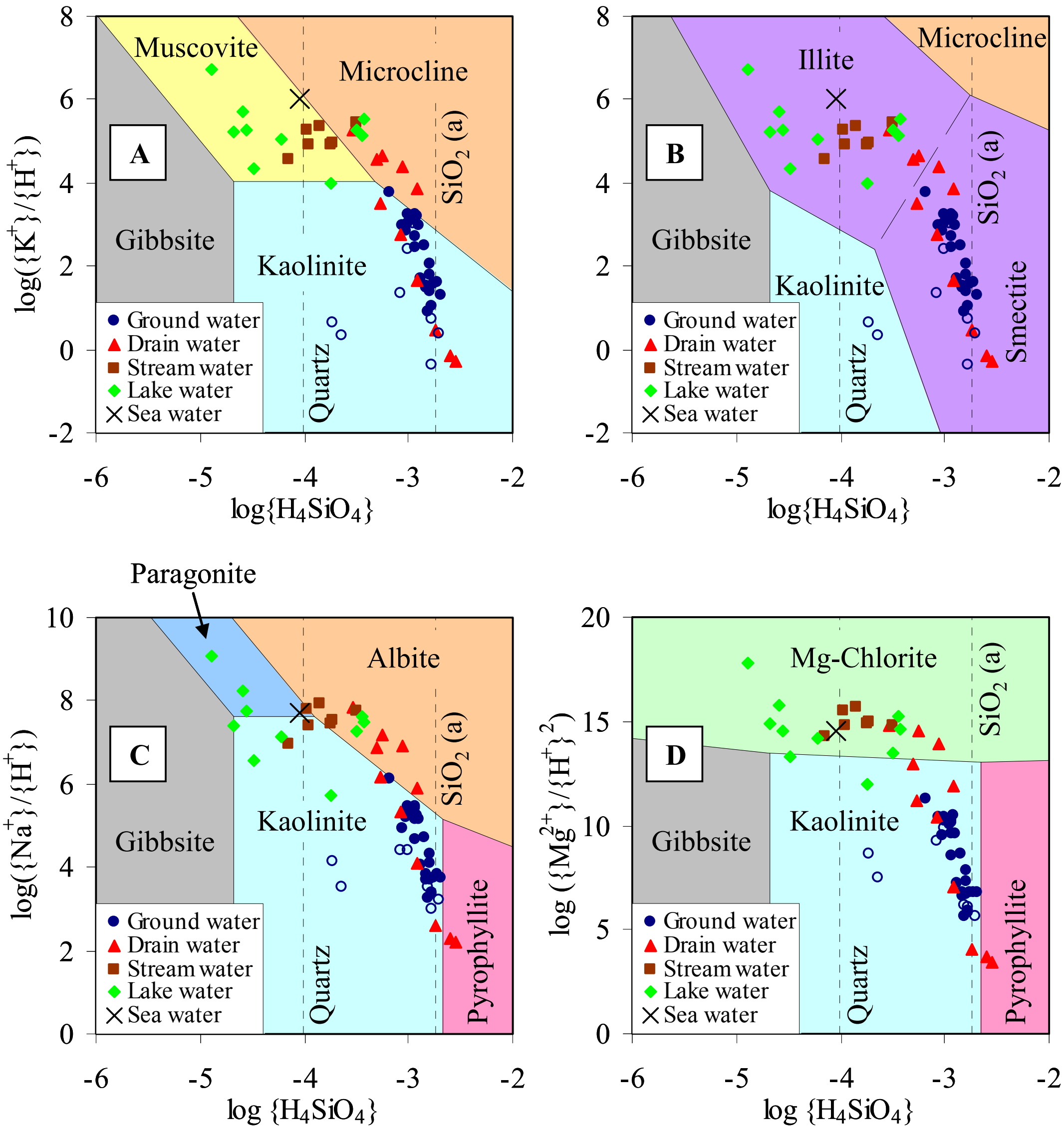


Figure 3-10 Logarithmic ion-activity diagrams of the systems (A) & (B) K_2O-Al_2O_3-SiO_2-H_2O, (C) Na_2O-Al_2O_3-SiO_2-H_2O, and (D) MgO-Al_2O_3-SiO_2-H_2O, at 25° C, 1 bar and unit H_2O activity. Activities were calculated using PHREEQC with phreeqc.dat (i.e. Debye-Hückel method) although the ionic strength of most waters is >0.1 M. Stability boundaries were calculated using thermodynamic data from Faure (1998) and, for theoretical discrete illite ($K_{0.8}Al_{1.9}(Si_{3.5}Al_{0.5})O_{10}.(OH)_2$) and smectite ($K_{0.3}Al_{1.9}Si_4O_{10}.(OH)_2$) in (B), Garrels (1984). Open symbols represent groundwaters outside the Fence Road subcatchment.

conditions along with borehole storage and/or skin effects (see Rasmussen & Crawford 1997; Spane 2002; Toll & Rasmussen 2007). The presence of the groundwater mound indicates that localized recharge causes the reverse flow of groundwater toward the more elevated portions of the catchment where mixing could potentially occur with virtually stagnant, anoxic (<3% saturation with DO) groundwater of negative Eh (-78 mV SHE) and notable dissolved NH_4^+, NPOC, H_2S (pungent odour), HCO_3^- and PO_4^{3-} and relatively low Fe, SO_4^{2-} and NO_3^- concentrations (sample 20061594, Figure 3-17a).

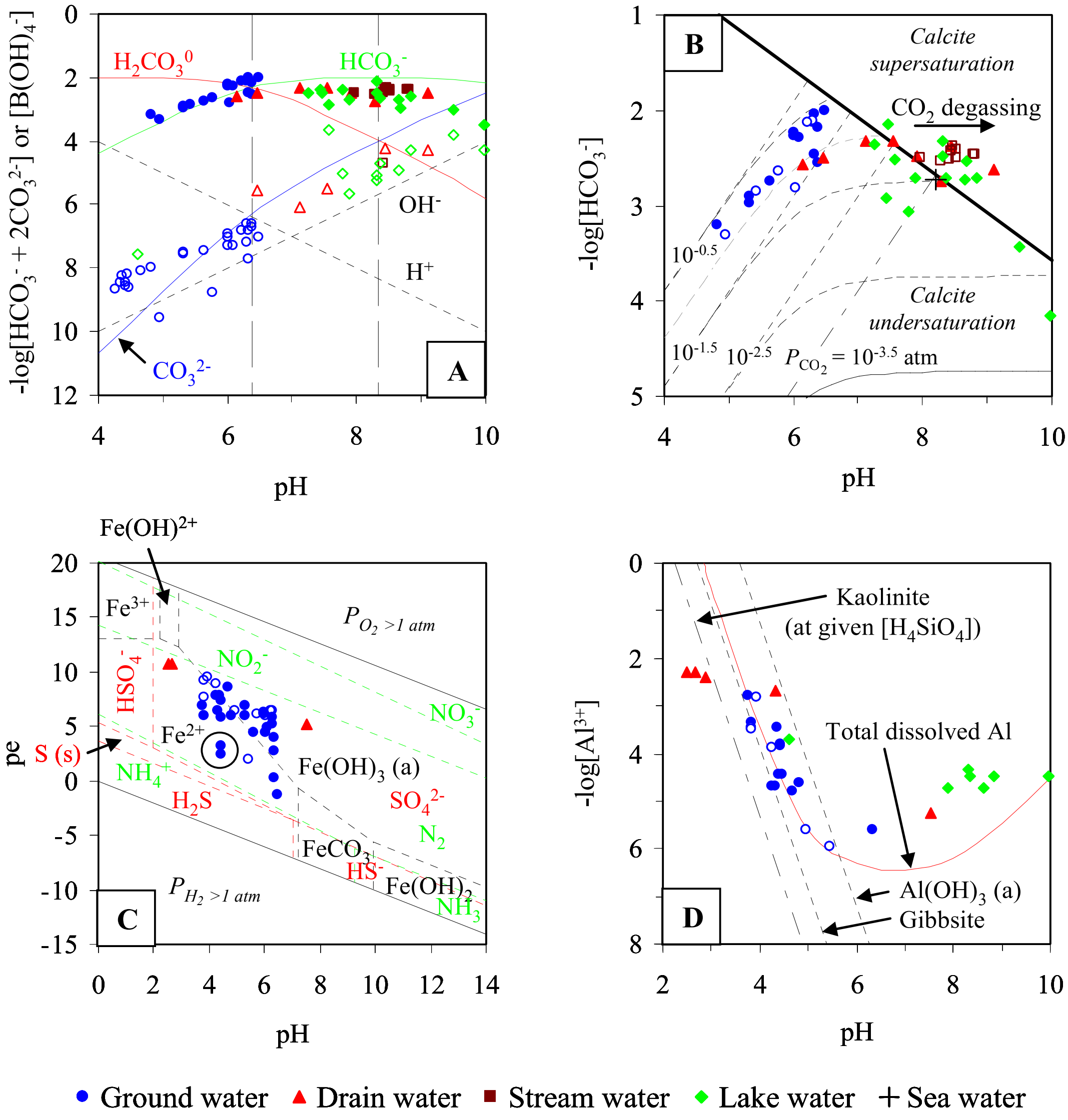


Figure 3-11 Changes in logarithmic solute molar concentrations [] and pe in ground, drain, stream and lake waters with pH; equilibrium and predominance-boundary lines for various solutes and minerals are shown for 25° C and 1 atm (after Stumm & Morgan). (A) [HCO_3^- + $2CO_3^{2-}$] (closed symbols) and [$B(OH)_4^-$] (open symbols); theoretical lines of $H_2CO_3^0$ (red), HCO_3^- (green), CO_3^{2-} (blue), H^+ and OH^- (black) concentrations for a CO_2-H_2O system closed to CO_2 (g) and at a total C concentration of 10^{-2} M and unit H_2O activity are shown for comparison. (B) [HCO_3^-]; lines of constant P_{CO_2} for CO_2-H_2O systems open (straight dashed lines) and closed (curved dashed lines) to CO_2 and the calcite saturation (solid) line, all adjusted for the salinity of seawater (i.e. TDS of 35 ‰), are shown. Stream waters are shown as an open symbol for clarity. (C) pe - pH diagram of the system Fe-CO_2-H_2O at [Fe^{2+}] = [Fe^{3+}] = $10^{-5.0}$ M and C_{total} = 10^{-2} M. Predominance fields for S and N are also shown: S_{total} = 10^{-2} M; [NO_3^-] = [NH_4^+] = 10^{-3} M; P_{N_2} (in atm equilibrium) = 0.77 atm. Note that all waters are well within the Mn^{2+} predominance field (not shown). The two low pH, low pe groundwaters (circled) were from broken piezometers that contained backfilled topsoil. (D) [Al^{3+}]; also shown are saturation lines for kaolinite, at log[H_4SiO_4] = -3 M, crystalline (gibbsite) and amorphous $Al(OH)_3$ (s), and total dissolved Al (i.e. Al^{3+} + $AlOH^{2+}$ + $Al(OH)_2^+$ + $Al(OH)_3$ (aq) + $Al(OH)_4^-$) at unit H_2O activity. Open symbols in (B) - (D) represent groundwaters outside the Fence Road subcatchment.

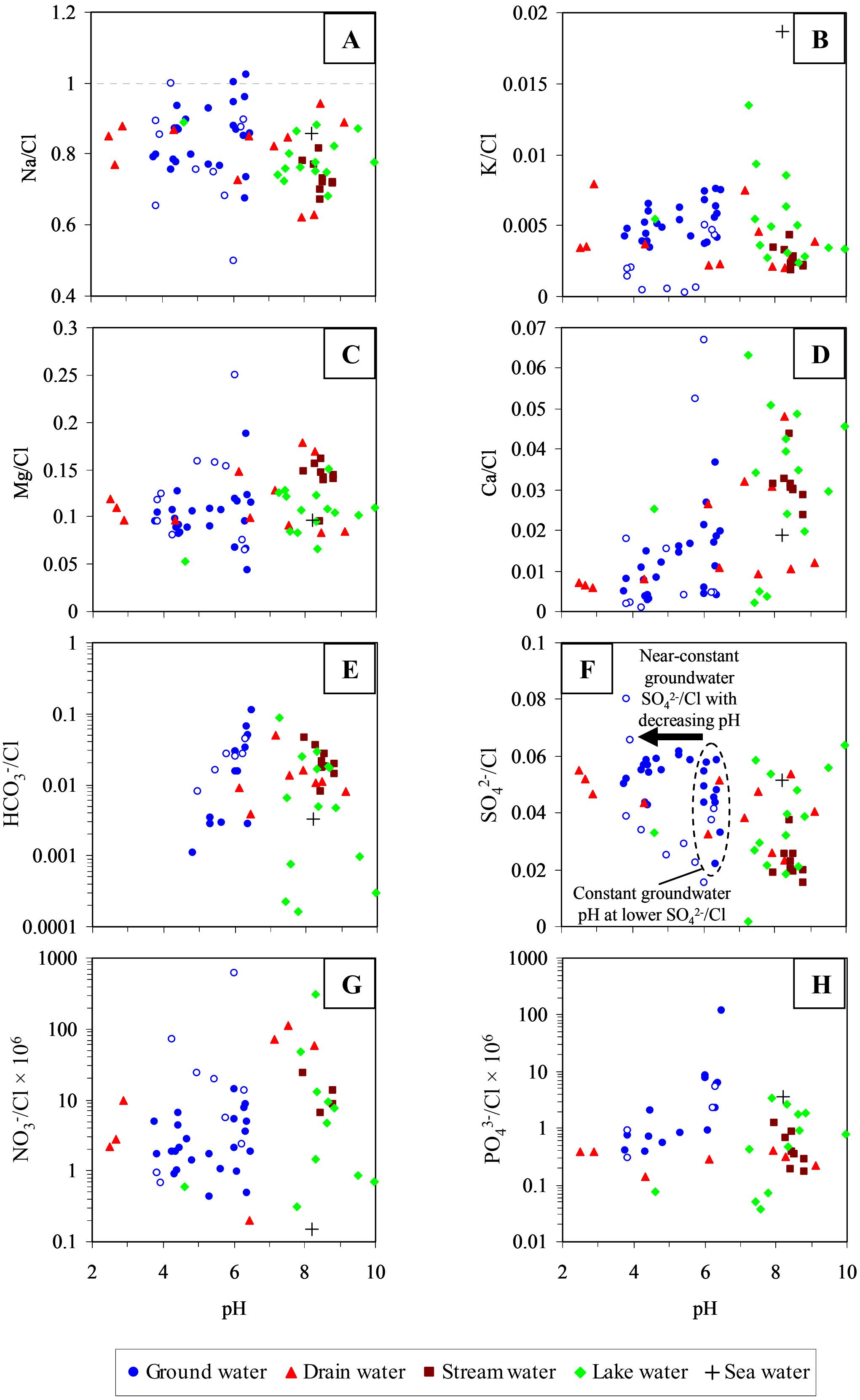


Figure 3-12 Variation in element-Cl molar ratios with pH; open symbols represent groundwaters outside the Fence Road subcatchment.

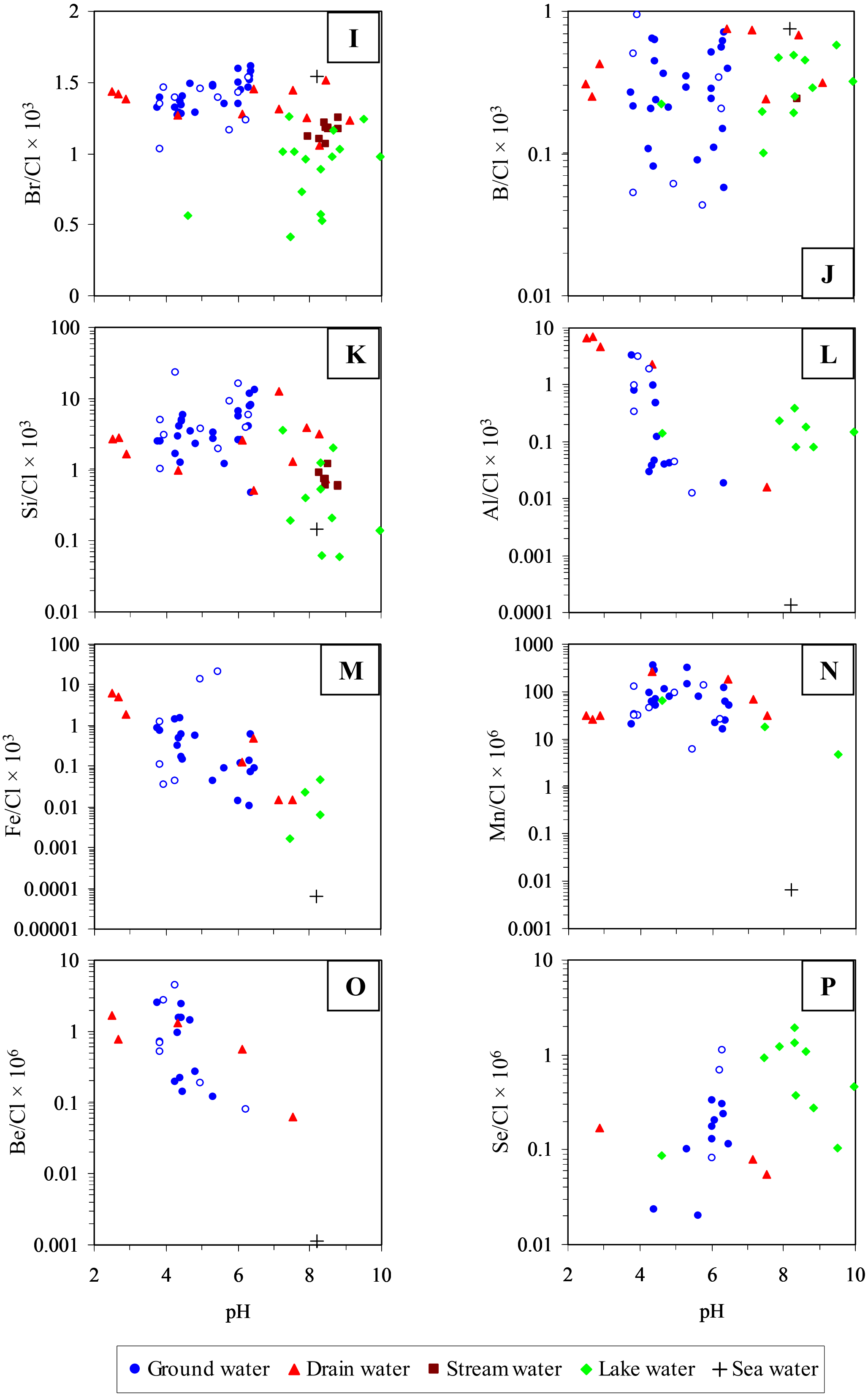


Figure 3.12, continued. Variation in element-Cl molar ratios with pH; open symbols represent groundwaters outside the Fence Road subcatchment.

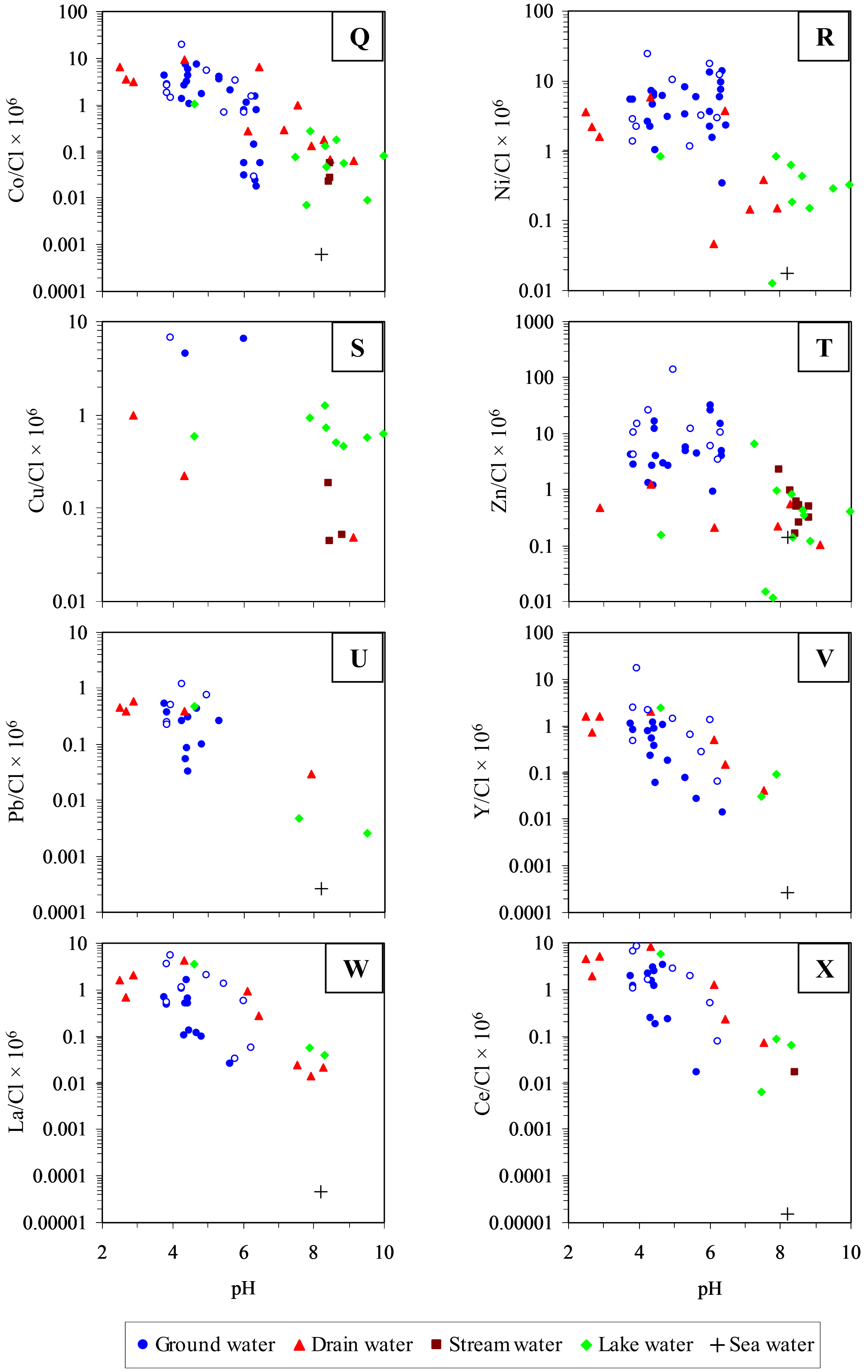


Figure 3.12, continued. Variation in element-Cl molar ratios with pH; open symbols represent groundwaters outside the Fence Road subcatchment.

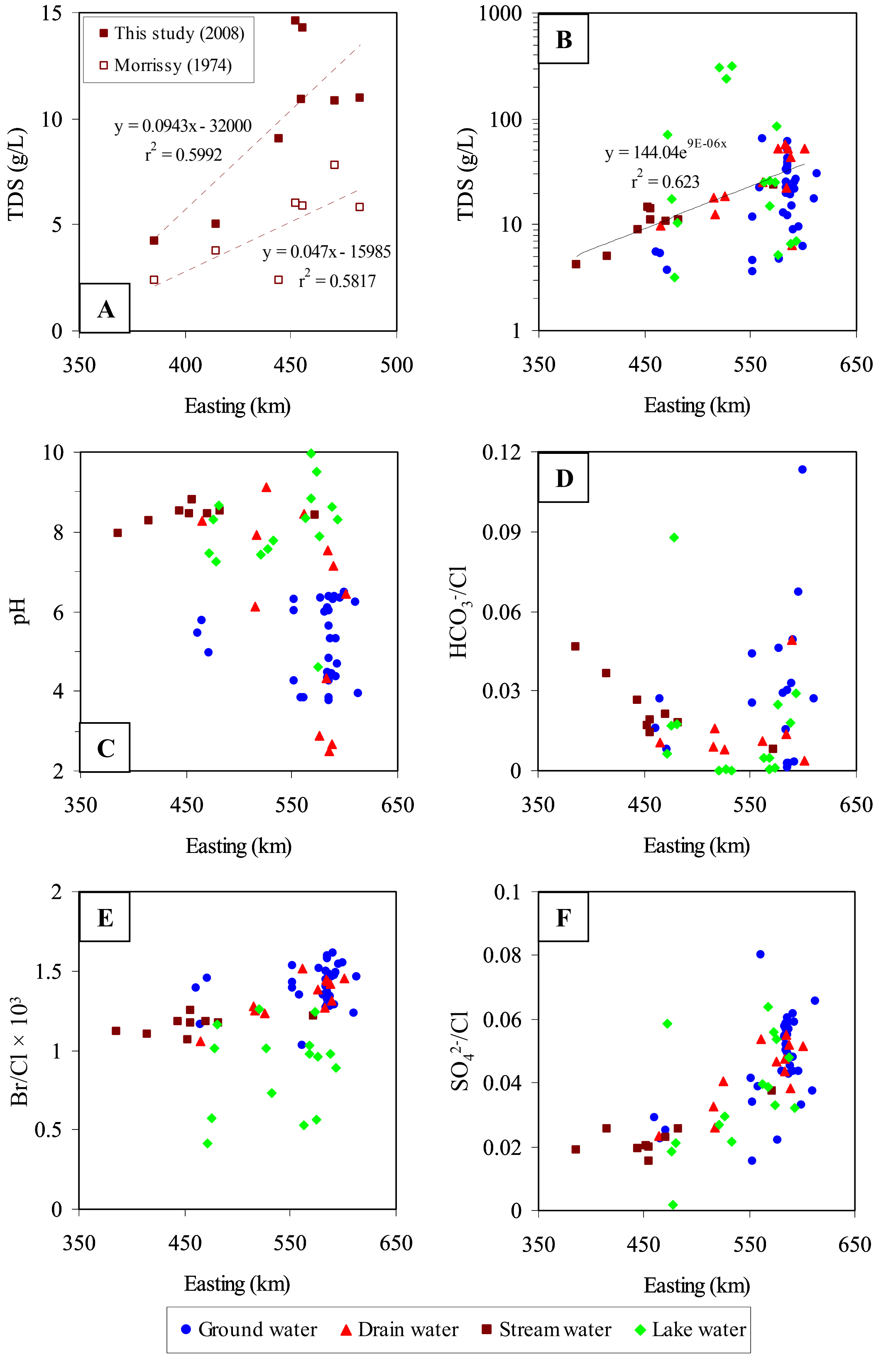


Figure 3-13 Change in surface- and ground-water chemistry with distance from the coast. (A) Salinity along the Blackwood River, from Nannup (southwest) to Eulin Crossing Road, and its tributary Arthur River at Moodiarrup Bridge (northeast). (B) Salinity of all waters, with a trend line (approximated by y = 0.1945x – 77732, r^2 = 0.5476) fitted to the stream and drain waters. (C) Water pH, and (D)-(F) molar element-Cl ratios.

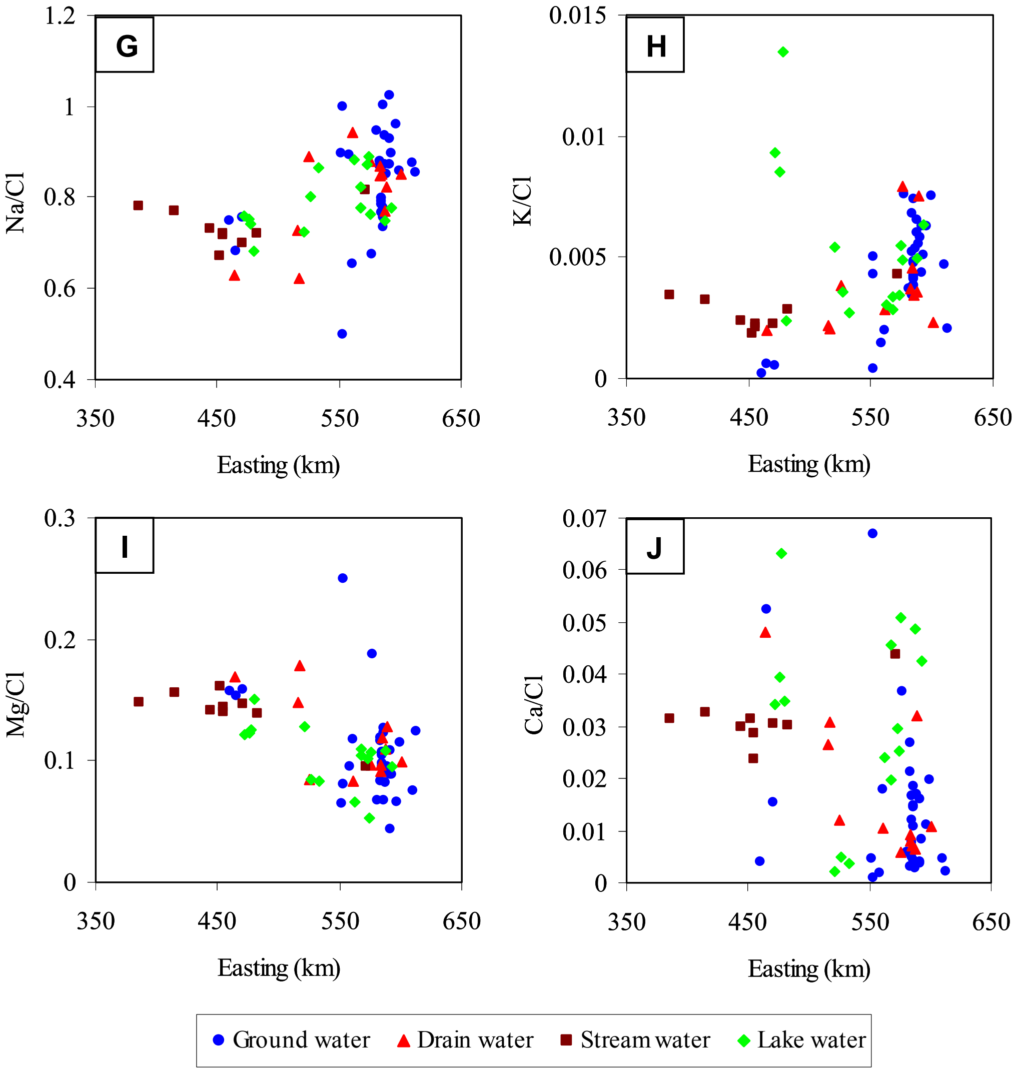


Figure 3.13 continued. Change in surface- and ground-water chemistry with distance from the coast. (G)-(J) molar element-Cl ratios.

The chemistry of groundwater in the sediments has evolved in response to preferential recharge. Groundwater salinity decreases slightly at and immediately down gradient from the crest of the recharge mound, but is still more than twice that of groundwater in the saprolite aquifer further up the catchment (Figure 3-17b). The valley floor, though, has accumulated salts during at least the Neogene and Quaternary, especially during previous phases of groundwater discharge (cf. George et al. 2008b) and by the direct deposition and evapoconcentration of cyclic salts. The recharge mound and sediments coincide with the existence of low-pH (<5.5) groundwater (**Figure 3-15**e and Figure 3-17b) with high Fe/TDS ratios and low DO concentrations compared to groundwater in the saprolite (e.g. Figure 3-17). Thus, the preferential recharge of oxic water into relatively permeable sediments directly promotes the lowering of groundwater pH in this catchment by Fe oxidation and hydrolysis, but these processes are limited due to the depletion of DO (Equations 3.2 & 3.3; Kirby et al. 2009).

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \qquad (3.2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\ \text{(amorphous/crystalline solid)}} + 3H^+ \qquad (3.3)$$

Groundwater in the sedimentary aquifer has relatively high Cl/TDS and low Br/TDS, Ca/TDS and SO_4^{2-}/TDS ratios. The groundwaters are undersaturated with respect to gypsum (Figure 3-9b), but possibly oversaturated with alunite (Fig. 3.9E; cf. McArthur et al. 1991; however, the samples were filtered using 0.45 µm membranes and hence may have contained particulate Al), although neither have been found in the regolith at discharge sites (Appendix 3.2). The Cl and Br ratios with TDS suggest that halite dissolution, or Br adsorption (cf. Davis et al. 1998) combined with the precipitation of non-chloride minerals, has occurred within the sedimentary aquifer.

Dissolved hydrolysable metals, particularly Fe and Al and not Mn, are sufficiently concentrated at only relatively shallow depths to enable the lowering of groundwater pH by metal oxidation (Fe only) and hydrolysis (e.g. Equations 3.2-3.4; Mann 1983; Shand & Degens 2008):

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (3.4)$$

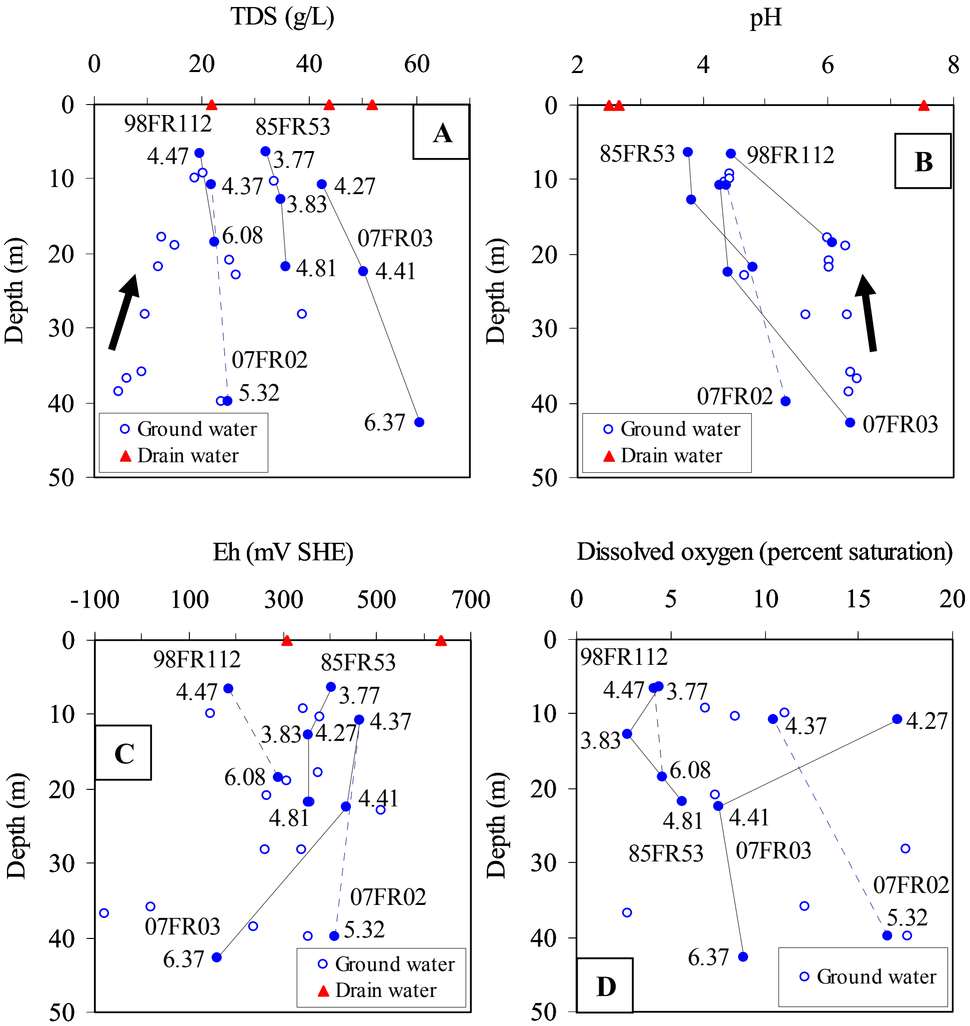


Figure 3-14 Changes in (A) TDS, (B) pH, (C) Eh, and (D) dissolved oxygen with groundwater depth in the Fence Road subcatchment. Data from nested piezometers, which are labelled, are shown as filled circles with adjoining solid or dashed (for visual distinction) lines. The pH values of samples from nested piezometers are labelled in (A). The arrows in (A) and (B) show down-catchment trends of groundwater from non-nested piezometers.

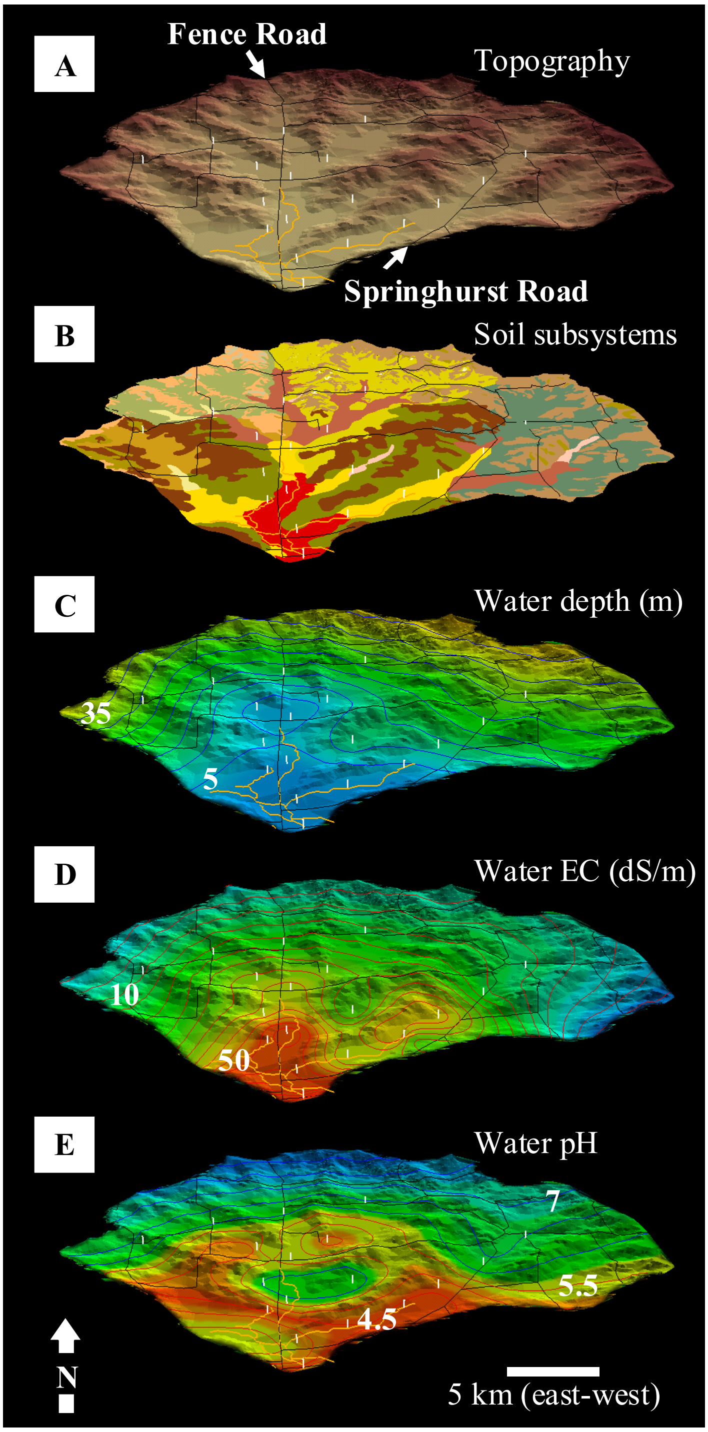


Figure 3-15 Three dimensional oblique views, from the south, of the Fence Road subcatchment vertically exaggerated 10 times and constructed with ArcView© 3D Analyst using a triangulated irregular network of surface topography (2 m contours). Shown are (A) landscape, (B) soil subsystems, which are saline in broad valley plains (southern red and yellow units; Percy 2000), and groundwater (C) depths with 5 m contours (blue zone is <5 m below the surface), (D) EC with 5 dS/m contours (deep orange zone is >50 dS/m), and (E) pH with 0.5 unit contours (red contours are pH 5.5 and less; the western extension of the acidic zone is an artefact of having no boundary data); selected contours are labelled. Groundwater bores and piezometers (white vertical lines), drains (orange lines) and roads (black lines) are also shown. The scale bar is strictly for an east-west direction only as the images are oblique views.

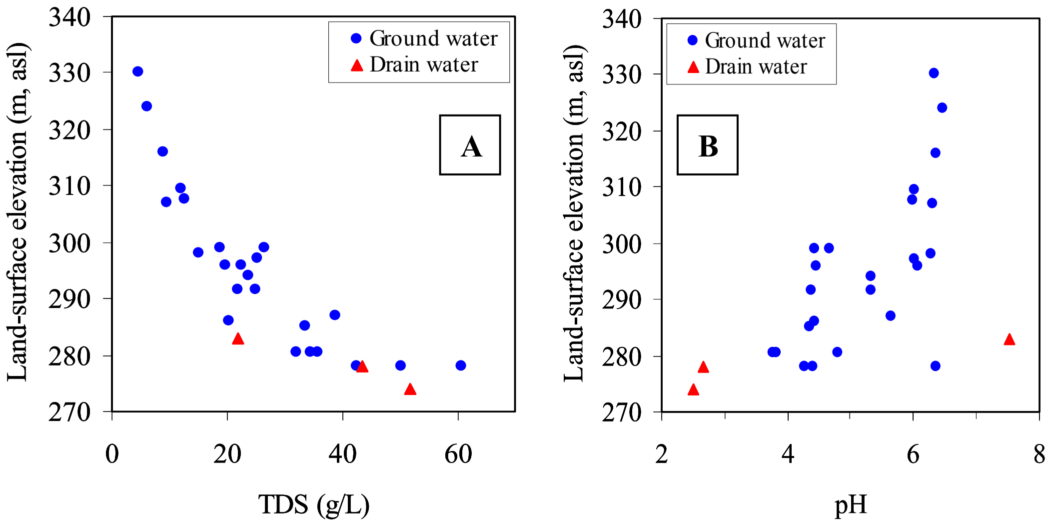


Figure 3-16 Changes in (A) TDS and (B) pH with land-surface elevation in the Fence Road subcatchment.

The shallower groundwaters have a pH <5 (Figure 3-14 and **Figure 3-15**e) and, correspondingly, relatively high dissolved Al and Fe concentrations (cf. pH in Figure 3-12 l and m), which result in a positive net potential non-CO_2 acidity (Figure 3-4b-d). In contrast, the deeper groundwaters have a pH >5 (Figure 3-14b and **Figure 3-15**e), low dissolved Al, Fe and Mn concentrations (cf. pH in Fig. 3.12L-N) and a negative Acy_{net}. These deeper waters therefore cannot significantly change in pH by oxidation and hydrolysis, as shown by the results of modelling using PHREEQC (see Table 3.2). Moreover, if mixing occurred with recharging groundwater of relatively low CO_2 partial pressure (P_{CO_2}), the deeper waters could undergo CO_2 degassing and a consequent increase in pH (Equations 3.5 & 3.6) potentially to values >6.3 (i.e. pK_1 for Equation 3.7; Table 3.2; cf. Kirby & Cravotta 2005; Kirby et al. 2009).

In a typical intensely weathered Western Australian regolith profile, comprising ferruginous overlying mottled and, in turn, bleached zones (e.g. Anand & Paine 2002; Anand et al. 2002), the groundwaters can source significant amounts of Fe from only relatively shallow depths by the dissolution of secondary Fe-bearing minerals. To potentially become acidified, the deeper groundwaters would therefore have to mix with shallower Fe-bearing waters or ascend in order to dissolve Fe-bearing minerals and to acquire DO from recently recharged, oxic groundwater or the vadose zone. Groundwater in the middle to lower reaches of the Fence Road catchment could ascend as it has a vertically upward hydraulic gradient of ~1 cm/m (average of four middle- to lower-catchment sites, after pressure-head normalization to freshwater density as suggested by Post et al. 2007) and, although largely to completely confined below a depth of about 10 m, hydraulic heads that are within a few metres of the sporadically salt-scalded land surface (**Figure 3-15**c). In addition, all but two (private and 98FR112I, the latter affected by piezometer damage) of the sampled groundwaters are undersaturated with respect to $Fe(OH)_{3\ (a)}$ (using phreeqc.dat; Figure 3-9f) and are therefore thermodynamically able to dissolve this compound, even without the aid of organic ligands or the onset of reducing conditions.

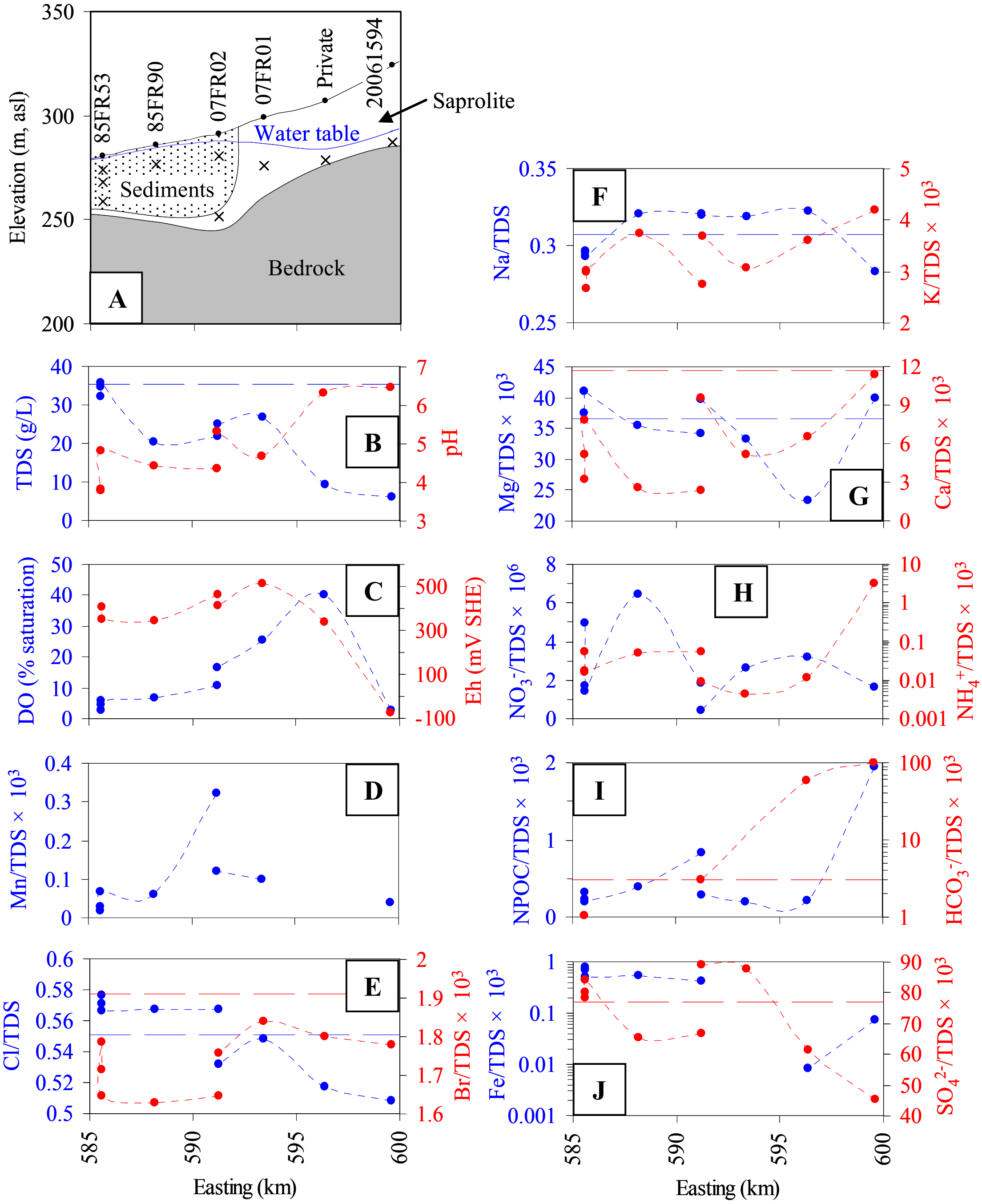


Figure 3-17 Groundwater chemical changes with distance down the Kukerin Gully valley alongside Springhurst Road, Fence Road subcatchment (see Fig. 3.15A for location). (A) Land surface (uppermost black line), labelled piezometers, hydraulic head (blue line; normalization to fresh-water density using the method of Post et al. 2007 resulted in 0.6-0.8 m change), sample depths (crosses), and sediments (dotted), saprolite (white) and bedrock (grey). (B) - (J) Chemistry. Element-TDS ratios are shown due to the variability in Cl- and Br-TDS ratios and hence the apparently nonconservative behaviour of Cl and Br. Samples from saprolite and the sediments are each shown as a set of points connected with short-dashed lines, which, for the sediments, extends down-gradient and then from greater to lesser depths in nested piezometer 85FR53; seawater values are shown as horizontal long-dashed lines.

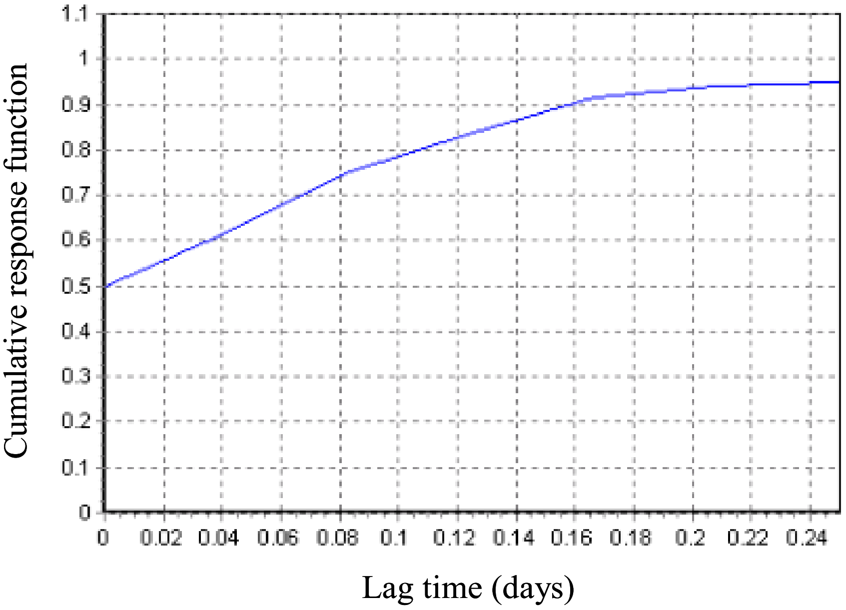


Figure 3-18 Step barometric response function calculated using the software BETCO (Toll & Rasmussen 2007) and groundwater levels and barometric pressure monitored hourly over two years at 50 m north of piezometer 07FR02I/D, indicating confined aquifer conditions (cf. Rasmussen & Crawford 1997; Spane 2002; Toll & Rasmussen 2007).

The concentration of DO decreases toward the land surface as it is used to oxidize Fe^{2+} and at some sites then increases at shallower depths (Figure 3-14d), presumably due to incomplete Fe oxidation under limiting (low) pH conditions or, following Fe oxidation, DO replenishment by infiltrating surface water. The halocline, upward hydraulic pressures and semi- to complete confinement directly beneath the valley floor prevent significant vertical recharge and the downward advection or diffusion of dissolved Fe and DO. Rather, the groundwater system must be recharged laterally from the valley-floor margins or colluvial slopes and acidified by the interaction with relatively fresh, low-density, oxic water that flows above the interface with the deeper, more saline water.

$H_2CO_3^* \text{ Ÿ } CO_2 + H_2O$ (decrease in carbonic acidity) (3.5)
$HCO_3^- \text{ Ÿ } CO_2 + OH^-$ (increase in caustic alkalinity) (3.6)
$H_2CO_3^* \text{ Ÿ } HCO_3^- + H^+$ $K_1 = 10^{-6.35}$ (3.7)

The long-term production of CO_2 contributes to groundwater acidity (Figure 3-4b & d) and, consequently, the hydrolysis and depletion of acid-neutralizing primary silicate minerals (e.g. Equation 3.8; Appelo & Postma 2005) in the regolith:

$$2NaAlSi_3O_{8\,\text{(albite)}} + 2CO_{2\,\text{(aq)}} + 11H_2O \downarrow$$
$$Al_2Si_2O_5(OH)_{4\,\text{(kaolinite)}} + 4H_4SiO_4^0{}_{\text{(silicic acid)}} + 2Na^+ + 2HCO_3^- \qquad (3.8)$$

An increase to particularly high groundwater CO_2 partial pressures (P_{CO_2} >$10^{-0.5}$ atm; calculated using PHREEQC; cf. typical P_{CO_2} values given by Coudrain-Ribstein et al. 1998) with decreasing pH (Figure 3-19), which coincides with a decrease in depth (Figure 3-14b; cf. Acy_{CO_2} in Figure 3-4d), indicates that maximum CO_2 production occurs near the uppermost portion of the aquifer. Previous studies on natural (e.g. Wood et al. 1993) and effluent-irrigated (e.g. Affek et al. 1998) systems have identified the development of maximum P_{CO_2} in the suboxic zone immediately above the groundwater table (i.e. capillary fringe). The high P_{CO_2} in those studies was described as a product of increased microbial activity in response to the influx of dissolved organic matter via laterally recharging water (Equation 3.9):

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad \text{(i.e. } H_2CO_3^{*}\text{)} \qquad (3.9)$$

The CO_2 production rates are lower than those within the overlying sola, but low gas diffusion rates in fine-grained regolith allow the build up to high P_{CO_2} (Wood et al. 1993; Affek et al. 1998). The enrichment of CO_2 in southern Western Australia's groundwaters may occur, like in the above-cited examples, by the dissolution and irreversible oxidation of soil- or sediment-derived organic matter by infiltrating oxic water to produce a suboxic condition and carbonic acidity (Equation 3.9). Additionally or alternatively, CO_2 may be formed from Alk_{CO_3} during Fe oxidation and hydrolysis (Equation 3.10) or, prior to acidification via metal hydrolysis, by NO_3^- reduction (Section 3.2.1), calcite precipitation (Equation 3.11) or plant-root respiration. Calcite precipitation is evident from the common occurrence of vadose calcrete in the valleys. Calcite precipitation from infiltrating rain water could occur by the evapoconcentration of aqueous Ca^{2+} and HCO_3^-, and/or loss of CO_2 either through direct degassing or the mixing with infiltrate with a lower P_{CO_2} (e.g. Smith 2009).

However, the CO_2 efflux is likely toward the land surface rather than into the aquifer. Since rain water has a negative RA_{CO_3}, calcite precipitation results in a decrease in the proportion of Alk_{CO_3} available for neutralizing acidity. The relationship of calcrete with the groundwaters could be tested using stable isotopes and textural analysis. A portion of the Fe^{2+} and Alk_{CO_3} used in Equation 3.10, and the Alk_{CO_3} in Equation 3.11, could be supplied by organic-matter oxidation coupled with the reductive dissolution of Fe oxyhydroxide (Equation 3.12). Alk_{CO_3} may also be supplied from calcareous dust or by silicate hydrolysis (Equation 3.8; e.g. Smith 2009).

$$Fe^{2+} + 2HCO_3^- + 1/4O_2 + 1/2H_2O \rightleftharpoons Fe(OH)_3 + 2CO_2 \qquad (3.10)$$

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_{3\,(s)} + CO_{2\,(g)} + H_2O \qquad (3.11)$$

$$CH_2O + 4FeOOH + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O \qquad (3.12)$$

Preferential mid-landscape groundwater recharge (Fig. 3.17A) may supply oxygen to the downslope portions of anoxic water in the upper reaches of the catchment, if hydraulically connected, and oxidize the contained organic matter (NPOC), H_2S, Fe^{2+} and NH_4^+ (e.g. Equations 3.2, 3.3, 3.9, 3.13 & 3.14). However, the concentrations of dissolved Fe (~8 µmol/L), NH_4^+ (1 mmol/L) and NPOC (1 mmol/L) in the anoxic water, and of Fe in the other slightly acidic groundwaters (i.e. <0.6 mmol/L Fe where pH >6), are much lower than Alk_{CO_3} (10 mmol/L) and are therefore insufficient to substantially contribute to the lowering of pH via oxidation and Fe hydrolysis (Table 3-2).

Table 3-2 Groundwater (locations given in Appendix 3.1) oxidation to atmospheric concentration, dissolved-Fe hydrolysis, $CO_{2\,(g)}$ degassing to atmospheric concentration, and calcite precipitation modelled using PHREEQC and phreeqc.dat at 20° C. Concentrations are given in mmol/L.

Modelling condition & results		**85FR53D** (I = 0.74)	**07FR02D** (I = 0.48)	**98FR106D** (I = 0.48)	**98FR104I** (I = 0.81)	**98FR110D** (I = 0.24)	**98FR108I** (I = 0.23)	**98FR107I** (I = 0.53)	**98FR112I** (I = 0.47)	**98FR105I** (I = 0.30)	**private** (I = 0.18)	**98FR111D** (I = 0.10)	**98FR109D** (I = 0.16)	**07FR03D** (I = 1.33)	**20061594** (I = 0.12)
Initial solution	pH	4.81	5.32	5.33	5.64	6.00	6.01	6.02	6.08	6.29	6.32	6.33	6.37	6.37	6.48
	Log $P_{CO_2\,(atm)}$	-0.48	-0.66	-0.72	-0.86	-0.62	-0.65	-0.69	-0.80	-0.81	-0.71	-1.15	-0.91	-1.47	-0.83
	Log $SI_{calcite}$	-3.37	-2.58	-2.65	-1.92	-1.83	-1.99	-1.08	-1.01	-0.91	-1.11	-1.18	-1.67	-0.82	-0.79
	Log $SI_{Fe(OH)_{3(a)}}$	-3.84	-	-3.53	-2.15	-	-	-1.97	-0.88	-	-1.54	-0.50	-0.53	0.99	-0.28
	Fe_{total}	0.33	b.d.	0.02	0.06	b.d.	b.d.	0.01	0.04	b.d.	<0.01	0.01	0.01	0.61	0.01
	Net non-CO_2 acidity	0.22	-1.14	-0.80	-1.60	-5.72	-5.38	-5.94	-5.06	-7.57	-9.23	-3.38	-6.47	-1.51	-9.96
Equilibration with $O_{2\,(atm)}$ (i.e. log O_2 = -0.679)	pH	4.61	-	5.32	5.62	-	-	6.02	6.07	-	6.32	6.33	6.37	6.05	6.48
	Log $SI_{calcite}$	-3.77	-	-2.67	-1.95	-	-	-1.08	-1.02	-	-1.11	-1.19	-1.67	-1.24	-0.79
	Log $SI_{Fe(OH)_{3(a)}}$	1.88	-	1.37	2.21	-	-	1.58	2.51	-	1.28	2.16	2.16	3.70	2.17
Equilibration with $O_{2\,(atm)}$ & $Fe(OH)_{3(a)}$ (i.e. $SI_{Fe(OH)_{3(a)}}$ = 0)	pH	4.10	-	5.32	5.60	-	-	6.02	6.07	-	6.32	6.32	6.37	5.80	6.48
	Log $SI_{calcite}$	-4.78	-	-2.68	-1.98	-	-	-1.08	-1.03	-	-1.11	-1.19	-1.67	-1.61	-0.80
	$Fe(OH)_{3(a)}$ produced	0.31	-	0.02	0.06	-	-	0.01	0.04	-	<0.01	0.01	0.01	0.61	0.01
Equilibration with $O_{2\,(atm)}$, $Fe(OH)_{3(a)}$ & $CO_{2\,(atm)}$ (i.e. log CO_2 = -3.414)	pH	4.60	8.02	7.96	8.10	8.68	8.67	8.59	8.55	8.75	8.88	8.51	8.77	8.02	8.92
	Log $SI_{calcite}$	-6.72	0.06	-0.09	0.44	0.73	0.55	1.34	1.31	1.38	1.28	0.91	0.61	0.53	1.46
	CO_2 outgassed	11.59	7.79	6.78	4.79	9.63	8.93	8.08	6.38	6.92	8.66	3.07	5.42	2.36	7.24
	$Fe(OH)_{3(a)}$ produced	0.02	-	<0.01	<0.01	-	-	<0.01	<0.01	-	<0.01	<0.01	<0.01	<0.01	<0.01
Equilibration with $O_{2\,(atm)}$, $Fe(OH)_{3(a)}$, $CO_{2\,(atm)}$ & calcite (i.e. $SI_{Calcite}$ = 0)	pH	-	7.99	-	7.88	8.57	8.59	7.99	7.94	8.30	8.76	8.16	8.73	7.76	8.79
	Calcite produced	-	0.05	-	0.37	0.79	0.50	2.44	2.08	2.74	1.42	1.03	0.37	0.42	1.65
	CO_2 outgassed	-	0.04	-	0.29	0.51	0.32	1.57	1.41	1.71	0.82	0.78	0.24	0.33	0.92

NOTE: I = ionic strength (mmol/kg); SI = saturation index; b.d. = below detection limit.

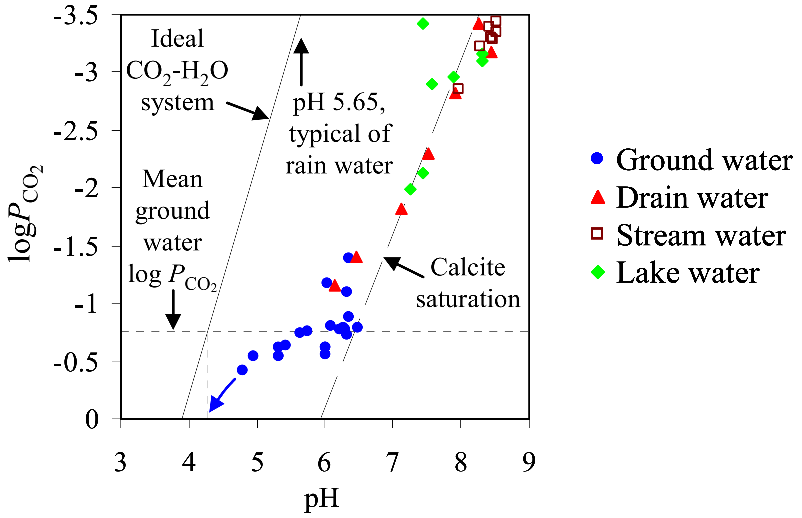


Figure 3-19 Comparison of groundwater pH and P_{CO_2} with those of an ideal CO_2-H_2O system at 25° C and 1 atm. (solid line). Calcite equilibrium is shown by the long-dashed line.

Oxidation immediately downslope from the anoxic groundwater has not appreciably changed the pH. Conversely, a decrease in pH by nearly two units slightly further downslope (<4 km) coincides with the start of a progressive decrease in DO and an increase in SO_4^{2-}/TDS while dissolved Fe decreases to below detectable concentrations (Figure 3-17) through oxidation and precipitation. An increase in SO_4^{2-}, also seen with increasing low salinity in Fig. 3.7F, and decreases in pH and DO correspond with pyrite oxidation (Equation 3.15; Appelo & Postma 2005). Sulfide minerals may exist at depth, like those in nearby auriferous Archaean greenstone (e.g. Griffin's Find, <25 km E of bore 20061594 and 14 km W of Lake Grace; Yeats & Vanderhor 1998; Ridley & Hagemann 1999), and subsamples for $\delta^{34}S_{SO_4^{2-}}$ and $\delta^{18}O_{SO_4^{2-}}$ analyses were taken during groundwater collection to investigate the possible role of sulphur oxidation in acidification (reported elsewhere).

$$H_2S_{(g)} + 2O_{2\,(g)} \rightarrow SO_4^{2-} + 2H^+ \qquad (3.13)$$

$$4NH_4^+ + 3O_{2\,(g)} \rightarrow 2N_{2\,(g)} + 4H^+ + 6H_2O \qquad (3.14)$$

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \qquad (3.15)$$

3.2.3. pH control mechanisms

The pH of the ground and surface waters in the upper Blackwood catchment ranges from 2.5 to 10, but is commonly about 4.3, 6.3 or 8.3-8.4 (Figure 3-3) due to buffering by water-mineral interactions, even though granitic rocks have an inherently low acid-neutralizing capacity (i.e. have a high SiO_2 wt. %) and feldspars in much of the derived regolith, at least in the Fence Road subcatchment, have been largely lost through weathering (Appendix 3.2). The maximum pH of 10 was present in those lake waters where the contribution of Alk_{CO_3} ($[HCO_3^- + 2CO_3^{2-}]$) to the total alkalinity was nearly matched in order of magnitude by borate alkalinity ($[B(OH)_4^-]$), which closely follows the total $[OH^-]$ with changes in pH (Figure 3-11a). A pH of about 8.3-8.4 is common for the natural surface (stream and lake) waters (Figure 3-2a and

Figure 3-4a). This pH corresponds with that of the ideal CO_2-H_2O system at 25° C and 1 atm when $[HCO_3^-]$ peaks (Figure 3-11a), $[H_2CO_3^*] \approx [CO_3^{2-}]$ and, hence, the pH is approximated by the mean of the negative logarithms of the first and second equilibrium constants K_1 and K_2 for reaction Equations 3.7 and 3.16, respectively. This pH can be attained by calcite dissolution (Equation 3.11) in water open to CO_2 at atmospheric partial pressure ($P_{CO_2} = 10^{-3.5}$ atm), or at higher P_{CO_2} (depending on salinity) where partially to fully closed to CO_2 (e.g. Figure 3-11b). This pH is also about the maximum soil pH attainable in the presence of gypsum due to that mineral's dissolution to precipitate Alk_{CO_3} as calcite (Equation 3.17).

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad K_2 = 10^{-10.33} \qquad (3.16)$$

$$CaSO_4.2H_2O + 2HCO_3^- \rightleftharpoons CaCO_3 + SO_4^{2-} + CO_2 + 3H_2O \qquad (3.17)$$

The pH of the groundwaters is commonly about 6.3 and invariably <6.5 (Figure 3-2 and Figure 3-11). The pH of 6.3 is defined by the first dissociation constant (K_1) for dissolved inorganic carbon (DIC; Equation 3.7). Groundwaters with a pH of about 6-6.5 lie on or near the boundary between the feldspar and kaolinite predominance fields (Figure 3-10 a and c) and have the largest Si/Cl and HCO_3^-/Cl ratios (Figure 3-12e and k), suggesting that feldspar hydrolysis and consequent HCO_3^- production (cf. Equation 3.8) are controlling these pH values. Groundwaters with a pH sufficiently high to provide field-titratable quantities of alkalinity, which thus essentially comprises $[HCO_3^-]$ (Figure 3-11a), increase in log $[HCO_3^-]$ nearly linearly with increasing pH under conditions of very high P_{CO_2} (range $10^{-0.4}$-$10^{-1.4}$ atm, i.e. larger than the typical maximum value of $10^{-1.5}$ atm. in soils; e.g. Appelo & Postma 2005) and effectively open to CO_2. The increase in $[HCO_3^-]$ with pH continues up to virtually calcite saturation and suggests the influence of calcite dissolution on groundwater chemistry (Figure 3-11b). However, the groundwaters near calcite saturation commonly exist at relatively large depths (i.e. >20 m) where calcite is absent (Appendix 3.2). Moreover, an addition of dissolved metals to the aquatic system can result in a net acid solution after metal oxidation and hydrolysis and CO_2 degassing, that is, $[metals] + [H_2CO_3^*] + [H^+] > [HCO_3^-]$ and pH <6.3 (Kirby & Cravotta 2005). The decrease in pH through groundwater acidification drives the $[HCO_3^-]$-pH trend in the reverse direction to that which results from calcite dissolution. Thus, HCO_3^- formation by feldspar hydrolysis (Equation 3.8) is probably maintaining the pre-acidified groundwaters at near calcite saturation.

Drain waters follow an apparent evolutionary path of constant P_{CO_2} in a system closed to CO_2 and into calcite saturation or supersaturation (Figure 3-11b), suggesting that acidic groundwaters discharging into the drains increase in pH through regolith calcite dissolution. However, the drain and stream waters are exposed to the atmosphere open to CO_2 and together show an increase in pH into calcite supersaturation without major changes in log $[HCO_3^-]$, in accordance with CO_2 degassing and consequent calcite precipitation from the highly CO_2-charged groundwaters. The lake waters have probably also evolved at least partly from groundwaters (cf. Bowen & Benison 2009) through an increase in pH by CO_2 degassing. Saturation of the lake waters with respect to calcite, though, is highly variable likely due to irregularity in the mineralogy, stoichiometry and kinetics of the alkaline-earth carbonate minerals (e.g. low-Mg and high-Mg calcite and high-Ca and stoichiometric dolomite) being formed.

Groundwater pH, ranging from 3.8 to <6.5, generally changes inversely with Eh in agreement with an influence of the Fe^{2+}-$Fe(OH)_{3\ (s)}$ redox couple (Figure 3-11c). However, many waters appear to slightly deviate from the theoretical Fe^{2+}-$Fe(OH)_{3\ (s)}$ boundary, shown in Figure 3-11c, due to their disequilibrium with the field Eh electrodes during the limited monitoring time, and perhaps the effect of other redox couples (cf. Lindberg & Runnells 1984). The geochemical behaviour of dissolved Fe in the system under study appears to be governed essentially by (1) the dissolution of secondary Fe-bearing minerals, either directly by $Fe(OH)_3$-unsaturated, suboxic groundwaters or coupled with the oxidation of organic matter, to decrease Eh and increase pH (Equation 3.12; cf. Kortatsi et al. 2008) and (2) the oxidation and hydrolysis of dissolved Fe^{2+} to increase Eh and decrease pH (Equations 3.2 & 3.3). Thus, during groundwater discharge and prior to evaporation, the extent of decrease in water pH is dependent on the initial Eh and pH; and can be partially by CO_2 degassing. For example, whilst in storage, considerable to trace amounts of orange Fe oxyhydroxide (and perhaps Fe sulphate in drain waters) had precipitated in several of the non-acidified water samples (Figure 3-20) of relatively large dissolved Fe concentration (11-282 mg/L) and low DO concentration (<1.5 mg/L; Table 3-3; cf. modelling results in Table 3-2). However, oxidation of the dissolved iron was probably incomplete due to limited dissolved oxygen in the waters after sampling.

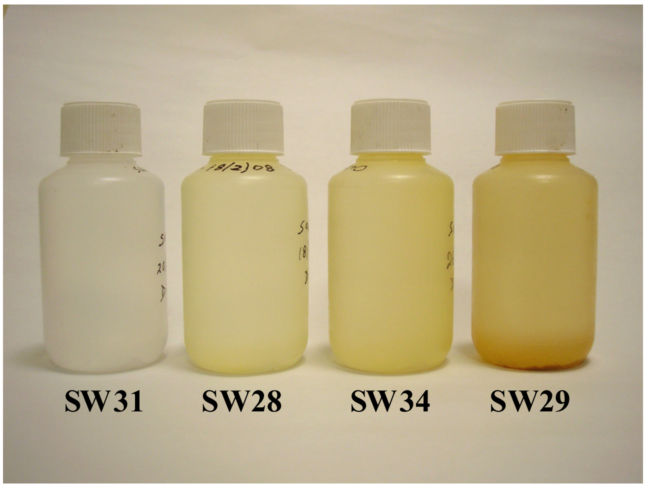


Figure 3-20 Groundwater samples (not acidified during collection) containing, from left to right, an increasing concentration of an Fe-bearing mineral, which precipitated whilst in storage at 4° C.

The pH of the more acidic groundwaters has a mean of about 4.3 and ranges 3.8-5.5 due to buffering by the dissolution of Al-bearing minerals in the regolith, such as $Al(OH)_{3\ (a)}$, gibbsite and kaolinite (Figure 3-11d), as is typical for low-pH waters (e.g. Zhu et al. 2001). A value of about 4.3 is also the theoretical pH of an ideal CO_2-H_2O system at the mean P_{CO_2} of the groundwaters that were field titrated for alkalinity, and although $H_2CO_3^0$ is a weak acid, easily buffered by calcite, and is not directly controlling the actual pH of the groundwaters (Figure 3-19) it could contribute over geological time to the depletion of bases in the regolith. The lowest groundwater pH of 3.8 is also about the theoretical value for water saturated with CO_2 (Figure 3-19). Only the higher of the lowest water pH values of 2.5-2.9, met by some drain waters, is approximated by buffering via kaolinite dissolution (Figure 3-11d), even after re-calculating the kaolinite saturation line using the maximum dissolved silica concentration of these waters ($\log[H_4SiO_4] = -2.67$ M). The slight decrease in drain-water pH away from the kaolinite saturation line is caused by dissolved Fe^{3+} hydrolysis and the evapoconcentration of acidity in water that has no contact with acid-neutralising regolith minerals.

Table 3-3 Dissolved-Fe precipitation and pH changes during water-sample storage.

Sample	Fe-mineral precip-itation	TDS (g/L)	Fe (mg/L)	Fe/TDS (g/g)	Eh (mV SHE)	DO (mg/L)	pH_{field}	pH_{lab}
Drain water								
SW21	C	51.8	22	0.4			6.45	7.28
SW24	O	51.8	282	5.4			2.50	2.52
Ground water								
SW29	C	60.9	32	0.5	161	0.7	6.37	6.76
SW54	C	5.6	107	19.2	118	0.4	5.44	5.75
SW34	M	35.8	18	0.5	353	0.4	4.81	5.36
SW37	M	20.3	11	0.5	345	0.5	4.44	4.71
SW28	O	50.3	67	1.3	436	0.6	4.41	4.70
SW30	O	42.6	55	1.3	464	1.4	4.27	4.30
SW31	N	26.6	<0.1	-	510	2.1	4.67	6.32
Mean of ground waters with no visible Fe precipitation		20.5	8.8	0.2	339	1.2	5.27	6.14

NOTE: Fe-mineral precipitation is described as C considerable, M moderate, O orange-coloured water, N none. Sample SW49, containing an Fe-mineral precipitate in storage, is excluded due to uncertainties in field parameters caused by a very low aquifer yield.

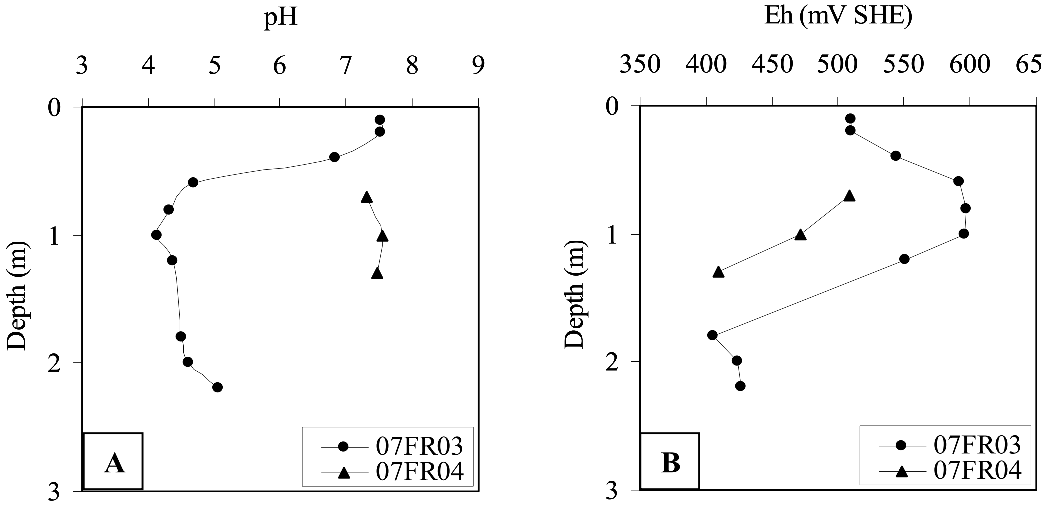


Figure 3-21 Soil (A) pH and (B) Eh at sites 07FR03 and 07FR04, measured immediately after sampling using Ionode™ IJ44 pH and IJ64 Eh double junction electrodes inserted into the matrix of 50 mm diameter push-tube soil cores via access holes drilled through the polybutyrate casing.

The pH of the deeper regolith at acidic-groundwater discharge sites equals that of the groundwater, but increases to pH >7 in the topsoil and, in places, subsoil (Figure 3-21). This may be due to the Mn^{2+} - Mn-oxide redox couple (Figure 3-22) and, locally, presence of calcite.

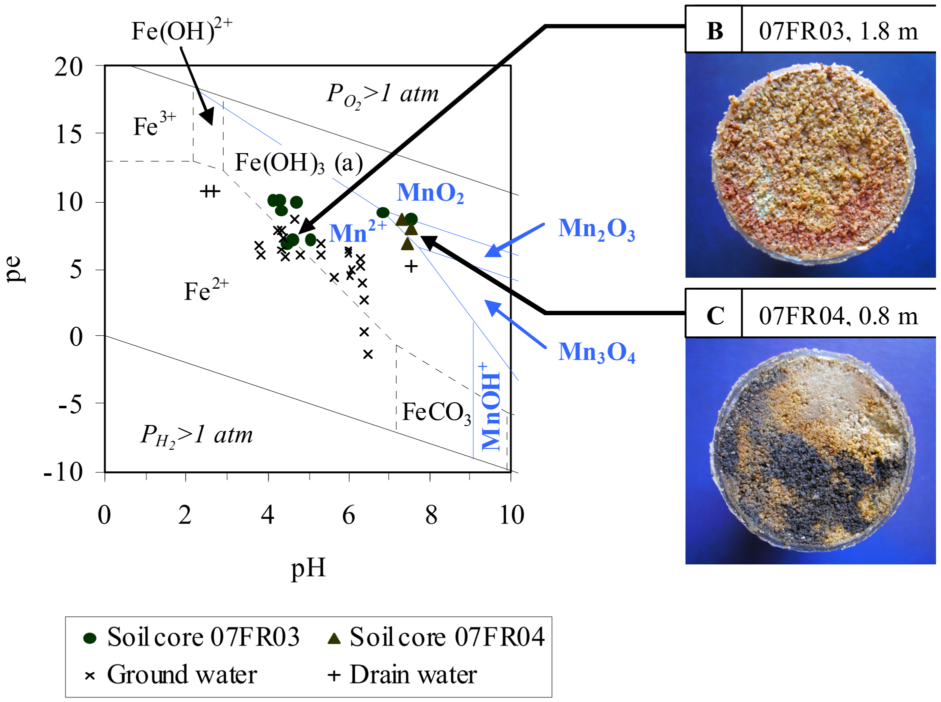


Figure 3-22 Soil pH-control mechanisms at groundwater discharge sites. (A) pe - pH diagram of the system Fe-CO_2-H_2O at $[Fe^{2+}] = [Fe^{3+}] = 10^{-5.0}$ M and $C_{total} = 10^{-2}$ M and the system Mn-H_2O at $[Mn^{2+}] = 4 \times 10^{-5}$ M (mean groundwater [Mn]). The Mn_2O_3 field is more likely manganite (γ-MnOOH). (B) Ferruginous (yellow and red) mottles at 1.8 m depth, from site 07FR03, and (C) manganiferous (black) and ferruginous (yellow) mottles at 0.8 m depth, from site 07FR04 (where calcite exists at 0.7-0.9 m depth), in 50 mm diameter push-tube soil cores from which pH and Eh were measured using Ionode™ IJ44 pH and IJ64 Eh double junction electrodes inserted through drilled holes in the polybutyrate casing.

3.3. Risks of acidic groundwaters to potential receiving environments

The acidic groundwaters in the upper Blackwood catchment can attain very low pH values and contain dissolved Al, Si, Be, Fe, Co, Ni, Zn, Pb, Y and the lanthanides at high concentrations (Section 3.2.1), which are comparable (apart from Zn) to those in groundwaters of similar pH in the Avon catchment (Shand & Degens 2008) and exceed moderate species protection limits for fresh and marine aquatic ecosystems (ANZECC & ARMCANZ 2000a). The acidic groundwaters therefore pose a threat to potential receiving environments. Three broad classes of potential acid-receiving environments have been defined for the southwest region, namely (1) Blackwood River and its tributaries; (2) lakes in landscapes of rejuvenated drainage west of Albany Highway; and, (3) lakes in internally drained landscapes of low relief, low rainfall and high evaporation rates, east of Albany Highway. The Blackwood River and lakes west of Albany Highway are circumneutral to alkaline in pH and, at the time of sampling, showed no sign of encroaching acidity due to the general paucity of, or capacity to neutralize, acidic groundwater. These waters are generally not located in broad valleys underlain by voluminous alluvial aquifers, such as those that exist further east, and the rivers flow frequently or continuously due to relatively steep gradients and ample rainfall. Potential does exist, though, for these waters to mix with acidic groundwaters, which exist in the vicinity (Figure 3-1) and at least locally have a water table within 1 m of the land surface. The river waters have clearly received sufficient highly saline baseflow, and probably saline-surface wash off, since land clearing to at least double in salinity, as described in Section 3.2.1 above, and further baseflow could place the Blackwood River at risk of acidification.

Lake waters near Dumbleyung, Wagin and east of Katanning, and the seasonally flowing creek in Doradine Gully northeast of Dumbleyung, are virtually all slightly to highly alkaline (pH >7.5 to 10) and Halse et al. (2000) reported a neutral pH for three water samples from Lake Toolibin in late 1996. The single exception is a relatively small lake southeast of Dumbleyung, which receives very little overland flow and has a pH of 4.6. A comparison with pH values recorded in 1972 (Williams & Buckney 1976) indicates that the waters of Lakes Dumbleyung and Parkeyerring, the latter near Wagin, have not been affected by acidic ground or drain waters (Table 3-4). The pH of water in Lake Norring, also near Wagin, has decreased by 1.8 units to pH 7.6, but this change coincides with a large increase in salinity, which is caused by intense evapoconcentration following rainfall input and strongly affects the accuracy of the measured pH values (e.g. Dickson 1993; Millero et al. 1993). Moreover, these pH values are only temporal snapshots of a dynamic system that is strongly geochemically influenced by evaporation, dilution, mineral precipitation and dissolution, and microbially-related redox processes. Irrespective, the water in Lake Norring has remained alkaline. The valley-floor soils are typically alkaline and calcareous (e.g. Percy 2000, 2003), but may be temporarily buffering and hence concealing the effects of ascending acidic groundwaters; large and permanent geochemical changes may result when their acid neutralizing capacity is reached.

Table 3-4 Snapshots of lake salinity and pH.

	Williams & Buckney (1976)			This study (2008)	
	Sample Number	**TDS (g/L)**	**pH (field)**	**TDScalc (g/L)**	**pH (field)**
Lake Dumbleyung	13	66.6	8.1	25.2	8.3
Lake Norring	14	16.7	9.4	237.5	7.6
Lake Parkeyerring	15	259.9	6.9	313.7	7.8

Ephemeral water courses extend from subcatchments underlain by acidic groundwater to Lakes Dumbleyung and Toolibin and, by their very nature, these courses must flow at least during major flood events and would potentially transmit acidity toward the lakes. Although the acidic stream and drain waters may be substantially diluted by weakly acidic rain water and during entry into alkaline lakes, previous modelling by Douglas & Degens (in Shand & Degens 2008) has shown that mixing with virtually neutral to slightly alkaline (pH 7.1-7.6) lake water of up to 100 times the mass of the acidic water is commonly needed for acid neutralization; the residual acid-neutralizing capacity of the receiving basin is therefore likely to be readily exceeded (Shand & Degens 2008). The Fence Road catchment, in particular, has recently (from November 2007 to April 2008) had installed an extensive (~55 km combined length) deep open arterial drainage system, where the central conveyance channel lies within the trunk valley and terminates within Dongolocking Creek 40 km upstream from Lake Dumbleyung. Measurements of pH recorded in August and

September 2007, prior to drain installation, were respectively pH 8.6 and 7.3 in the creek near Dumbleyung-Lake Grace Road and pH 7.0 and 5.0 near a railway crossing 13 km downstream (Department of Water 2008). Thus, the net exported surface water from the Fence Road catchment was alkaline, but acidic groundwater was discharging further downstream. Water in the trunk drain had, at the time of sampling, soon after drain installation, a pH of 2.5, a total acidity of 38 meq/L (1900 mg $CaCO_3$/L), TDS of >50 g/L, very high dissolved metal concentrations (Figure 3-12) and a flow rate of about 3.5 L/s. This acidity is about 18 times the Alk_{CO_3} measured during a late drying phase at Lake Dumbleyung, which accordingly would use about 2 gigalitres of water per year to directly neutralize this acidity, assuming a constant drain flow rate and no acidity loss or gain en route through sediment interaction or additional water inputs (clearly not so); the lake has a water capacity of 192 gigalitres. Aside from acidity, the lake would receive salinity, silica, metals and ammonium from the drain water (Table 3-5), although likely small in comparison with natural surface-water inputs.

High groundwater P_{CO_2} values, with a mean $\log P_{CO_2}$ = -0.81 atm for waters with field-measurable Alk_{CO_3}, indicate that CO_2 outgassing from shallow and discharging groundwaters will occur and may be a significant environmental (climatic) hazard. The rate of CO_2 outgassing from the part of the alluvial aquifer that exists beneath the saline soil subsystem (subsystem 259Cb3; Percy 2000) in the Fence Road catchment was estimated using the software PHREEQC and the database phreeqc.dat (Parkhurst & Appelo 1999). The CO_2 outgassing rates were calculated by modelling the equilibration of groundwater P_{CO_2} with that of the atmosphere ($\log P_{CO_2}$ = -3.414 atm) followed by calcite and, in turn, sepiolite saturation.

Table 3-5 Partial comparison of the Fence Road drain and Lake Dumbleyung water compositions.

Attribute	Fence Road drain (SW24)	Lake Dumbleyung (C6)
TDS	51.77 g/L	25.31 g/L
pH	2.50	8.35
Acidity/alkalinity[1]	38.3 meq/L_{Acy} (1915 mg $CaCO_3$/L)	2.135 meq/L_{Alk} (107 mg $CaCO_3$/L)
Si	60.6 mg/L	0.7 mg/L
Al	142 mg/L	0.9 mg/L
Fe	282 mg/L	<0.05 mg/L
Ce	525 µg/L	<0.4 µg/L
Co	298 µg/L	1.1 µg/L
La	183 µg/L	<0.4 µg/L
Nd	180 µg/L	<0.4 µg/L
Ni	171 µg/L	4.4 µg/L
Y	113 µg/L	<0.4 µg/L
Pb	74 µg/L	<0.5 µg/L
NH_4^+	3 mg/L	0.04 mg/L

The result was used with the aquifer discharge, approximate using Darcy's law (discharge = transmissivity × hydraulic gradient × aquifer width), the mean saturated hydraulic conductivity measured by Whitfield (1999; HC_{sat} = 0.21±0.06 m/day, n = 3), and aquifer physical measurements taken from GIS and during borehole drilling and water sampling. The amount of CO_2 released from the three groundwaters that were sampled from the saline-soil subsystem and which contained field-measurable DIC was 0.25±0.13 g/L with CO_2 degassing and 0.28±0.12 g/L with degassing and mineral saturation.

Considering the mean groundwater discharge rate of 26.76 kL/km^2/year, these figures equate, respectively, to about 6.7 kg CO_2/km^2/year and 7.5 kg CO_2/km^2/year from an aquifer portion of about 13.6 km^2 in areal extent. By comparison, the mean CO_2 release from 14 DIC-bearing (field measurable) Fence Road groundwater samples via the equilibration with atmospheric P_{CO_2} (Table 3-6) was estimated as 0.30±0.03 g/L and, along with subsequent calcite and sepiolite saturation, 0.36±0.03 g/L. The CO_2 degassing rate estimates ignore diffusion rates through the vadose zone and, due to the same constraint, CO_2 outgassing rates from groundwater at depths too great for discharge have not been estimated. Moreover, the P_{CO_2} of the shallower, relatively low-pH groundwaters is larger than those of the higher-pH, DIC-bearing waters (Figure 3-19), potentially resulting in a larger mass of CO_2 released from the more acidic waters. Hence, these estimates are considered to be minimum rates of CO_2 outgassing from the catchment's groundwater system. The mean result from the 14 waters using the databases phreeqc.dat and pitzer.dat, but excluding sepiolite saturation, was identical at 0.33±0.03 g/L, indicating that the ionic strength of these waters is typically insufficient to significantly influence the modelled results. This aquifer is tentatively, based on crude estimates, not considered to be a significant emitter of CO_2 to the atmosphere when compared to, for example, the estimated mean agricultural greenhouse gas (CH_4 and N_2O) emission of 25,000-50,000 kg/km^2/year from the same catchment (Bennett 2009). Moreover, motor vehicles produce between about 0.1-0.4 kg CO_2/km in exhaust (i.e. 2.3 kg CO_2 per L petrol; e.g. http://rac.com.au; http://www.mynrma.com.au; accessed online: June 2009). Carbon-dioxide degassing may, at least initially, offset the pH decrease of groundwaters discharging to drains and floodways.

3.4. Summary and recommendations

Acidic groundwaters exist throughout the upper Blackwood catchment and are characterized by positive Acy_{net}, low pH (<3.8), low DO saturation (3-25%), and high salinity (4-65 g/L TDS), P_{CO_2} (>$10^{-0.64}$ atm) and dissolved Al, Si, Fe, Be, Co, Ni, Pb, Zn, Y and rare-earth element concentrations. The discharge of these groundwaters, by rising water levels or flow induced by deep open drains, presents a threat to surface ecosystems and the quality of surface waters, which are naturally neutral to highly alkaline (pH >10, due to elevated Alk_{CO_3} and $Alk_{B(OH)_4^-}$) and typically less saline. The ground and surface waters in the region are of Na-Cl- or Na-Mg-Cl-type chemistry and negative RA_{CO_3}. These waters exist in a terrain of granitic rocks and derived regolith, which have low acid neutralizing capacity, and primarily acquired their dissolved Na, Mg, Cl, SO_4^{2-} and Br from seawater through intense rain-water evaporation. However, dissolved Si, Al, Fe, Mn and, in lower-salinity waters, HCO_3^- were probably sourced by the dissolution of primary and secondary regolith minerals. Silicate hydrolysis most likely drives the maximum groundwater pH to typically 6.3 whereas calcite dissolution over the long term, and perhaps gypsum dissolution with concomitant calcite precipitation, promotes the common surface-water pH of 8.3-8.4.

Table 3-6 Groundwater $CO_{2\,(g)}$ degassing modelled using PHREEQC and phreeqc.dat at 20° C. Concentrations are given in mmol/L.

Modelling condition & results	**85FR53D** (*I* = 0.74)	**07FR02D** (*I* = 0.48)	**98FR106D** (*I* = 0.48)	**98FR104I** (*I* = 0.81)	**98FR110D** (*I* = 0.24)	**98FR108I** (*I* = 0.23)	**98FR107I** (*I* = 0.53)	**98FR112I** (*I* = 0.47)	**98FR105I** (*I* = 0.30)	**private** (*I* = 0.18)	**98FR111D** (*I* = 0.10)	**98FR109D** (*I* = 0.16)	**07FR03D** (*I* = 1.33)	**20061594** (*I* = 0.12)
Initial solution														
pH	4.81	5.32	5.33	5.64	6.00	6.01	6.02	6.08	6.29	6.32	6.33	6.37	6.37	6.48
Log $P_{CO_2\,(atm)}$	-0.48	-0.66	-0.72	-0.86	-0.62	-0.65	-0.69	-0.80	-0.81	-0.71	-1.15	-0.91	-1.47	-0.83
Log $SI_{calcite}$	-3.37	-2.58	-2.65	-1.92	-1.83	-1.99	-1.08	-1.01	-0.91	-1.11	-1.18	-1.67	-0.82	-0.79
Log $SI_{sepiolite}$	-8.62	-7.10	-7.48	-5.93	-5.51	-5.44	-4.47	-4.53	-4.13	-4.53	-4.27	-4.74	-2.91	-3.59
Equilibration with $CO_{2\,(atm)}$ (log P_{CO_2} = -3.414)														
pH	7.59	8.02	7.96	8.11	8.68	8.67	8.59	8.55	8.75	8.88	8.51	8.77	8.21	8.92
CO_2 lost	11.12	7.79	6.77	4.72	9.63	8.93	8.08	6.32	6.92	8.66	3.07	5.43	1.36	7.24
Log $SI_{calcite}$	-0.75	0.06	-0.08	0.47	0.73	0.55	1.34	1.32	1.38	1.28	0.91	0.61	0.91	1.46
Log $SI_{sepiolite}$	2.48	3.67	3.02	3.94	5.10	5.08	5.72	5.28	5.56	5.53	4.40	4.73	4.41	5.96
Equilibration with $CO_{2\,(atm)}$ & calcite (i.e. $SI_{calcite}$ = 0)														
pH	-	7.99	-	7.89	8.57	8.59	7.99	7.94	8.30	8.76	8.16	8.73	7.76	8.79
CO_2 lost	-	0.04	-	0.31	0.51	0.32	1.57	1.42	1.71	0.82	0.78	0.24	0.72	0.92
Calcite formed	-	0.05	-	0.41	0.79	0.50	2.44	2.11	2.74	1.42	1.03	0.37	1.01	1.65
Log $SI_{sepiolite}$	-	3.55	-	3.04	4.68	4.81	3.41	2.92	3.86	5.10	3.01	4.57	2.65	5.52
Equilibration with $CO_{2\,(atm)}$, calcite & sepiolite (i.e. $SI_{calcite}$ & $SI_{sepiolite}$ = 0)														
pH	7.04	7.96	7.46	7.88	8.47	8.49	7.97	7.93	8.24	8.68	8.11	8.65	7.76	8.71
CO_2 lost	0.34	0.80	0.69	0.48	1.01	1.12	0.65	0.54	0.69	1.06	0.56	1.03	0.28	1.17
Sepiolite formed	0.09	0.39	0.19	0.24	0.35	0.38	0.32	0.27	0.29	0.35	0.25	0.34	0.14	0.39
TOTAL CO_2 lost	11.46	8.63	7.47	5.51	11.16	10.37	10.30	8.29	9.32	10.54	4.41	6.70	2.37	9.32

NOTE: *I* = ionic strength (mmol/kg); SI = saturation index.

Groundwater acidification in the Fence Road subcatchment, whereby the acidity produced exceeds Alk_{CO_3}, occurs predominantly and sequentially by Fe-mineral dissolution, Alk_{CO_3} immobilization and Fe hydrolysis, although the evolution of this groundwater is unclear. The following hypothesis is forwarded as one possible model of low pH groundwater evolution, based on data in the Fence Road sub-catchment. Secondary Fe-bearing oxide/oxyhydroxide minerals stored in the ferruginous and mottled regolith are dissolved by temporarily rising groundwaters, which are unsaturated with respect to $Fe(OH)_3$ $_{(a)}$, and perhaps by mineral-structural Fe reduction coupled with the oxidation of dissolved organic matter in recharging water. Much of the resultant alkalinity (mostly Alk_{CO_3}) is probably removed by $CaCO_3$ precipitation in the vadose zone during pore-water evaporation and, perhaps, CO_2 degassing. Fresh, oxic water, recharging perhaps at valley-floor margins or colluvial hillslopes, flows over the interface with relatively dense, saline, sub-oxic groundwater and promotes limited Fe oxidation and hydrolysis and the consequent lowering of groundwater pH and depletion of dissolved oxygen. Low-pH groundwaters typically occur at depths <20 m, especially in Cenozoic alluvium, and in the middle to lower reaches of third-order catchments where groundwaters are slowly ascending through aquitards.

The CO_2 produced from Alk_{CO_3} by Fe oxidation and hydrolysis, and possibly by organic-matter oxidation, plant-root respiration and other geochemical reactions, accumulates partly as carbonic acidity. With metal-derived, the carbonic acidity dissolves primary silicate minerals in the regolith to exhaustion, enabling additional CO_2 accumulation to very high P_{CO_2}. Groundwater pH is controlled within the range 3.8-<6.5 largely by the Fe^{2+}-$Fe(OH)_3$ redox couple, and the common low pH value of 4.3 and limit of 3.8 are controlled by the dissolution of $Al(OH)_3$ $_{(a)}$/gibbsite and kaolinite, respectively. Groundwater acidification has developed by geochemical processes other than evaporite-mineral precipitation and therefore cannot strictly be depicted as a separate branch in the continental-brine conceptual evolutionary model of Hardie & Eugster (1970) and Eugster & Jones (1979), contrary to that proposed by recent workers (Bowen & Benison 2009; Long et al. 2009). The decrease in the pH of the groundwaters coincides with large changes in element-Cl ratios, including increases in ratios of Al, Fe, Be, Co, Ni, Pb, Zn, Y and rare-earth elements and decreases in ratios of Si, Ca, K, Mn, Ni, Se, Br, HCO_3^-, SO_4^{2-} and PO_4^{3-}.

The degassing of CO_2 initially offsets a decrease in the pH of discharging groundwaters caused by dissolved-metal hydrolysis and evapoconcentration, but does not prevent further fall in pH. Groundwater CO_2 degassing above the aquifer, and where groundwaters discharge into drains, streams and lakes, may promote calcite precipitation as calcrete in the vadose zone, but apparently does not significantly contribute to the total greenhouse gas emission from agriculture. The soils at acidic-groundwater discharge sites are most likely maintained at pH >7 by the Mn^{2+} - Mn-oxide redox couple as well as the local presence of calcite. The hydrolysis of dissolved Fe, and Al released from dissolving Al-hydroxide minerals and kaolinite, and the evapoconcentration of acidity without contact with acid-neutralizing minerals enables drain water pH values to decrease to 2.5. Drain waters with such low pH values exist in the lower reaches of subcatchments in the north-eastern part of the region and, although typically having low flow rates of <2 L/s, potentially add acidity, salinity and dissolved silica, metals and ammonium to floodways via wet-seasonal or event-driven pulses of flow. Surface waters in the higher-rainfall, western part of the region, and typically the lakes in the eastern part of the region, have not undergone acidification, but have received saline baseflow and are susceptible to, and at risk of, acidification.

A more thorough and definitive interpretation on the geochemical processes of groundwater acidification and CO_2 formation could be realized through:

1) a vastly improved understanding of the vadose- and phreatic-zone hydrology in the Fence Road catchment, especially regarding groundwater recharge and the

interactions between infiltrating surface water, vadose pore waters, groundwater, solutes and the regolith; and,

2) a focused examination of Fe, C and S sources, cycling and reaction kinetics.

Moreover, the effects of discharging acidic groundwater and its high metal concentrations on soil development and plant growth and quality in agricultural and natural ecosystems need to be investigated.

4. REGIONAL GROUNDWATER GEOCHEMISTRY (OVERVIEW) - SOUTH COAST

Adam Lillicrap and John Simons
ARWA Centre for Ecohydrology, Department of Agriculture and Food, 444 Albany Highway, WA 6330

4.1. Introduction

Naturally occurring acidic-saline groundwaters are widespread across the south-west of Western Australia (Lillicrap and George 2008). These groundwaters have been disturbed as a result of land use change (clearing) and agricultural practices such as drainage. This has resulted in increased discharge of acidic, saline groundwaters to the environment, with consequent impacts.

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 2007). However, the effects of acidification are interrelated and often operate in combination. This consequently results in multiple stresses, both direct and indirect, leading to loss of biodiversity (Grey 2007).

There has been increased drainage in the Avon catchment, particularly arterial drainage (i.e. regional drainage networks over hundreds of kilometres) to manage salinity (Shand and Degens, 2008). However, the potential impacts of this arterial drainage was poorly understood. This led to an acidic groundwater geochemical risk assessment being conducted for the Avon catchment (Shand and Degens 2008). As part of the Avon study, a review of existing groundwater data was conducted across the whole agricultural region (Lillicrap and George 2008). The review identified other areas, including the South Coast region, where acidic-saline groundwaters potentially posed a risk to the environment and infrastructure, if disturbed.

Lillicrap and George (2008) identified that acidic-saline groundwaters in the South Coast region were concentrated in the central and eastern areas, with the highest concentration of acidic-saline groundwaters occurring in the mallee region located north of Esperance (Figure 4-1). Many rivers have their headwaters in this region, including the Dalyup River system which flows into Lake Gore, a Ramsar-listed wetland of international significance. Groundwaters in the South Coast region are being disturbed by agricultural practices such as clearing and drainage. The South Coast region lacks the arterial drainage of the Avon, but agricultural drainage is discharged directly to water courses. Therefore acidic-saline groundwaters in the South Coast potentially pose an even greater threat to the environment than in the Avon, as the rivers and streams on the South Coast externally drain to coastal wetlands and estuaries which have high environmental values. These coastal wetlands include two Ramsar listed wetlands; Lake Gore and Lake Warden. Therefore it is necessary to assess the potential geochemical risks acidic-saline groundwaters may pose to the rivers and high value coastal wetlands and estuaries of the South Coast.

This study focussed on the central and eastern areas of the south coast where there was the highest concentration of acidic-saline groundwaters (as identified in Lillicrap and George, 2008) to assess the potential geochemical risks to the environment. Furthermore, in order to more fully understand the potential threat acidic-saline groundwaters may pose to sensitive environments such as Ramsar wetlands and the processes involved, the Dalyup River – Lake Gore system was used as a case study (Figure 4-2).

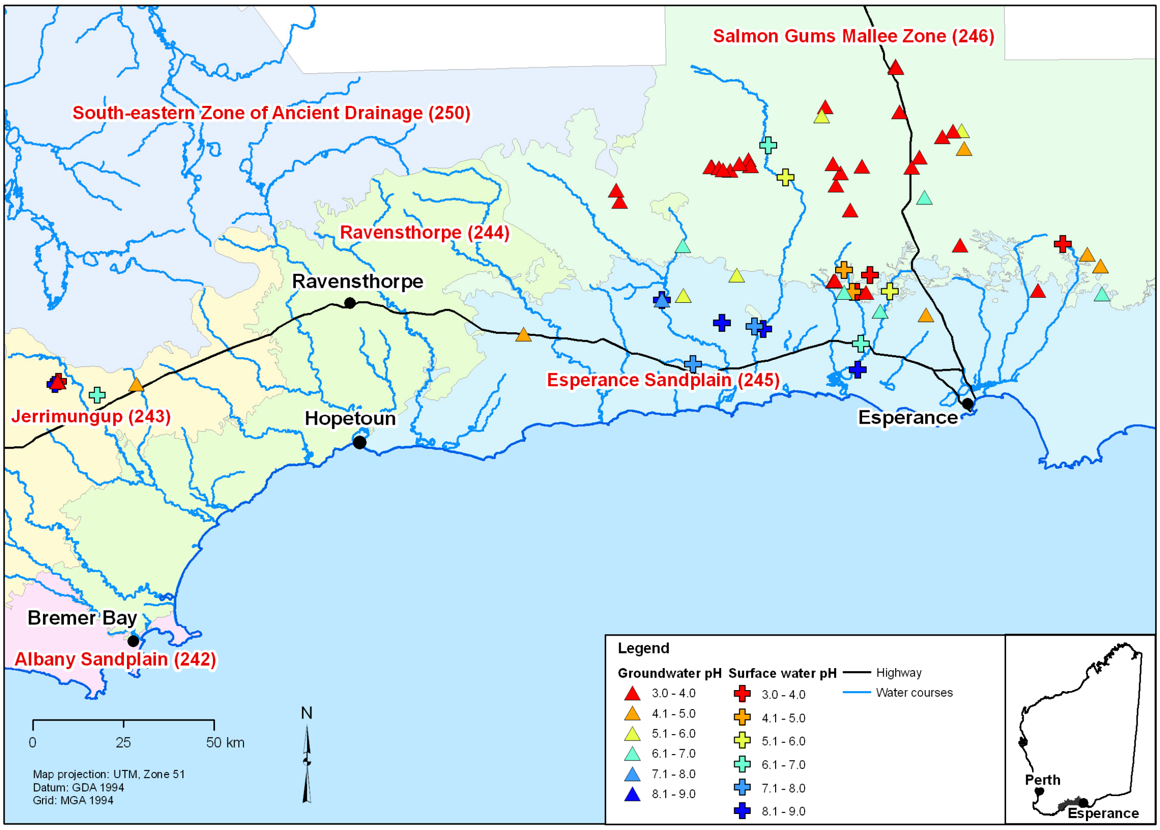


Figure 4-1 Map of groundwater and surface water sampling sites for the South Coast, classified by sampling pH. Soil-landscape zones are shown in red.

4.2. Methods and results

4.2.1. Study area

Soil-landscape zones (SLZ) are spatial units that have similar geology and geomorphology. Given most groundwater processes in WA are controlled by the geologic and regolith properties, these zones have been used to assign broad hydrological attributes (George et al 2005).

The central and eastern south coast of Western Australia has a temperate climate with cool, wet winters and warm to hot, dry summers. The average annual rainfall on the coast is about 600 mm and declines with distance from the coast to less than 400 mm. Rainfall varies throughout each sub-region. Rainfall reliability also decreases with distance away from the coast. Evaporation increases from 1,500 mm/yr on the coast at Bremer Bay to nearly 1,800 mm/yr in the north. Further east, annual evaporation ranges from 1,800 mm/yr at Esperance to 2,200 mm/yr at Salmon Gums. While winter evaporation in the Mallee is only slightly higher than that in the Esperance Sandplain, summer evaporation is significantly higher.

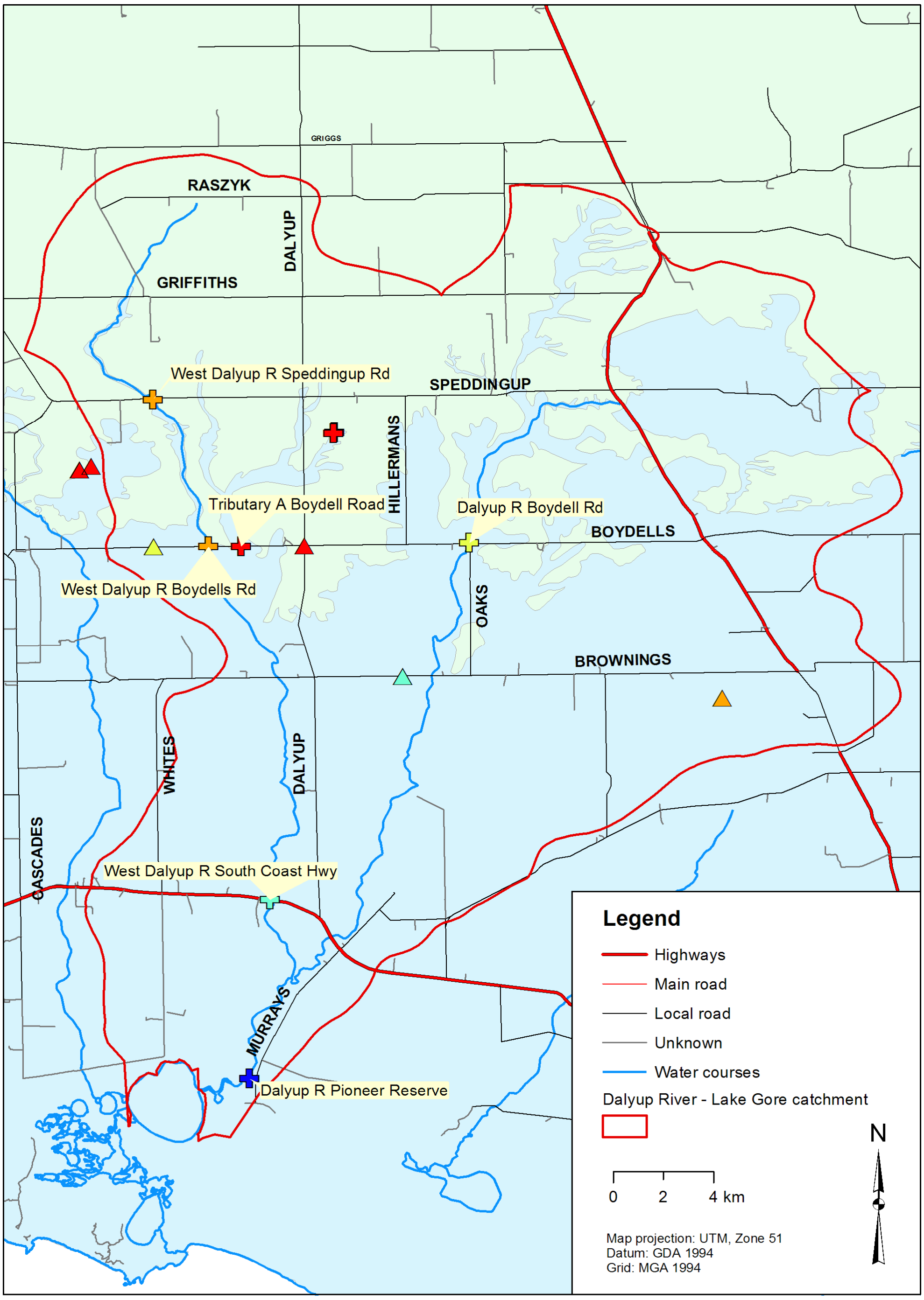


Figure 4-2 Map of the Dalyup River – Lake Gore catchment showing sampling sites. The key to pH values see Figure 4-1.

The main soil-landscape zones of the central south coast are the Jerramungup Plain Zone (243) and the Ravensthorpe Zone (244) (Figure 4-1). The Jerramungup Plain Zone (243) consists of a level to gently undulating plain, which forms the upper catchments of the southerly-flowing rivers. The plain consists of sands overlying deeply weathered marine sediments, granites and gneisses. The southern margin of the plain drops away towards the coast, forming a set of low hills. The valleys are typically broad with very gently inclined slopes (1–3%) except where rivers have been rejuvenated through uplift, then the valleys are more dissected, forming V-shaped valleys with gently to moderately inclined slopes (greater than 3%). The basement rock of granites and gneisses can be exposed in valleys and hillsides (Lillicrap 2004).

The groundwater flow systems are local to intermediate and discharge into low-lying areas, such as valley floors. The groundwater usually flows in the same direction as the surface water. Groundwater movement is slower in the broader valleys than the more dissected valleys as they have a lower groundwater gradient. The depth to groundwater ranges from less than 1 m to greater than 20 m, depending on the depth to the basement and the landscape position. Although the groundwater salinity ranges from 1,200-1,500 mg L^{-1} to 40,000 mg L^{-1}, most of the groundwater is saline (5,000 – 35,000 mg L^{-1}). The groundwater pH ranges from 2.8 to 7.6, although typically the groundwater pH is neutral (Figure 4-3) (Lillicrap 2004).

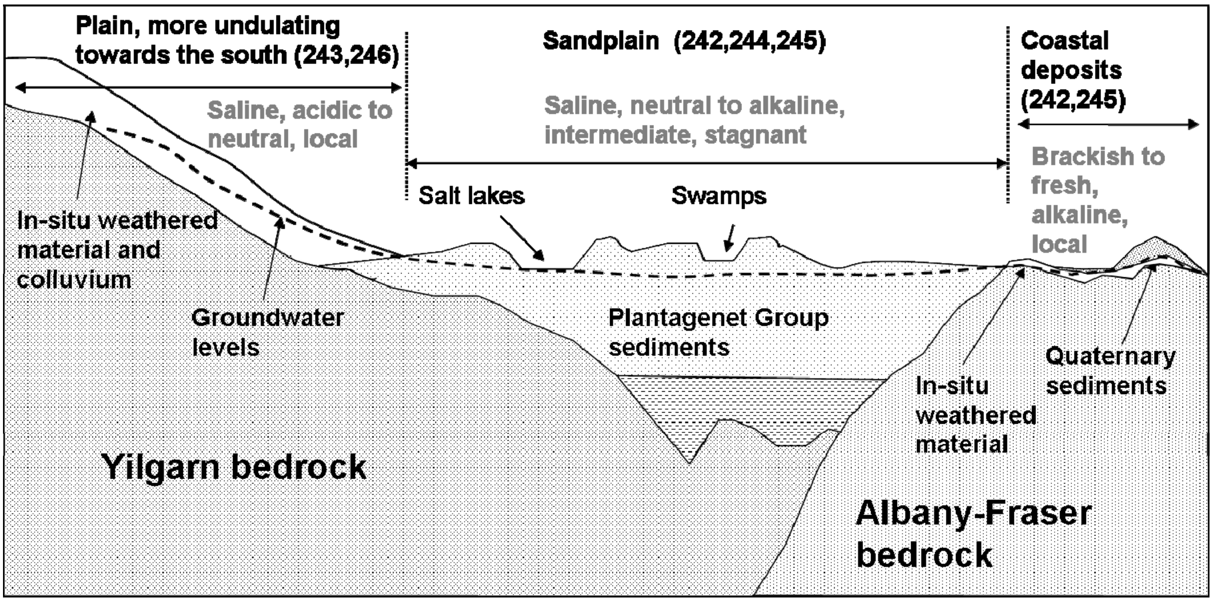


Figure 4-3 General conceptual north-south cross-section of the central and eastern South Coast showing the physiography, zones (e.g. 243) and hydrogeology of the study area (after Lillicrap 2004).

The Sandplain zones (242 and parts of 244) are characterised by a level to very gently undulating sandplain that extends inland for 15 to 20 km. The sandplain has poor drainage with intermittent lakes and swamps. Southerly-flowing rivers that cross the sandplain have cut through sediments and exposed granitic and gneissic basement. The groundwater systems on the sandplain are intermediate and stagnant with very low groundwater gradients, except near the margins of incised rivers. The groundwaters in these systems discharge into rivers and lakes. The depth to groundwater varies from 10 m to greater than 20 m in the stagnant aquifers. The groundwater is saline (up to 30,000 mg L^{-1}) and has typically neutral pH that ranges from 6.1 to 6.6 (Figure 4-2).

The groundwater systems on the coastal deposits are local to intermediate systems that have some connection to the ocean. The groundwater salinity ranges from fresh to brackish in these coastal deposits and are usually alkaline (greater than pH of 7.5) (Figure 4-2) (Lillicrap 2004). The aquifers in the coastal deposits are often developed as water resources.
The Ravensthorpe Zone (244) consists mainly of rolling to undulating low hills formed on a greenstone belt of mafic, ultra-mafic and meta-sedimentary rocks. The rest of the Zone contains Proterozoic granitic and metasedimentary rocks, and Tertiary sediments (see above for sandplain).

The eastern South Coast encompasses the Esperance agricultural district, and has two Soil-landscape zones, the Esperance Sandplain (245; Figure 4-1) in the south and Salmon Gums Mallee in the north (246, Figure 4-1). The natural drainage systems reflect the geological history of the area. West of Esperance, the landscape has been rejuvenated and is externally drained through a number of well-defined rivers and creeks that flow into wetlands and estuaries located in coastal reserves. East of Esperance and in the north and east of the Mallee where the landscape has not been rejuvenated, drainage systems are poorly defined and internally drain into paperbark (*Melaleuca spp.*) and yate (*Eucalyptus occidentalis*) swamps (Simons 2004).

Esperance Sandplain Zone (245; Figure 4-1) is characterised by a level to undulating sandplain that forms a 40–60 km wide strip along the coast. The sandplain consists of a sheet of fine sand of varying thickness overlying gravel or clay. Grey, deep sandy duplex and grey, shallow sandy duplex soils are dominant and both of these often contain gravel. The Salmon Gums Mallee Zone (246; Figure 4-1) is characterised by its mallee vegetation and contains a level to gently undulating plain with numerous salt lakes. The dominant soils are alkaline grey sandy duplexes that overlie predominantly marine sediments. The headwaters of the southerly-flowing rivers and creeks are located in the west and south central parts. The northern and eastern areas internally drain into playa lakes (Simons 2004).

In areas with well-defined external drainage, groundwater flow systems are local to intermediate, separated by basement highs and ridges. Where drainage is poorly defined the groundwater flow systems are intermediate to regional. Local groundwater flow systems occur in areas with shallow basement. Areas with deep sands have localised, perched groundwater flow systems overlying intermediate groundwater flow systems (Simons 2004).

The depth to groundwater ranges from less than 2 m to deeper than 10 m. Groundwater levels less than 2 m commonly occur in areas with shallow basement, at the headwaters of the rivers and creeks, and in low-lying areas adjacent to the playa lakes. Shallow watertables fluctuate seasonally and the deeper groundwater levels are currently rising at rates between 0.05 and 0.30 m/yr. Groundwater salinity increases with distance away from the coast and ranges from 500 mg L^{-1} in the perched aquifers to 80,000 mg L^{-1} in the intermediate aquifers. The median groundwater salinity in the Sandplain is 10,000 – 15,000 mg L^{-1} and 30,000-35,000 mg L^{-1} in the Mallee (Simons 2004).

The Ramsar-listed Lake Gore and surrounding Dalyup River catchment being used as a case study is located 35km west of Esperance and covers approximately 83,000 ha (Figure 4-2). The Dalyup River has it headwaters in the Salmon Gums Mallee Zone and discharges into Lake Gore in the Esperance Sandplain Zone. Dalyup River Catchment has been extensively cleared of native vegetation and its dominant land use is broadacre dryland agriculture. In 1999 landholders mapped 6.3% of the total catchment area as being affected by salinity (Simons 2000). Groundwater levels are still rising in the upper reaches of the Dalyup River Catchment and deep open drains (> 1 m deep) are extensively used in these areas to manage secondary salinity. The Dalyup River Catchment contains 340km of drainage works, most of which are excavated deep open drains, with some banks and shallow drains (Komarzynski 2000).

4.2.2. Sampling methods

Groundwater monitoring bores (n=39), agricultural drains (n=4) and rivers (n=14) were sampled for chemical analysis across the central and eastern south coast to ascertain the geochemical risk. Surface and groundwaters were more extensively sampled in the Dalyup River-Lake Gore catchment as it is being used as a case study to a gain more detailed understanding of geochemical risks and processes. The sites were sampled in October –

November 2007 and the sampling methodology followed sampling protocols developed for the project (reference?). Water samples were prepared for analysis in the same manner as Shand (2008). The flows of surface waters were estimated where possible by measuring velocity of the flow and measuring cross-sectional area of water. Measurement of surface waters occurred under high flow and base-flow conditions. The sampling sites are shown in Figures 4.1 and 4.2 with further details shown in Appendix 4.1.

4.2.3. Overview of the hydrogeochemical characteristics of the central and eastern south coast

The surface and groundwaters showed a wide variance of TDS (total dissolved solids) values ranging from stock quality (less than 10,000 mg/L) to greater than seawater (35,000 mg L^{-1}) (Figure 4-4). Surface and groundwaters had different distributions and ranges of TDS values with groundwaters having a wider range of TDS values compared to surface waters. Though groundwaters had the highest TDS values, on average surface waters were more saline than groundwaters (Figure 4-4).

Surface and groundwaters also had different pH distributions. Groundwaters were mostly acidic whereas surface waters were mostly neutral to alkaline (Figure 4-4). The oxidation-reduction potentials (Eh) were measured for most sites. Surface waters had a median Eh of 240mV and groundwaters had a median value of 320 mV. This reflects the generally acidic and oxidising nature of the groundwaters compared to the alkaline surface waters.

The most common or major ions in water are the cations: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}), and the anions: chloride (Cl^{-}), sulfate (SO_4^{2}) and bicarbonate/ carbonate (HCO_3^{-}/ CO_3^{2-}). The surface and groundwaters were mostly of similar composition to seawater, Na-Cl dominated or type waters, with some minor variations. There was one notable exception, a groundwater bore on the central south coast that had Na-Cl-SO_4 type water (Figure 4-5).

The major ions for surface and groundwaters showed a large variation in concentration (Figure 4-6), which is to be expected given the wide range of salinities encountered during the sampling. Most ions show similar range distributions except for calcium and the bicarbonate-carbonate species in groundwaters.

Chloride is a conservative ion which means is not involved in other types of chemical reactions except being added or removed from waters through dissolving with inundation of water or precipitation through evaporation. Therefore other ions are compared against chloride to see if they are involved in other geochemical processes other than dissolution or precipitation. The major ions were plotted against Cl concentration (Figure 4-6), with most ions showing a strong correlation with Cl and having a similar trend to the seawater dilution line. Na had the strongest correlation with Cl. The exceptions were K and Ca, which mostly showed depletion in both surface and groundwaters relative to seawater.

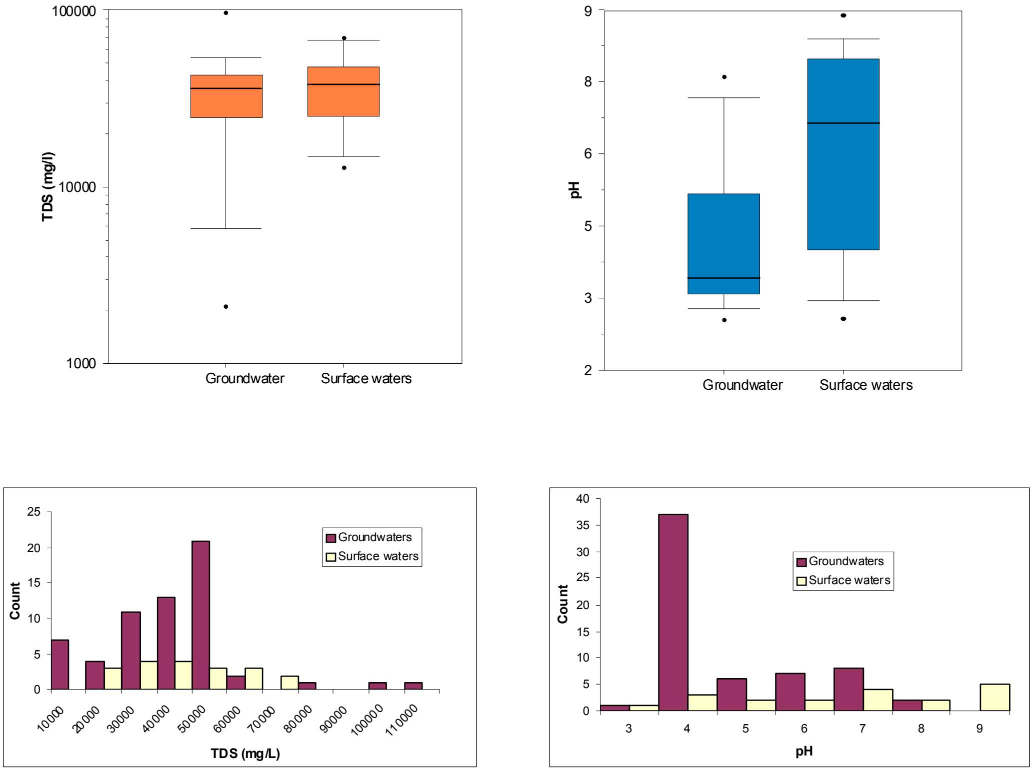


Figure 4-4 Boxplots (showing median and interquartiles) and histograms showing TDS (left) and pH (right) for groundwater and surface waters.

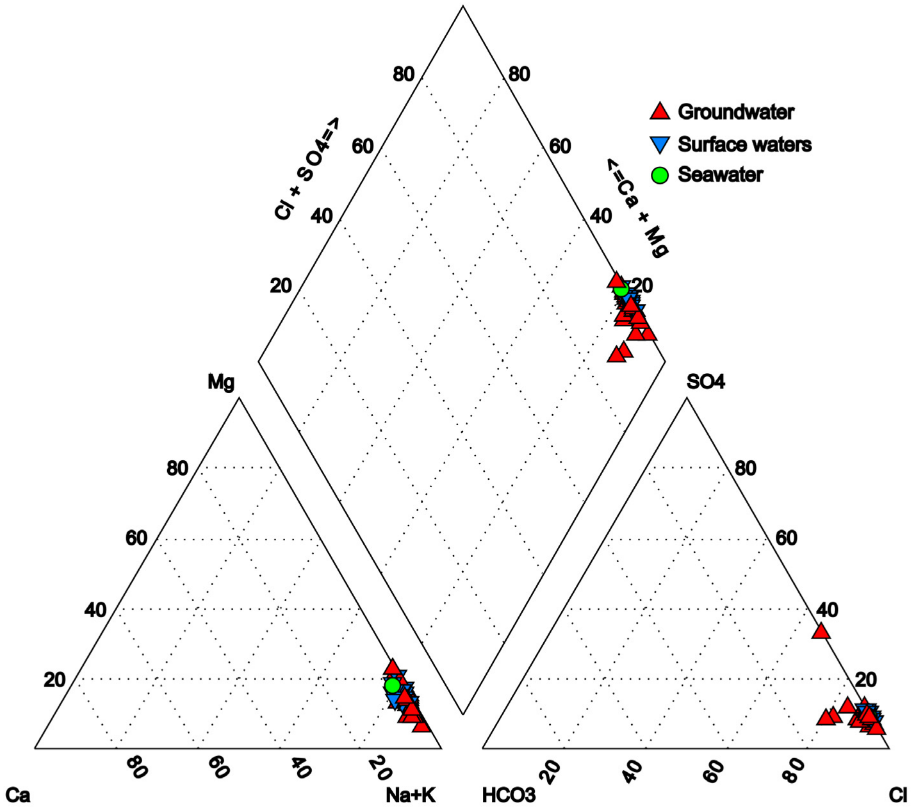


Figure 4-5 Piper plot for surface waters and groundwaters of the central and eastern South Coast.

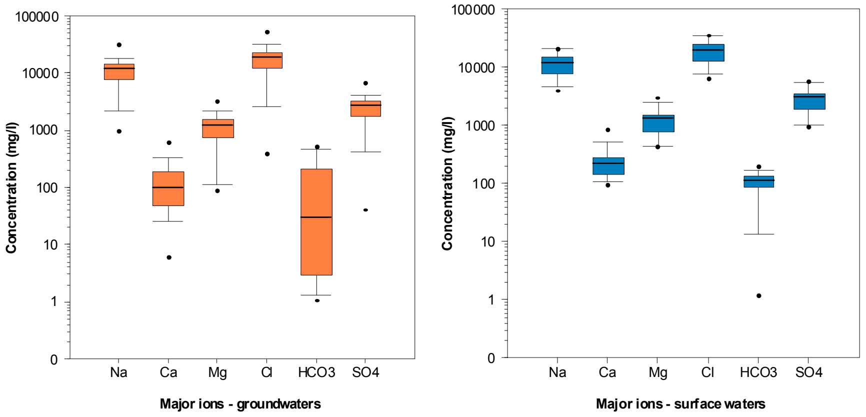


Figure 4-6 Boxplots showing the distribution of concentrations of the major ions for surface waters (left) and groundwaters (right). The middle line of the boxplot is the median value and middle 50% or inter-quartile range between the 25th and 75th percentile is shown by the extremities of the coloured box. The bars show the 10th and 90th percentiles and the points show the maxima and minima.

The degree of acidity, as measured by pH, has a strong bearing on the solubility of many ions. Many metals and other ions are more soluble under acidic conditions. The major ions were plotted against pH (Figure 4-7). Most major elements show a poor correlation with pH, except silica which shows enrichment under acidic conditions (Figure 4-7). The minor and trace elements were also plotted against pH (Figure 4-8 to Figure 4-10). Most trace metal ions showed a strong correlation with pH, having their highest concentrations under acidic conditions and being at negligible concentrations under alkaline conditions. Some trace elements, such as nickel (Ni) zinc (Zn) and copper (Cu) plus the rare earth elements lanthanum (La) and cerium (Ce), had some very high concentrations under acidic conditions, and were in the mg/L range.

Iron (Fe) and aluminium (Al) showed high concentrations under both acidic and alkaline conditions. The high Fe values at neutral pH are probably dominated by ferrous iron which is highly soluble. This is supported by Eh values, where available, which indicate moderately reducing groundwater conditions. The highest Al concentrations occurred under acid conditions. High Al concentrations, above theoretical maximum concentrations, occurred under both neutral and alkaline conditions. This could be due to Al forming complexes and that Al is amphoteric in nature (soluble under both acidic and alkaline conditions).

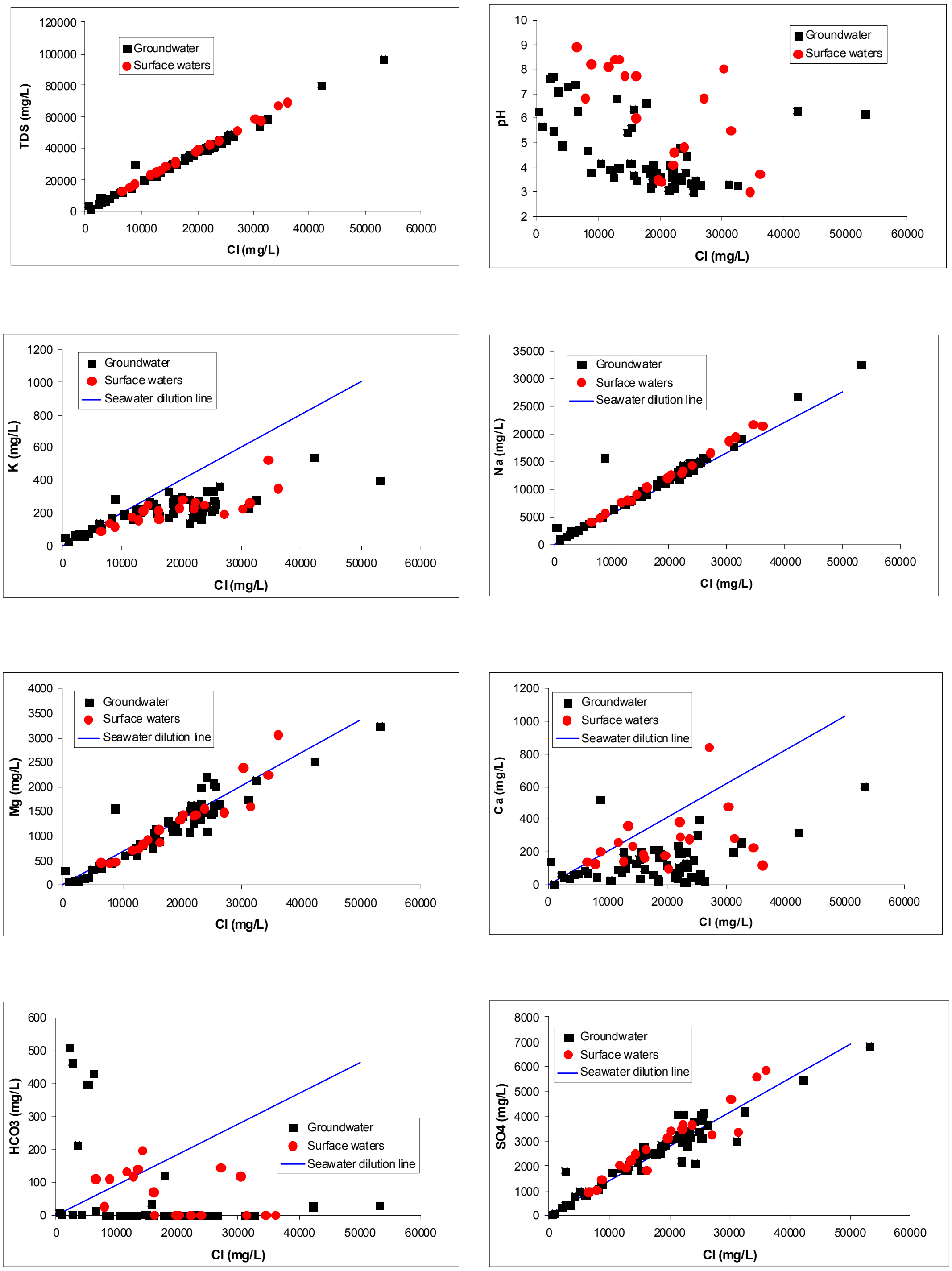


Figure 4-7 The relationship of TDS, pH and major ion concentrations to Cl in surface and groundwaters from the central and eastern South Coast. The solid blue line is the seawater dilution line.

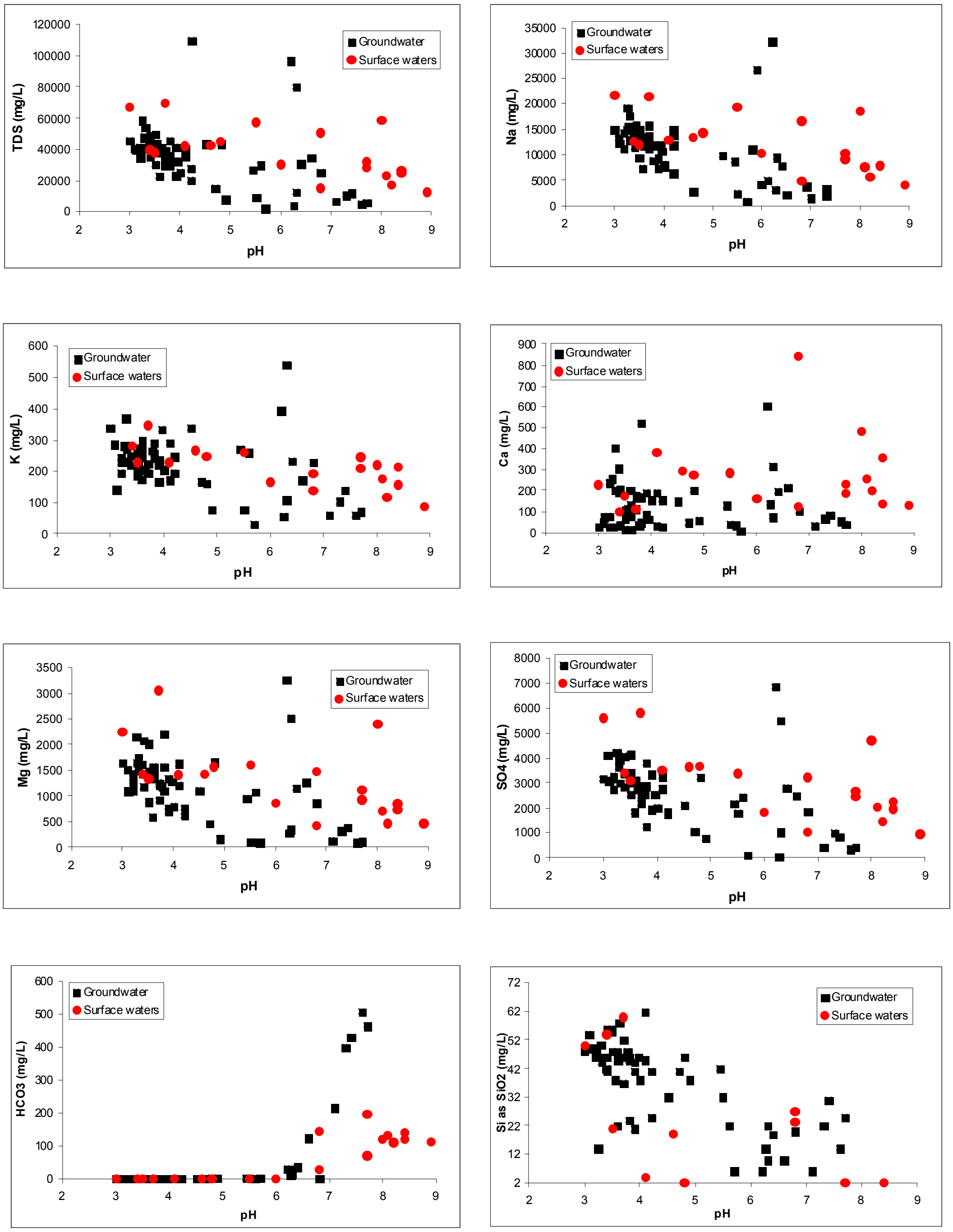


Figure 4-8 Relationship of TDS and major ions with pH for surface and groundwaters from the central and eastern South Coast.

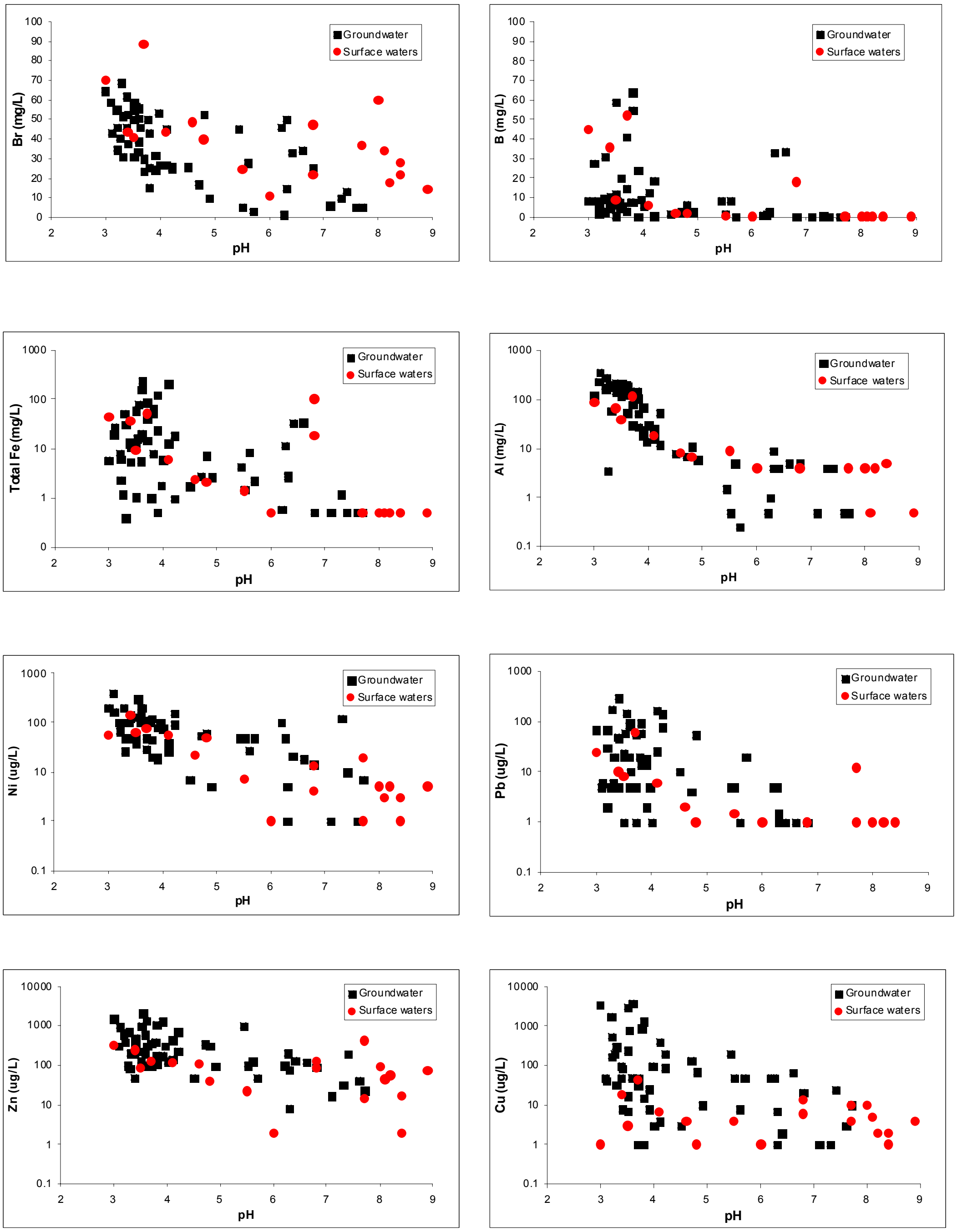


Figure 4-9 Concentration of minor elements and trace metals plotted against pH. Note log scales except for Br and B.

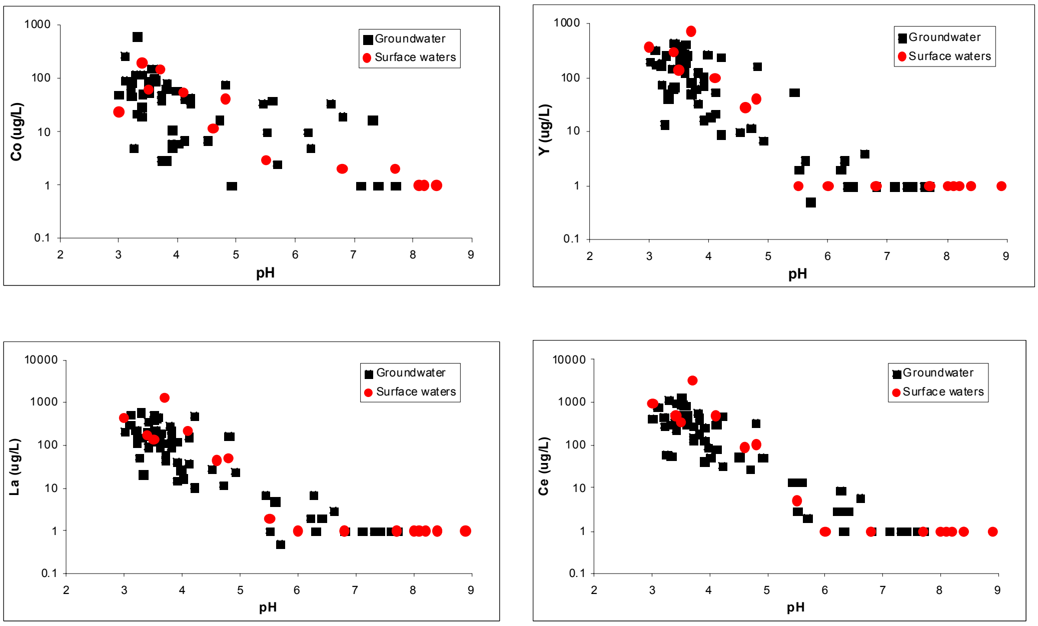


Figure 4-10 Concentration of trace elements plotted against pH. Note the log scale.

4.2.4. Case study: Dalyup River – Lake Gore catchment

Some of the results from sampling in the Dalyup River-Lake Gore catchment are shown in Table 1. Groundwater samples north of Boydells Road (Figure 4-2) were acidic with an average pH of 3.8 (see Table 4-1and Figure 4-2). The surface waters in the upper catchment, north of Boydells Road were also acidic with a pH range between 3.4 and 4.8. Surface waters in the lower catchment, from the South Coast Highway and further south, the waters were alkaline.

Trace metals such as Al, Fe, Ni, Zn and Cu had the highest concentrations in the more acidic ground and surface waters in the upper catchment. The concentration of most trace metals decreased to below detection limit at Lake Gore with the exception of Al which was still at high concentrations (5 mg/L).

Table 4-1 Water quality at select sites in the Dalyup River – Lake Gore Catchment (sites shown in **Figure 4-2**).

Parameter	Unit	Average groundwater values for bores North of Boydells Rd (n = 3)	Tributary	Dalyup R West	Dalyup R West	Drain – E of Dalyup Rd	Dalyup R	Dalyup R West	Dalyup R	ANZECC/ ARMCANZ (2000) 80% Freshwater
			Boydells Rd	Boydells Rd	Speddingup Rd	S of Speddingup Rd	Cnr Oaks & Boydells Rd	South Coast Hwy	Pioneer Reserve	
Date sampled			9 Oct 2007	11 Oct 2007	9 Oct 2007	16 Oct 2007	9 Oct 2007	17 Oct 2007	17 Oct 2007	
Flow estimate	L/s		100 -500*	6	<100*	4	> 500*	>100*	>100*	
Rainfall previous 48 hrs	mm		19.4	5	19.4	0.8	19.8	0	0	
pH		3.8	3.5	4.8	4.1	3.4	4.8	7.7	8.4	6.5 – 8
E.C.	dS/m	42	49.4	53.4	53	51	57	42	30	
Alkalinity	mg (CaCO$_3$)/L	0	0	0	0	0	1.5	100	180	
Acidity	mg (CaCO$_3$)/L	460	245	55.5	110	420	48	0	0	
Aluminium	mg/L	64	39	8	18	66	7	4	5	0.15
NPDOC	mg/L		13	11	20	13	13	14	15	
Boron	mg/L	39	6	5	6	10	4	5	4	1.3
Iron	mg/L	39	9	2	6	36	2	<1	<1	
Manganese	mg/L	1.1	<1	<1	<1	<1	3	<1	<1	3.6
Silica	mg/L	38	21	19	4	54	2	<2	2	
Nickel	µg/L	67	63	22	55	144	49	19	3	17
Copper	µg/L	56	3	4	7	18	<1	10	<1	2.5
Zinc	µg/L	400	90	106	115	240	38	424	<3	31
Arsenic	µg/L	2.2	1	<1	<1	5	<1	<1	<1	360
Selenium	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	34
Molybdenum	µg/L	<10	<10	<10	<10	<10	<10	<10	<10	
Silver	µg/L	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.2
Cadmium	µg/L	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	0.8
Tin	µg/L	<5	<5	<5	<5	<5	<5	<5	<5	
Lead	µg/L	3.8	8	2	6	10	<2	12	<2	17
Chromium (total)	µg/L	3.6	2	<1	<1	6	<1	2	<1	40 (CrVI)

* Flow estimated, as could not be measured reliably

4.3. Discussion

The salinities of surface and groundwaters measured in the South Coast study area were considerably lower than salinities measured for the Avon catchment (Shand 2008). In surface waters, this could be due to the time of year the sampling was conducted as well as the South Coast having a higher rainfall and being externally drained.

Another major difference between the South Coast and Avon studies was in the pH distribution for waters. In the Avon catchment, both groundwaters and surface waters showed a bimodal pH distribution with distinct peaks at acidic and cirum-neutral pH (Shand 2008) whereas in the South Coast study the bimodal nature of pH distribution was not evident. The groundwaters showed a distinct acidic peak and surface waters showed a peak towards alkaline conditions (Figure 4-3). This is part due to sampling methodology of the study that mainly targeted acidic bores in the Salmon Gums Mallee soil landscape zone. It also reflects the nature of the hydrology and geochemical processes of the eastern south coast. The groundwaters in the upper catchments are acidic, but tend towards neutral or alkaline in the lower catchment (Lillicrap and George 2008) (Figure 4-1). Surface waters were acidic only in parts of the upper catchments but in the lower catchments all surface waters measured were alkaline, partially reflecting a larger surface runoff component in waters in the lower catchments.

Even when rivers and streams were acidic in the upper catchment, they tended towards alkaline in the lower catchment (Figure 4-1 and Figure 4-2). This would suggest that in the streams sampled, the lower reaches of the rivers have sufficiently alkalinity to neutralise the acidic input that occurred in the upper reaches.

Most of the potentially toxic minor and trace elements such as Al, Cu, Zn, Pb, Ni and B (ANZEEC and ARMCANZ 2000b) had the highest concentrations under acidic conditions (Figure 4-9 and Figure 4-10) which exceeded ANZEEC and ARMCANZ aquatic ecosystem guideline values (80% level of protection for freshwater). The concentration of elements mostly dropped below guideline values under neutral and alkaline conditions. This would suggest that acidic, saline groundwaters represent only a geochemical risk in the upper catchments where surface waters were acidified, but the risk diminished towards the lower catchment as pH increased due the buffering capacity of streams in lower catchments. Further insight can be gained into the nature of the geochemical risks by looking at more detailed sampling in the Dalyup River - Lake Gore catchment.

Groundwaters in the upper Dalyup catchment, north of Boydells Road, were acidic with an average of 3.8 (Table 4-1 and Figure 4-10). At Boydells Road and further north, the Dalyup River West, the Dalyup River and tributaries were acidic (Table 4-1 and Figure 4-2). There were high flows in the tributary on Boydells Road at the time of measurement (estimated between 100 and 500 L/s) and the West Dalyup River was measured during low flow conditions (6 L/s). The surface waters had high concentrations of Al, B, Ni, Zn and Cu exceeding ANZEEC and ARMCANZ aquatic ecosystem guideline values (80% level of protection) (Table 4-1). At these levels, the acidification impacts on aquatic ecosystems within this part of the catchment would most likely be through the toxic effects of metals.

The acidity of surface waters in the upper catchment could be due to a number of different factors. Firstly, the catchment has been extensively cleared and this has resulted in rising watertables which increased baseflow to surface waters in the upper catchment. Additionally, there are hundreds of kilometres of drains for salinity management in the upper catchments which drain groundwater to drainage lines. The discharge of acidic saline groundwaters to streams and rivers from agricultural drainage could also have contributed to acidification of surface waters. Ultimately, the acidic saline groundwaters would have been the source of acidification of surface waters in the upper catchment.

When sampled, lower down the catchment, the pH of the Dalyup River West, at the South Coast Highway had increased to 7.7 though Al, B, Ni, Zn and Cu were still above aquatic ecosystem guideline values. The pH of the Dalyup West River increased from 4.8 at Boydells Road to 7.7 at the South Coast Highway. The only other stream that contributes any significant flow to the West Dalyup River between Boydells Road and the South Coast Highway is the tributary that had acidic surface waters. The catchment of the West Dalyup River also becomes more steeply incised between Boydells Road and the South Coast highway, with the side slopes only contributing small volumes of water compared to flows from the upper catchment. There was a significant increase in pH over a distance of 16 kilometres which could not be explained by dilution alone. Therefore, there had to be an additional source of alkalinity input to the river to raise the pH so substantially. The hydrogeology changes substantially between Boydells Road and the South Coast Highway, going from weathered Proterozoic-Archaean granite/gneiss aquifers to Plantagenet group aquifers. The change in hydrogeology is the most likely reason for the substantial increase in pH observed in the West Dalyup River. Biogeochemical processes in the hyporheic zone could also be a significant source of alkalinity.

At the mouth of the Dalyup River (at Pioneer Park), the pH had further increased to 8.4 and all minor and trace elements (excluding nutrients) with the exception of Al and B were below guideline values. The extremely high concentration of Al (5 mg L^{-1}) in the Dalyup River at Pioneer Park is of concern as Al is toxic to aquatic species such as fish, amphibians, crustaceans, molluscs and worms (ANZEEC and ARMCANZ 2000b), particularly as it is entering a Ramsar wetland of international importance.

The confluence of the Dalyup and West Dalyup Rivers occurs up stream of Pioneer Park. High Al concentrations that might have been present in the West Dalyup River, for example as organically complexed aluminium, should have been significantly diluted as the rivers merged. This should result in lower concentrations of Al at Pioneer Park, however the measured Al concentration was slightly higher than measured in the West Dalyup River. at the South Coast Highway. High Al concentrations are not expected to occur in the lower Dalyup River as its upper catchment does not have as significant acidification issues as the upper catchment of the West Dalyup and Dalyup receives greater inflows in from tributaries in its lower catchment. This suggests that another process might be involved in controlling the Al concentration in the Dalyup River catchment. Therefore a conceptual model has been developed as a possible explanation for the high Al concentrations at the mouth of the Dalyup River.

The main key to the conceptual model is amphoteric nature of Al, that is, it is soluble under both acidic and alkaline conditions, but relatively insoluble around neutral conditions. In the proposed conceptual model, naturally occurring acidic saline groundwaters dissolve Al from the surrounding matrix in the headwaters of the catchment, where it is discharged to weakly buffered surface waters (that become acidic). The Al is transported downstream, and as the pH increases due to mixing with alkaline surface and groundwater discharges, the solubility of Al decreases favouring precipitation as flocs. The Al flocs are then carried in suspension in the river and transported downstream (increasing turbidity). As the pH of the river starts to rise even further due to alkaline inputs towards the lower catchment, the solubility of Al increases. The Al flocs transported from the upper catchment then go back into solution, resulting in the increased Al concentration at the mouth.

In order to test this conceptual model, a simple geochemical model was developed using the geochemical package PHREEQC for Windows (v2.15.07, Parkhurst and Appelo, 2006). It was assumed the main source of Al was from the upper catchment of the West Dalyup River as the greatest extent of acidification in its upper catchment. The water quality parameters from the tributary on Boydells Road (Table 4-1) were used as the starting solution and alkalinity ($NaHCO_3$) was added to the solution incrementally to simulate alkalinity being added along the river until a pH of 8.4 was reached, which is the same pH as recorded for the Dalyup River at Pioneer Park. The model was run to determine the concentrations of Al, Fe and pH as the alkalinity was added to the starting solution. Amorphous aluminium hydroxide ($Al(OH)_3a$) and gibbsite were used as the solid phases to control the solubility of aluminium. Amorphous Fe (III) hydroxide (Fe(OH)3a) was used as the solid phase to control the solubility of iron. The solid phases were allowed to redissolve. The results are shown in Figure 4-11. The PHREEQC modelled results approximates the measured values in the Dalyup River catchment (Figure 4-11). Therefore the geochemical modelling indicates that the conceptual model developed to explain the fate of Al in the catchment could be a possible explanation for the increase in Al measured at the mouth of the Dalyup River. This has implications for the management of acidic saline groundwaters in catchments as it suggests even though rivers and streams of the central and eastern south coast have some capacity to buffer pH and remove acidity, unless Al or Al flocculants are removed from the system, Al potentially poses an environmental risk to final receiving environments.

However, these results are based on a single sampling event. Further monitoring is required to more fully assess the likely threat that acidic saline groundwaters, and particularly the fate of Al, pose to final receiving environments before management implications can be reasonably determined.

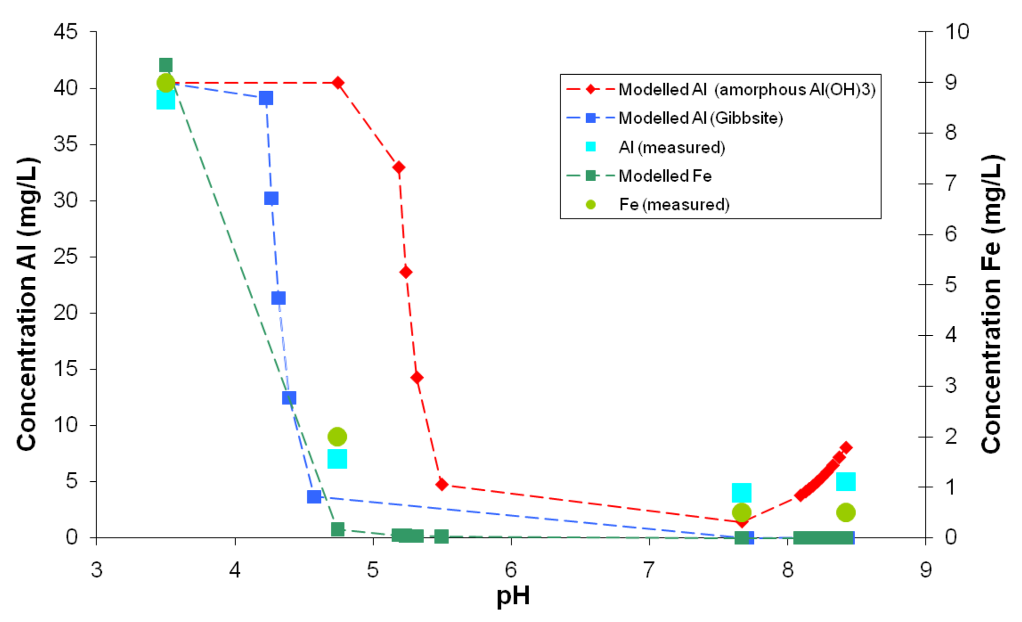


Figure 4-11 PHRREQC modelled Al, Fe and pH compared with measured values.

4.4. Main findings and management implications

- Acidic saline groundwaters (median pH = 3.6) are present in the upper catchments of the central and eastern south coast. There has been acidification of surface waters in headwaters of some catchments with concentrations of some potentially toxic minor and trace elements such as aluminium, copper, zinc, nickel, lead and boron exceeding ANZEEC and ARMCANZ aquatic ecosystem guideline values (80% level of aquatic fresh water species protection). Therefore acidic saline groundwaters (when discharged to streams) pose a geochemical risk where surface waters have become acidified in the upper catchments
- Surface waters measured in the lower catchments were alkaline and contained the capacity to buffer pH.
- Minor and trace metals elements (excluding nutrients) were all below ANZEEC and ARMCANZ aquatic ecosystem guideline values (80% level of aquatic fresh water species protection) in the lower catchment of Dalyup River – Lake Gore, a Ramsar wetland of international importance except for aluminium and boron.
- High levels of aluminium (5 mg L^{-1}), an element known to be highly toxic to aquatic species, was found to be entering Lake Gore. Sampling suggests the high aluminium concentrations are the result of acidification in the upper catchment. This implies acidification in the upper catchment could have an impact of final receiving bodies.
- As the results are based on a single sampling program no management implications can reasonably be inferred and further investigation is required to better ascertain the geochemical risks acidic saline groundwaters pose in the South Coast region.

5. CASE STUDY ASSESSMENTS OF REGIONAL DRAINAGE GEOCHEMICAL RISKS USING ACID-ALKALINE MIXING EXPERIMENTS, GEOCHEMICAL ANALYSIS AND MODELLING

Grant Douglas[1] **and Brad Degens**[2]
[1] Water Resources Protection, CSIRO Land and Water, PB 5, Wembley WA 6913
[2] Salinity and Water Resource Recovery Branch, Water Resource Management Division Department of Water, P.O. Box K822 Perth WA 6892

5.1. Introduction

A geochemical model has been constructed using the geochemical package PHREEQC for Windows (v2.12.05, Parkhurst and Appelo, 2006) to simulate batch mixing of acidic-saline waters present in deep drains with surface waters in receiving basins or stream channels in the Western Australian (WA) Wheatbelt. Two types of neutralisation of acidic waters have been used in this model – mixing of acidic drainage waters with either (i) naturally-occurring alkaline water from Ski Lake in the Yenyening Lakes system or with (ii) Indian Ocean seawater. The acidic-saline drain waters neutralised in this study were sampled from Boodarockin, Elachbutting, East Cowcowing, Beacon and Trayning. Previous discussion of modelling of the mixing behaviour of some of these waters (including locations) is given in Chapter 7 of Shand and Degens, 2008.

A number of empirical factors and geochemically-based assumptions are inherent in the batch mixing model. These assumptions are discussed in detail in Douglas and Degens (2008). This chapter describes results of bench-top mixing trials under controlled conditions undertaken with the samples of acidic-saline drain waters and alkaline waters and associated modelling using PHREEQC, based on a refined version of the model developed in earlier work (Douglas and Degens 2008).

5.2. Approach

Acidic-saline waters from deep drains the WA Wheatbelt (Table 5-1) were mixed with either naturally-occurring alkaline water from Ski Lake in the Yenyening Lakes system or with Indian Ocean seawater in the following proportions: 66.67, 80, 90.9, 95.24, 97.56, 99 and 99.5 alkaline component. These corresponded with the mixing ratios: 1:3, 1:4, 1:10, 1:20, 1:40, 1:99 and 1:100 and were compared with unmixed waters (Table 5-1). Reactions were undertaken in simple batches in acid-washed, continuously stirred 2L beakers. The required volumes of acidic-saline water were added to 200mL volumes of either the Yenyening Lakes or Indian Ocean seawater to achieve range of mixing ratios. In all mixing experiments, vessels were open to the atmosphere, maintained at laboratory room temperature (~22°C) and were stirred for two hours with pH recorded at both the commencement and end of the experiment. Where precipitates formed, these were allowed to briefly settle and *ca.* 50mL of supernatant was filtered through a 0.22 μm syringe filter and stored without headspace in an acid-washed polyethylene screw top container and refrigerated prior to analysis for metals. A second sample was also collected for major ion analysis. Where samples had a pH>4.5 an additional sample was collected for alkalinity analysis.

Analysis of solutions was undertaken at either the Chemistry Centre of Western Australia or at Genalysis Laboratories, Western Australia using ICP-OES, ICP-MS or titrimetric methods A comprehensive suite of major and trace elements were analysed including: Na, K, Ca, Mg, Cl, SO_4, total alkalinity, HCO_3, CO_3, Br, Al, B, Fe, Mn, P, Si, Sr, V, Cr, Co, Ni, Cu, Zn, As, Se, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, Th, U. Due to the saline to hypersaline nature of the waters analysed (sample salinity was sometimes more than double that of seawater), considerable dilutions were often necessary for ICP-MS analyses limiting the lower detection limits for some elements.

Modelling of the behaviour of pH during mixing of acidic and alkaline waters was undertaken using PHREEQC code (as described in Douglas and Degens 2008) with improvements achieved using the results of the bench-top mixing and modelling calibration (data not shown here).

5.3. Results

Diagrams plotting the response of various water quality parameters after mixing between Elachbutting drainwater and Indian Ocean seawater have been used to illustrate general mixing trends (Figure 5-1). The general similarity in the shape of the mixing curves, irrespective of the type of acidic-saline Wheatbelt drain water and the type of alkaline water, is exemplified in grouped pH-titration plots for both the Yenyening Lakes and Indian Ocean seawater (Figure 5-2).

Table 5-1 Details and summary initial water chemistry of acidic saline drain waters and alkaline lake and seawater used in mixing experiments.

Location	Site	pH	TDS (mg/L)	Total Alkalinity (mg $CaCO_3$/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
Boodarockin	Drain, Daddow Rd, NE of Merredin	2.84	33798	0	0.03	123.0	1.94
Elachbutting	Drain, Rabbit Proof Fence Rd, NE Mukinbudin	3.22	52890	0	0.010	105.3	2.0
Beacon	Drain, Beacon Rock Road, Beacon	2.89	38966	0	0.02	60.8	0.79
Trayning	Drain, Lee Rd, SE Trayning	2.52	49144	0	0.12	182.5	0.76
East Cowcowing	Drain, Gambles Rd, North Wyalkatchem	2.86	59265	0	0.82	113.3	0.48
Yenyening Lakes	Ski Lake, Ski Lake Rd,	7.61	36828	48.0	<0.005	0.010	<0.005
Indian Ocean seawater	City Beach, Perth	8.10	32546	98.7	<0.005	0.080	<0.005

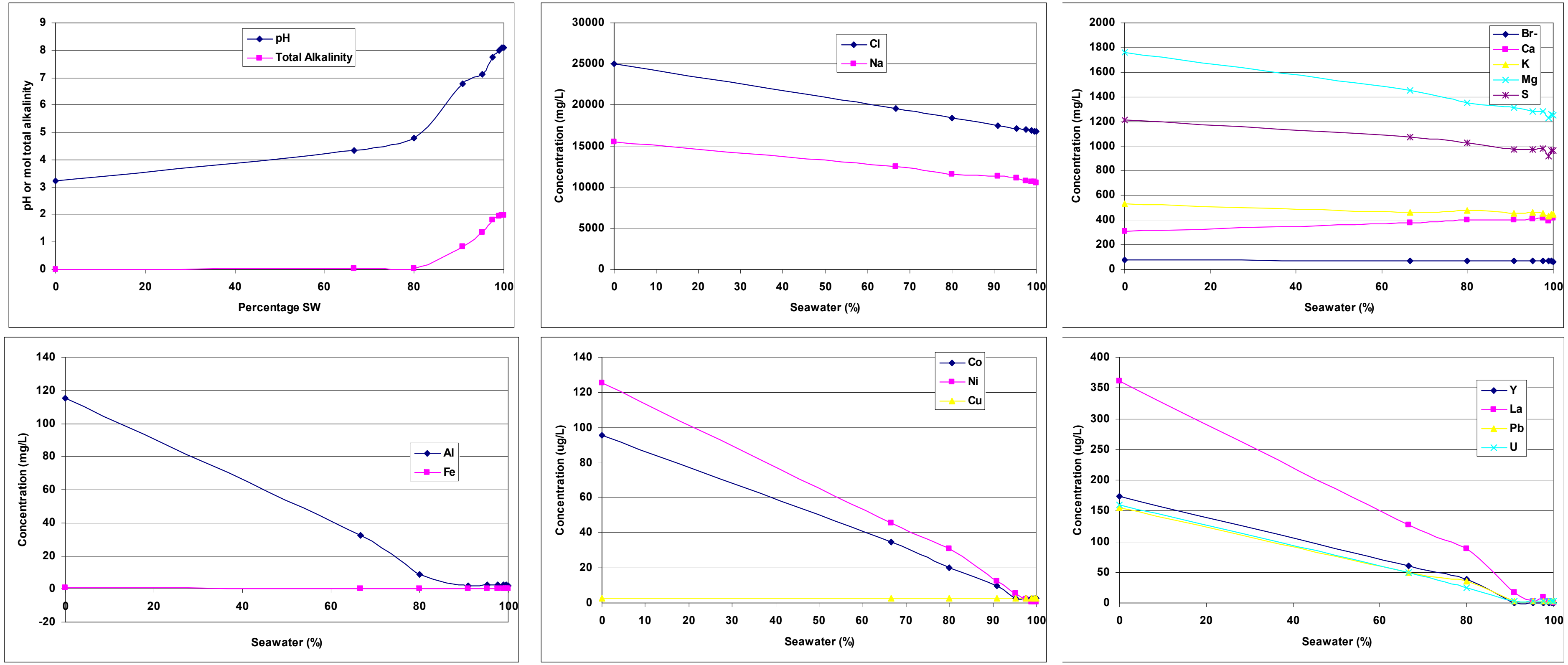


Figure 5-1 Changes in chemical characteristics of water resulting from batch mixing of Elachbutting drainwater and Indian Ocean seawater.

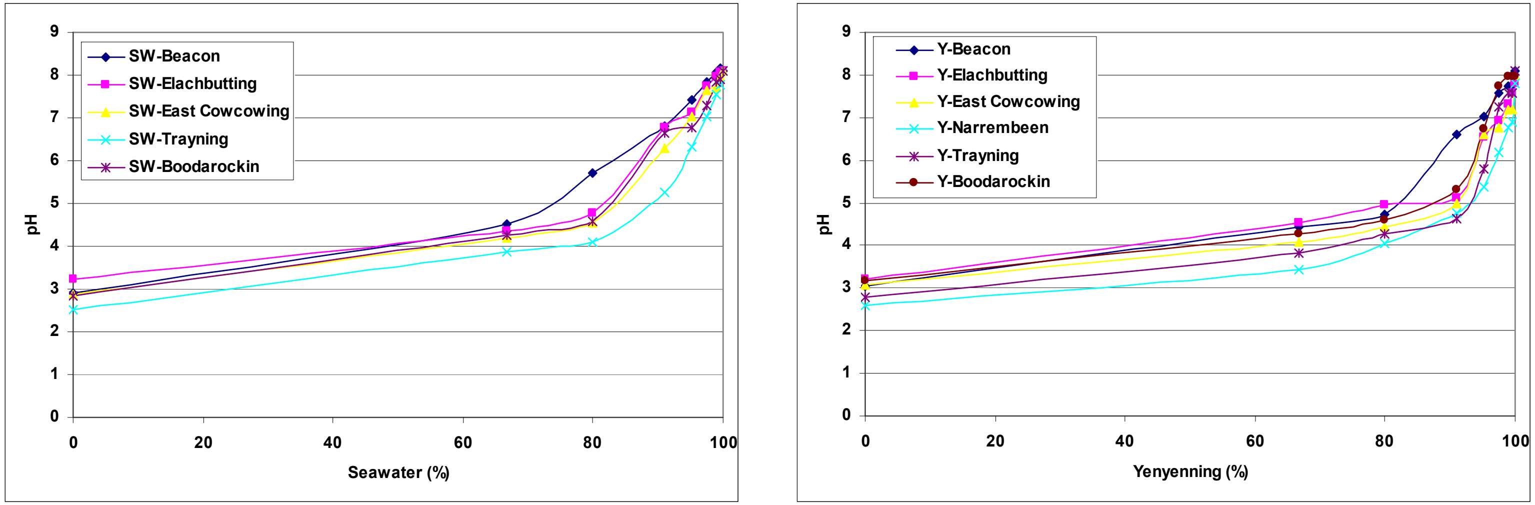


Figure 5-2 pH – mixing diagrams for bench-top mixing of Indian Ocean seawater (code SW, left plot) and Yenyening Lakes water (code Y, right plot) with acidic-saline drain waters from the WA Wheatbelt.

Mixing of Elachbutting drain water and Indian Ocean seawater resulted overall in a distinctly non-linear trend comprised of both linear components and plateaus. Mixing of acidic-saline drain water with up to 80% Indian Ocean seawater generally resulted in a linear change from pH 3.22 (100% Elachbutting drain water) up to *ca.* pH 5 (Figure 5-2). Thereafter, a more rapid increase in pH was observed, interspersed by one plateau at *ca.* pH 7 and then a non-linear increase to pH 8.10 (100% Indian Ocean seawater). This general trend in mixing between acidic-saline waters and either Yenyening Lakes water or Indian Ocean seawater is also generally apparent in other mixing experiments (Figure 5-2). However, where Yenyening Lakes water was used the initial linear section of the pH trend curve persisted up to about a 90% Yenyening Lakes composition, as the Yenyening Lakes water has approximately half the alkalinity of the Indian Ocean seawater.

A more detailed description of the nature of mixing between acidic-saline drain waters and alkaline waters from either the Yenyening Lakes or Indian Ocean seawater can also be made using the model developed with PHREEQC (see Douglas and Degens, 2008 for details). Five separate batch mixing scenarios were modelled: mixing of a simple acid with Indian Ocean seawater (SW); mixing of a simple acid solution with Yenyening Lakes water (Y); a simple acid-base batch mixing; mixing of Elachbutting water (EB) with Indian Ocean seawater (SW); and mixing of Elachbutting water (EB) with Yenyening Lakes water (Y) (Figure 5-3).

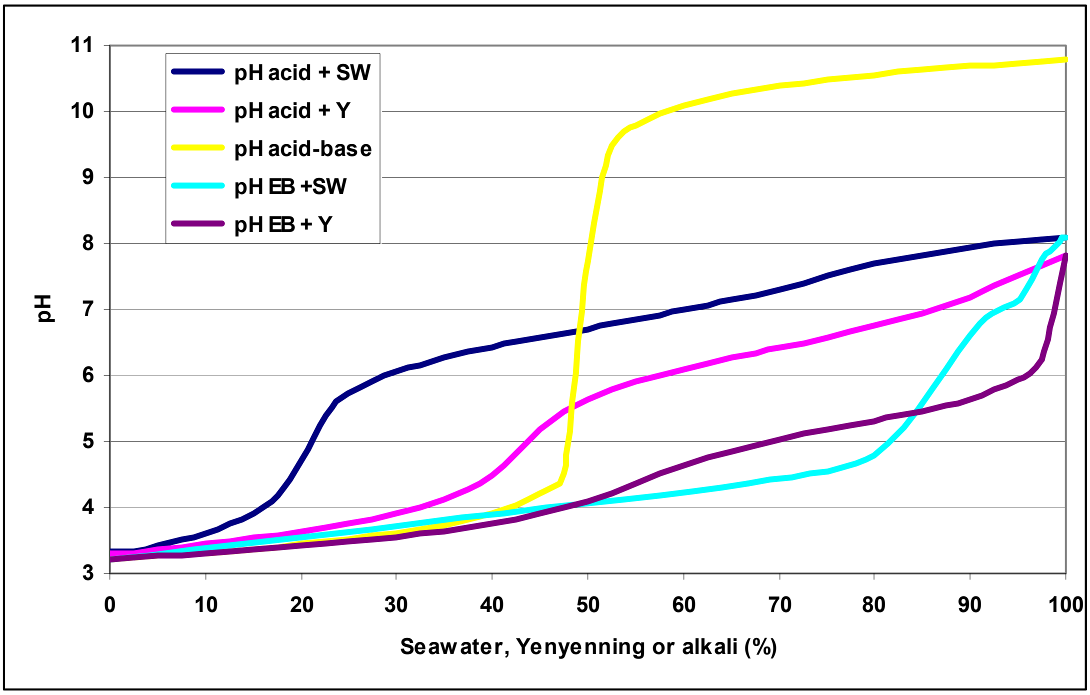


Figure 5-3 pH-mixing diagrams modelled using PHREEQC of mixing of a simple acid with Indian Ocean seawater (acid + SW), mixing a simple acid with Yenyening Lakes water (acid + Y), a simple acid-base batch mixing (acid-base), mixing of Elachbutting water with Indian Ocean seawater (EB + SW) and mixing of Elachbutting water with Yenyening Lakes water (EB + Y).

In the simplest case, that of mixing a simple acid (HCl) and base (NaOH) in a range of different proportions as a series of batches, as base is added a gradual increase in pH was modelled to occur until just prior to 50% of the mixture being comprised of the alkaline solution Figure 5-3). Thereafter, there was a turning point, a rapid increase in pH with the maximum rate of change occurring at pH 7 (inflexion point), followed by a gradual plateauing with addition of increased base after 55%. This uniform sigmoidal curve represents an ideal case where equal amounts of an identical molarity (strength) of acid and base are mixed in varying proportions as a series of batches, producing a classic sigmoidal shape with a mid-point of the inflexion at pH 7.

The classic sigmoidal acid-base batch mixing curve can, however, be modified in the case where the acid and base are of unequal molarity in terms of the position, height and slope of the turning points and inflexion. This is illustrated in the examples of mixing of acid with Indian Ocean seawater or Yenyening Lakes water, with the former exhibiting steeper and earlier turning points as it contains approximately twice the alkalinity of the latter (Figure 3). Mixtures of the acidic-saline Elachbutting water with alkaline waters showed slightly different sequences of turning points and inflexions due to the different alkalinities of the Indian Ocean seawater and Yenyening Lakes water (see Table 5-1).

An additional factor that can also modify the position and overall shape of the batch mixing-pH curve is the presence of other dissolved elements in the water, particularly Al, in the case of acidic-saline drain waters. This modification of the pH-neutralisation curve is primarily due to the production of additional acidity during Al hydrolysis which represents an additional inventory of acidity to that already present, and which is generated during neutralisation. The net effect is to endow the acidic-saline drain waters with an additional component of acidity that is pH-dependent. In addition, dissolution of Al-minerals (formed during the initial hydrolysis and precipitation of other secondary minerals) at increasingly alkaline pH that may also modify the pH-mixing curve. All of these aspects related to the non-ideal shape of the pH-mixing curve are discussed in more detail later.

It was apparent from these batch experiments that mixing of saline-acidic drain water from the WA Wheatbelt such as that in drains near Elachbutting and an alkaline surface water, such as water in the Yenyening Lakes, generally required ratios of between 10:1 and 20:1 of alkaline to acidic-saline water to achieve a pH of 7 and up to 50:1 or even 100:1 to achieve a final pH of 8. This is less than the mixing ratios estimated by modelling using PHREEQC in earlier studies where final pH was limited by the pH of the alkaline waters.

General trends resulting from mixing of Elachbutting drain water and Indian Ocean seawater were also apparent in both major cations and anions and trace elements (Figure 5-1), albeit different, apart from total alkalinity, to that observed for pH (Figure 5-1). The majority of major ions, and in particular Na and Cl, displayed conservative behaviour as a result of the mixing of Elachbutting drain water and Indian Ocean seawater. Similarly, K, Ca, Mg, S and Br also displayed mostly conservative mixing behaviour apart from small variations, generally where the proportion of the Indian Ocean seawater component was between 95 and 99% (also where pH was >6).

In contrast to the mostly conservative behaviour of the major ions, Al and the trace elements Co, Ni, Cu, Pb, Y, La, and U generally displayed a distinctly non-conservative mixing behaviour where the Indian Ocean seawater component exceeded *ca.* 80% (Figure 5-1). Until this point, the concentrations generally reflected a dilution pattern. The majority of these trace elements did not remain in solution above 95% mixing with the Indian Ocean seawater component. These 80 and 95% components of Indian Ocean seawater correspond to the major increase in pH and a pH range of *ca.* 4.8-8.1 (Figure 5-2).

5.4. Discussion

Batch mixing of a range of acidic-saline waters obtained from drains in the WA Wheatbelt with alkaline water from either Indian Ocean or the Yenyening Lakes generally demonstrated non-sigmoidal neutralisation behaviour consistent with the buffering and precipitation of secondary, probably transient minerals phases and/or the production of additional acidity during neutralisation. These mechanisms lead to a marked departure from a smooth sigmoidal curvature of simple acid-base systems often producing a series of unexpected changes in pH, plateaus or other non-uniform behaviour as observed in this study.

Development of a conceptual understanding of the major mechanisms involved in the neutralisation of acidic-saline waters based on the batch experiments conducted in this study was used to underpin the development of the PHREEQC mixing model. Key buffer mechanisms and the effect of mineral precipitation on solution pH in the batch mixing between acidic-saline drain waters and alkaline waters from the Indian Ocean or the Yenyening Lakes are discussed below.

Within acidic sulfate-rich waters, such as those studied, there are generally four buffer mechanisms present that will influence the type and extent of neutralisation (Totsche *et al.*, 2003). There are as follows:

(i) hydrogen sulfate buffer
(ii) iron hydroxysulfate buffer
(iii) aluminium hydroxysulfate buffer
(iv) an ion exchange buffer

Although the acidic-saline drain waters in this study are similar to Acid Mine Drainage (Degens et al. 2008) the concentrations of soluble iron were comparatively low in the drain samples and therefore unlikely to have a major influence in regulating acidity during neutralisation and precipitation reactions with alkaline waters in this study. Iron concentrations were uncharacteristically low, compared with previous samples of the drains where concentrations could be up to 2 orders of magnitude greater (Degens et al. 2008; Shand and Degens, 2008). This may have been due to oxidation and precipitation of secondary iron oxyhydroxide and hydroxy-sulfate minerals (e.g. akaganeite and schwertmannite; Fitzpatrick et al. 2008) during storage prior to the mixing trials being undertaken. Consequently, dissolved iron will not be further considered in this discussion. Similarly, ion-exchange buffering will not be considered as many of these reactions such as the ageing of schwertmannite and conversion to goethite with the consequent release of SO_4^{2-} and H^+ occur over a longer period than the 2 h mixing experiments undertaken in this study. These reactions, however, are likely to be relevant within the WA Wheatbelt in both perennial and ephemeral and intermittently inundated streams and artificial drainages.

Thus, the two mechanisms of most importance in this study are hydrogen sulfate consumption of hydroxyl alkalinity and Al-hydrolysis with the formation of aluminium hydroxysulfate minerals such as basaluminite ($Al_4SO_4(OH)_{10}.5H_2O$). With this in mind, the nature of the shape of the pH-mixing curve for batch mixing between Elachbutting drain water and Indian Ocean seawater can be further examined (Figure 5-1).

Addition of increasingly large volumes of alkaline Indian Ocean seawater to Elachbutting drain water (*i.e.* commencing from the acidic end of the mixing experiments) results in a gradual increase in pH reflecting the logarithmic nature of the pH scale and sulfate consumption of added hydroxyl alkalinity via the following reaction (1):

$$HSO_4^- + 2OH^- \rightarrow SO_4^{2-} + H_2O \quad (1)$$

The net result of this reaction is that acidity is consumed without the formation of a mineral precipitate. In particular systems, however, an increase in pH in the presence of abundant sulfate may lead to the precipitation of sulfate-bearing minerals.

Further addition of alkalinity (*i.e.* an increasing ratio of Indian Ocean seawater to Elachbutting drain water) invokes the second mechanism, that of Al-hydrolysis and a series of possible reactions leading to mineral precipitation (Table 5-2) that have also been verified as theoretically stable minerals by geochemical modelling as a function of pH and percentage Indian Ocean seawater (Figure 5-4).

Thus, a range of Al-hydrolysis reactions forming Al-hydroxy or Al-hydroxysulfate minerals may occur with the majority of mineral formation and transformation/dissolution occurring between pH 4 and 7. These Al-hydrolysis reactions correspond to the first pH change and plateau in the pH-Indian Ocean seawater batch mixing curve for the majority of acidic-saline drain waters in the WA Wheatbelt (Figure 5-2). Where sulfate ions are incorporated into the precipitating Al mineral, as in the case of hydroxysulfate minerals, the requirement for hydroxyl is substantially reduced. This then results in the enhanced neutralisation and hence greater increase in pH as observed in the pH-Indian Ocean seawater or pH-Yenyening Lakes curve for all systems examined in this study (Figure 5-2). Noteworthy is that this series of reactions corresponds to a slight decrease in dissolved SO_4 at *ca.* pH 4.8 or with the addition of approximately 80% Indian Ocean seawater (Figure 5-1).

Table 5-2 Al-hydroxy or Al-hydroxysulfate minerals potentially present as precipitates during the neutralisation of acidic-saline WA Wheatbelt drain waters as identified by geochemical modelling.

Mineral	*Reaction*	*H^+/Al^{3+} ratio*
Jurbanite	$Al^{3+} + SO_4^{2-} + H_2O \rightarrow AlSO_4OH + H^+$	1.0
Basaluminite	$4Al^{3+} + SO_4^{2-} + 15H_2O \rightarrow Al_4SO_4(OH)_{10}{:}5H_2O + 10H^+$	2.5
Alunite	$K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow KAl_3(SO_4)_2(OH)_6 + 6H^+$	2.0
Gibbsite	$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$	3.0

A small plateau at *ca.* pH 7 is suggestive of the production of additional acidity despite of an increasing proportion of Indian Ocean seawater (Figure 5-1 and Figure 5-2). Geochemical modelling suggests that the dissolution of alunite is theoretically possible as it becomes nominally undersaturated at *ca.* pH 7 (Figure 5-4). Alunite, amongst other Al-hydroxysulfate minerals is known to be a source of latent acidity (*e.g.* McElnea et al., 2002) via the following reaction (2):

$$KAl_3(SO_4)_2(OH)_6 + 3\,H_2O \rightarrow 3\,Al(OH)_3 + K^+ + HSO_4^- + 2H + SO_4^{2-} \quad (2)$$

thus, alunite dissolution in increasingly alkaline mixing combinations between Indian Ocean sweater and acidic-saline WA Wheatbelt drain waters may explain the small plateau in the pH-mixing curve.

In the specific example where Elachbutting drain water is mixed with Indian Ocean seawater, mineral reactions involving Al are theoretically saturated at pH of *ca.* 3-7 for alunite, pH 3-4.5 for jurbanite, greater than pH 4.5 for gibbsite and at *ca.* pH 4.5 for basaluminite (Figure 5-4). The greatest change in theoretical solubilities occurs at *ca.* pH 4.5 where a cascading sequence of theoretically precipitating minerals are generated. These minerals initially contribute H^+ via precipitation and then potentially OH^- via dissolution and/or H^+ as latent acidity (if OH^- or H^+ are not consumed in subsequent precipitation reactions) as the proportion of Indian Ocean water is increased.

The resistance to neutralisation of acidic-saline WA Wheatbelt drain water after mixing with alkaline Yenyening Lakes water or Indian Ocean seawater (as demonstrated in the batch mixing in this study) can be further explained by the following generalised example. As background, the pH and Al concentration for the five acidic waters used in this study was 2.87 ± 0.25 and 119 ± 43 mg/L (mean ± 1 standard deviation), respectively.

If a hypothetical acidic-saline water of pH 3 and 100 mg/L Al was to be neutralised, and if it is assumed that there is an average H^+/Al^{3+} ratio of 2 (Table 5-2) for precipitating minerals, and momentarily disregarding later possible partial neutralisation of acidity by minerals containing OH^-, then approximately 5-10 times the number of protons may potentially be produced during Al precipitation reactions than originally present in the solution.

Alternatively, net acidity can be calculated on the basis of pH and metals in solution using the equation (3) of Hedin *et al.* (1994):

$$\text{Acidity} = 50\{1000(10^{-pH}) + [2Fe^{2+}) + 3(Fe^{3+})]/56 + 2(Mn)/55 + 3(Al)/27\} \qquad (3)$$

where acidity is expressed in mg/L $CaCO_3$ with Al, Fe and Mn in mg/L. In this study it has been assumed that the majority if not all of the Fe will be in the trivalent form. Further independent application and analysis of this equation by Kirby and Cravotta (2005) suggests that it tends to overestimate the acidity of Fe^{3+} and Al^{3+} but underestimates contributions of HSO_4^- and H^+, which tend to cancel each other out. On this basis, the total acidity, and from this the net alkalinity required to neutralise acidic-saline drain waters, was estimated in both the presence and absence of the metals Al, Fe and Mn (Figure 5-5). In practical terms, however, within the drains of the WA Wheatbelt, the dissolved metal suite is generally dominated by Al such that it often constitutes >90% of these metals.

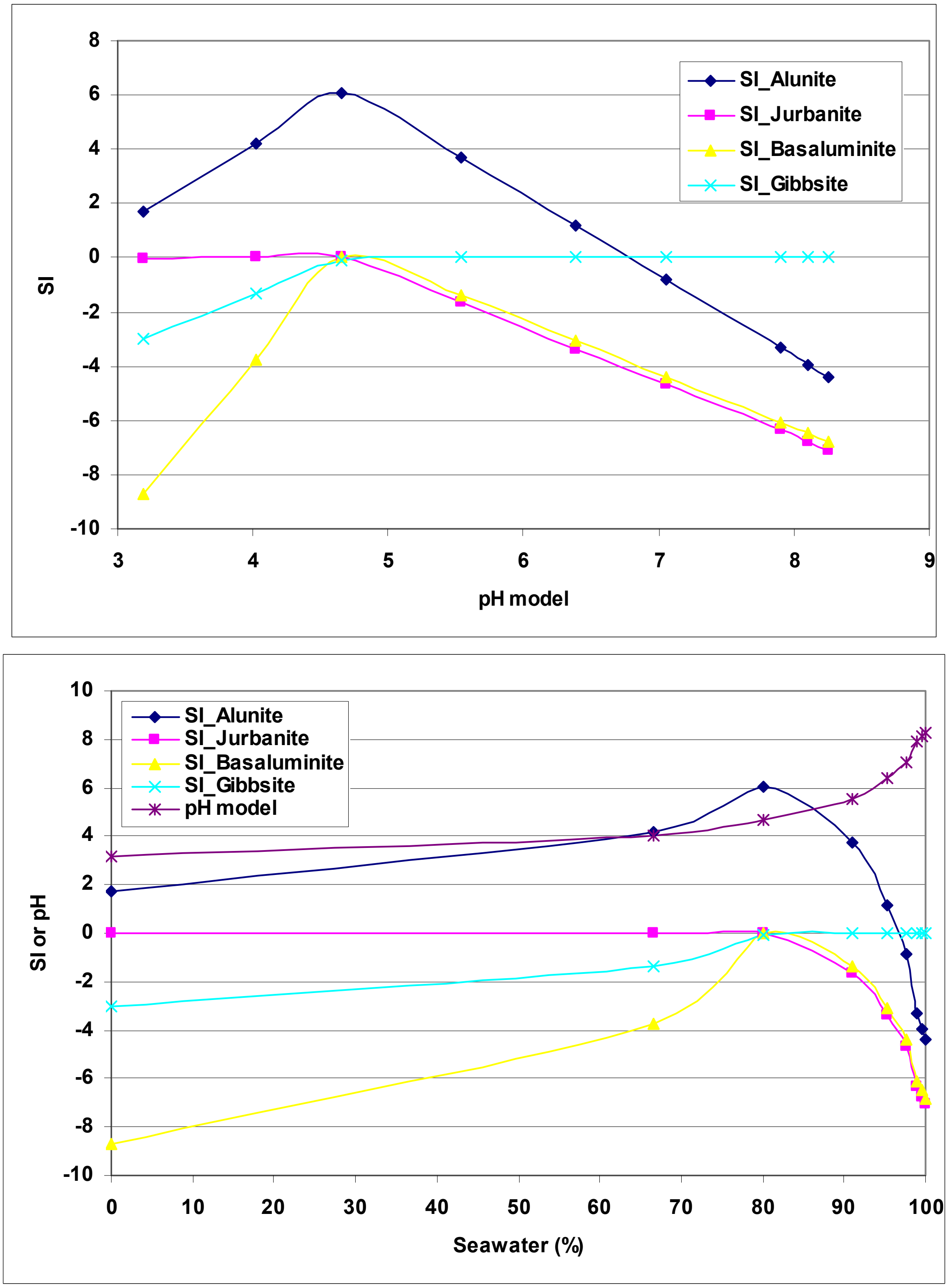


Figure 5-4 Modelling of the saturation index (SI) for selected Al-hydroxy and Al-hydroxysulfate minerals from the batch mixing of Indian Ocean seawater and Elachbutting drain water.

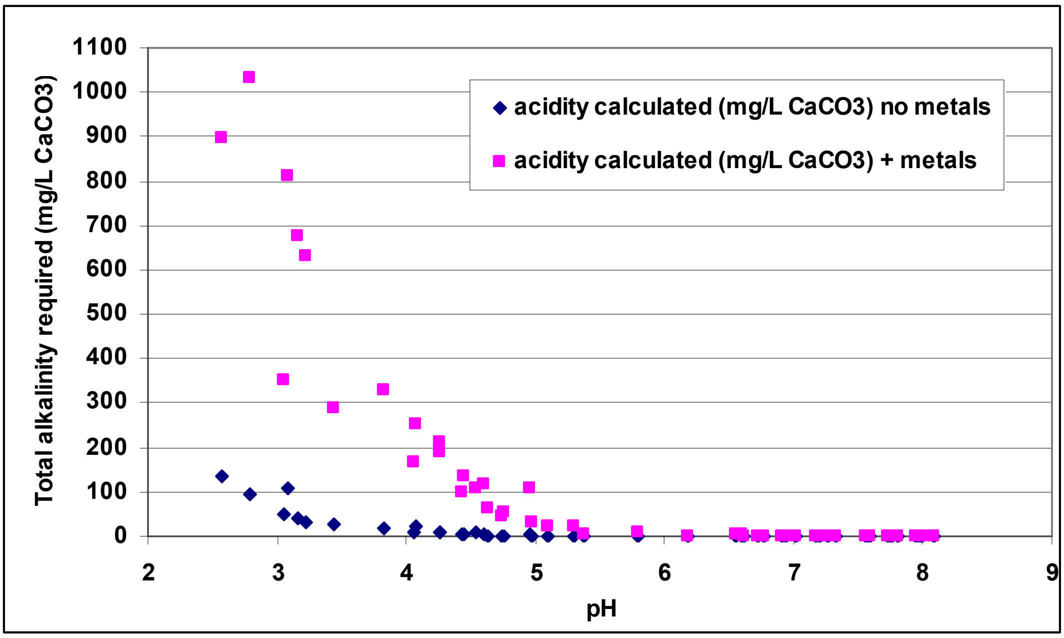


Figure 5-5 Estimated total alkalinity (mg/L $CaCO_3$) required to neutralise WA Wheatbelt drain waters based on actual pH (no metals) and with dissolved metals Al, Fe and Mn using the equation of Hedin *et al.* (1994).

Analysis of the aggregated estimates of total alkalinity required to neutralise acidic-saline waters from the Boodarockin, Elachbutting, East Cowcowing, Beacon and Trayning as presented in Figure 5-5 indicates there is a uniform curve-linear relationship with waters at pH 3 requiring up to 1000 mg/L of $CaCO_3$, waters at pH 4 approximately 200-300 mg/L of $CaCO_3$ as total alkalinity while waters at pH 5 require less than 50 mg/L of $CaCO_3$ as total alkalinity.

Importantly, the estimated total alkalinity required is approximately 10 times that required when dissolved metals are not included in the estimate (Figure 5-5). This factor, namely the presence of Al and its subsequent hydrolysis to a range of Al-hydroxy and Al-hydroxysulfate minerals, is the major contributor to the resistance of acidic-saline waters from the WA Wheatbelt to neutralisation.

Thus, the use of equation of Hedin *et al.* (1994), which accounts for acidity generated by dissolved metals, to estimate a total alkalinity requirement in an acidic-saline WA Wheatbelt drain water combined with a estimate of the total alkalinity present in an alkaline WA Wheatbelt waterways may be used as a first approximation to calculate the relative volumes required for neutralisation. While a broad data set is available from this and other work (Shand and Degens, 2008 and other chapters in this volume) for acidities in drain waters across the Wheatbelt there is little known alkalinity in Wheatbelt waterways and lakes. Values in surface waters (see other chapters in this volume) indicate that alkalinity can range from less than 50 mg $CaCO_3$/L up to more than 500 mg $CaCO_3$/L. Further work is required to characterise the range of alkalinity values likely to occur in Wheatbelt waterways and lakes and dominant landscape patterns that can be used to predict this during flow events.

5.5. Conclusions

Laboratory-based batch mixing studies of the addition of alkali as either Indian Ocean seawater or water from the Yenyening Lakes to acidic-saline Wheatbelt drain waters have provided an important insight into the process of alkalinity consumption and major and trace element behaviour during neutralisation. This understanding of the neutralisation process has also underpinned the development and on-going calibration of a geochemical mixing model designed to forecast the effects of mixing of acid and alkaline saline waters within the Wheatbelt.

Mixing ratios of acidic-saline drain water and an alkaline lake water of between 20:1 and 40:1 were necessary to achieve water with pH>7, although pH>6 could be achieved for some waters at less than 20:1. Surface waters with greater alkalinity are likely to result in similar, if not better mixing ratios, as indicated by the results of mixing with Indian Ocean Seawater, which exhibited an initially greater alkalinity than the Yenyening Lakes water.

The disproportionate requirement of alkaline waters required to achieve neutralisation (pH>7), often more than 10 times the initial volume of the acidic saline drain water, is primarily due to the presence of dissolved metals, and in particular Al which generates substantial acidity during hydrolysis. Further latent acidity contained within Al-hydroxy and Al-hydroxysulfate mineral precipitates as suggested by geochemical modelling may also be generated due to mineral formation and dissolution during neutralisation. The generation of intermediate mineral precipitates and resultant buffering of solution pH during neutralisation also probably contributes to the non-conservative behaviour of a range of major and trace elements. Importantly, the estimation of acidity from dissolved metals (Hedin *et al.* 1994) has been confirmed as providing a first approximation to calculate the relative alkalinity required for neutralisation of acidic-saline drain waters in the WA Wheatbelt.

6. ACIDIC SEDIMENT CHEMISTRY IN ACIDIFIED LAKES – CASE STUDIES.

Rob Fitzpatrick[1], Brad Degens[2], Warren Hicks[3] and Ian Fordyce[4]
[1] CSIRO Land and Water, Private Bag No. 2, Glen Osmond, SA, 5064, Australia.
[2] Salinity and Water Resource Recovery Branch, Water Resource Management Division Department of Water, P.O. Box K822 Perth WA 6892
[3] CSIRO Land and Water, Black Mountain, Canberra, ACT 2601.
[4] Yarra Yarra Catchment Management Group, P.O. Box 18, Kalannie WA 6468

6.1. Introduction

Rising water-tables caused by clearing of native vegetation in the south-west of Western Australia have brought saline and acidic water to land surfaces in much of the eastern WA Wheatbelt (Shand and Degens 2008). The interaction of the saline acidic water with surface environments has been accelerated in some areas by the use of deep (>2 m) drains to drain shallow groundwater from saline lands into lakes and floodways (Shand and Degens 2008). According to Degens *et al.* (2010), the effects of this acidic groundwater discharge via water-table rise on hydric soils in playas and claypans is not certain and may lead to the formation of conditions remarkably similar to those of inland acid sulfate soils (ASS). Potential ASS materials (sulfidic materials) may also have formed in previous decades of waterlogging under saline conditions (Degens *et al.* 2008; Fitzpatrick and Shand 2008). In this context, any soil that contains sulfides is regarded as an ASS, although the dominant acidity may not be ASS derived. These carry implications for the management of such waters, particularly since there is the risk of impacts of acidity on aquatic ecosystems compounding the existing impacts of salinisation (Degens *et al.* 2008; Stewart *et al.*, 2009). This investigation reports on the partitioning of acidity in two contrasting lakes – one receiving only local acidic groundwater discharge (MacPherson Lake), the other receiving acidic discharge from local groundwater drains (Green Lake).

6.2. Field survey and soil analysis methods

Transect surveys of shallow soil profiles were carried out in two secondary salinised lakes near Wubin (220 km northeast of Perth, WA), adjoining the Mongers Lake system in the northern Wheatbelt of Western Australia (Table 6-1). Representative pits were dug at 3 sites across the lakes and shallow (<30 cm) horizons, colours, textures, mottling, and major inclusions were described. Sampling depth was limited to the horizons interacting with shallow water-tables and on those most likely to influence ponded water quality. Samples were collected from major horizons, sealed in ziplock bags (with air excluded by rolling of the bag before sealing) and frozen on-site for transport to the laboratory for analysis. On arrival the samples were rapidly dried at 80 °C in a fan forced oven, crushed and sieved through a 2 mm sieve to prepare dry, <2 mm samples for analysis of selected acidity parameters including pH in a 1:40 solution of soil and 1M KCl, total actual acidity (TAA) determined by titration with NaOH solution to pH 6.5 (Australian standard acid sulfate soil analysis method 23F; Ahern *et al.*, 2004), sulfide-S using the chromium reducible S method (Australian standard acid sulfate soil method 22B Ahern et al. 2004) and available carbonate (acid neutralising capacity, ANC; see Australian standard acid sulfate soil method 19A2, Ahern et al. 2004).

Table 6-1 Location and characteristics of lake sampling sites in the Western Australian wheat belt geographic area region (Figure 6-1).

Name	Location	Zone	Easting	Northing	Hydrological characteristics
MacPherson Lake	Off Walsey Rd, North Jibberding	50	478 157	669 1521	Basin lake, local inflow from catchment
Green Lake	Intersection Carter Rd and Jibberding Hall Rd, Jibberding	50	483 639	667 3867	Basin lake, local inflow from catchment

6.3. Results

6.3.1. Soil profiles and local landscape patterns

Summary descriptions of the profiles surveyed at each site show a local pattern of sandy profiles surrounding the lakes overlying clay horizons that also extend beneath the lakes (Table 6-2 and Table 6-3; Figure 6-2and Figure 6-3). The lake beds characteristically contained halite crusts overlying thin, very soft gels with halite and gypsum and thicker, soft, silty hypersulfidic material, although the deeper clay across the site was not hypersulfidic (Table 6-2). Hypersulfidic materials at both sites were confined to the central basin, however, shallow horizons of soils fringing both lakes contained evidence of acidification and occurrence of sulfuric materials (Isbell 1996). This acidity and occurrence of sulfuric materials was only associated with thin lenses of sulfidic materials at Green Lake as illustrated in Figure 6-3. The new terms hypersulfidic and monosulfidic are defined in Sullivan *et al.* (2010).

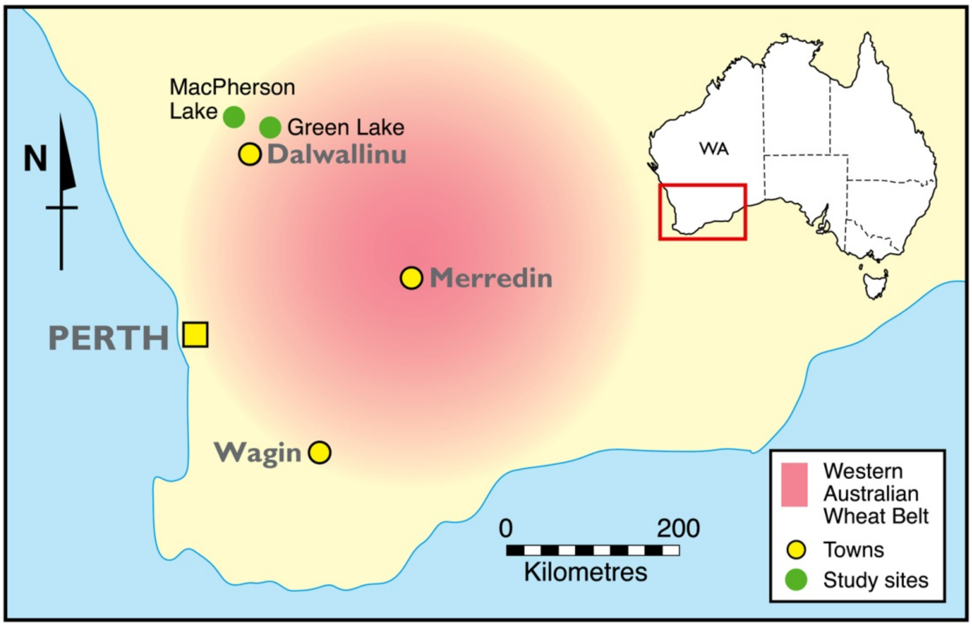


Figure 6-1 Map showing localities of MacPherson Lake and Green Lake in Western Australia.

Table 6-2 Summary descriptions of major horizons for MacPherson Lake

Depth (cm)	Horizon description
Dune – MacPherson Lake	
0 - 5	Loose grey sand, dry, weakly crusted.
5 - 10	Weakly cemented yellowish-brown sand with brown mottling.
10 - 55	Yellowish-brown sand.
55 – 60+	Grey-brown sand, moist.
Shoreline – MacPherson Lake	
0 - 5	Grey sand with black sulfidic mottles and reddish-brown mottles, moist.
5 - 15	Greyish-yellow, sandy with reddish-brown burrows. Moist (water-table at ~ 12 cm). Soil slurry pH 4.0.
15 - 25	Yellowish brown sandy loam. H_2S odour. Soil slurry pH 4.1.
25 - 50	Olive grey loamy sand to sandy loam. H_2S odour. Soil slurry pH 3.8.
60 - 70	Grey clay, with purplish-red mottles, sticky. Pit water pH 3.6, EC 134 mS/cm, Eh: 141 mV.
Lake bed – MacPherson Lake	
0 - 9	Hard halite crust with iron staining. Gypsum in crust in plate heaving zones.
9 - 10	Brownish-olive clayey gel with gypsum and halite on the surface of sulfidic materials and between hard halite crust, saturated (water-table at 9cm).
10 - 24	Black sulfidic gel (clayey silt) with many organic fibres (remnant straw/grass?) plus large cubic halite crystals. Pit water pH: 5.8. Eh: –108 mV.
24 – 50+	Greenish-grey sticky clayey sand with purple and red mottles.

6.3.2. Assessment of acid generation potential: acid-base accounting

The net acid generation potential (NAGP) of the soils in the lakes was assessed using a combination of chemical measurements supported by field observations and consideration of the geological and hydrological framework. This approach takes into account the mineralogical make-up of the soils, which may either enhance or neutralise production of acidity. The methods used to assess NAGP are based on those used with acid sulfate soils, however, can equally be applied to assessing acidity and alkalinity in Wheatbelt lakes (as has previously been achieved in Degens *et al.*, 2008). In acid sulfate soils, acidity is generated by oxidation of sulfide minerals (principally pyrite: FeS_2) and can result in the production of a range of secondary minerals, such as jarosite, sideronatrite and schwertmannite. Such minerals act as stores of acidity in that they may produce acidity upon dissolution. It is therefore important that soil catena investigations also include an assessment of whether these minerals occur. Soils can also contain alkalinity in the form of carbonates that can neutralise acid production.

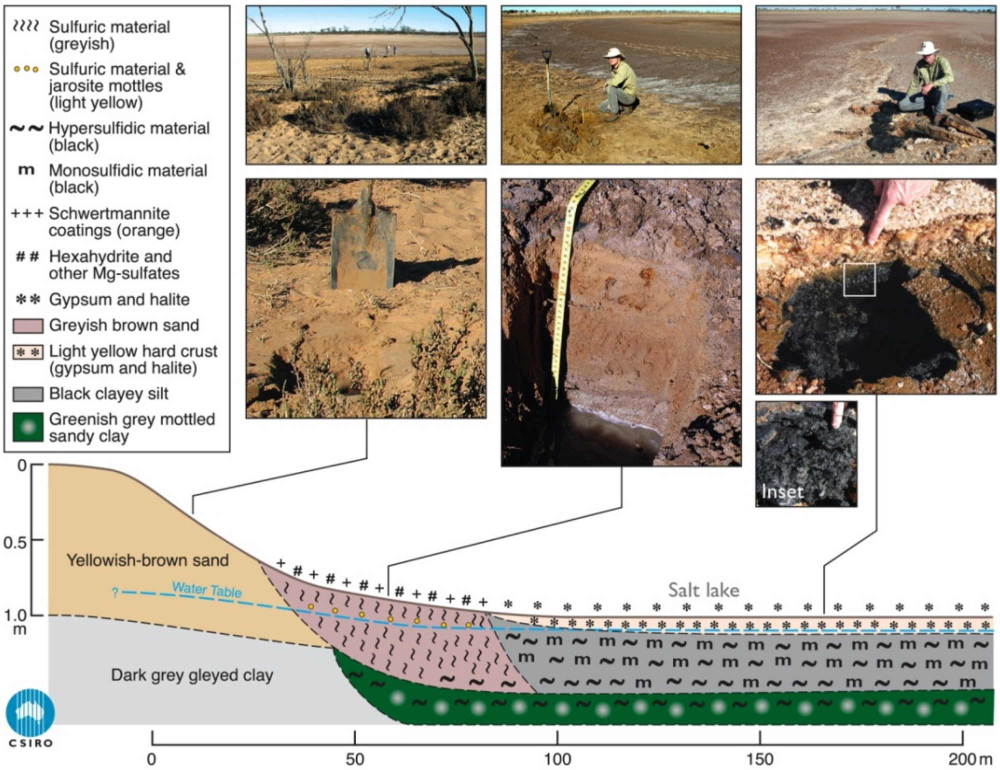


Figure 6-2 Descriptive soil-regolith toposequence model for transect across MacPherson Lake (site M3 in Figure 6-1) showing sequence of Inland ASS from lake lunette to the central basin. See Table 2 for profile descriptions of the dune, shoreline and lakebed.

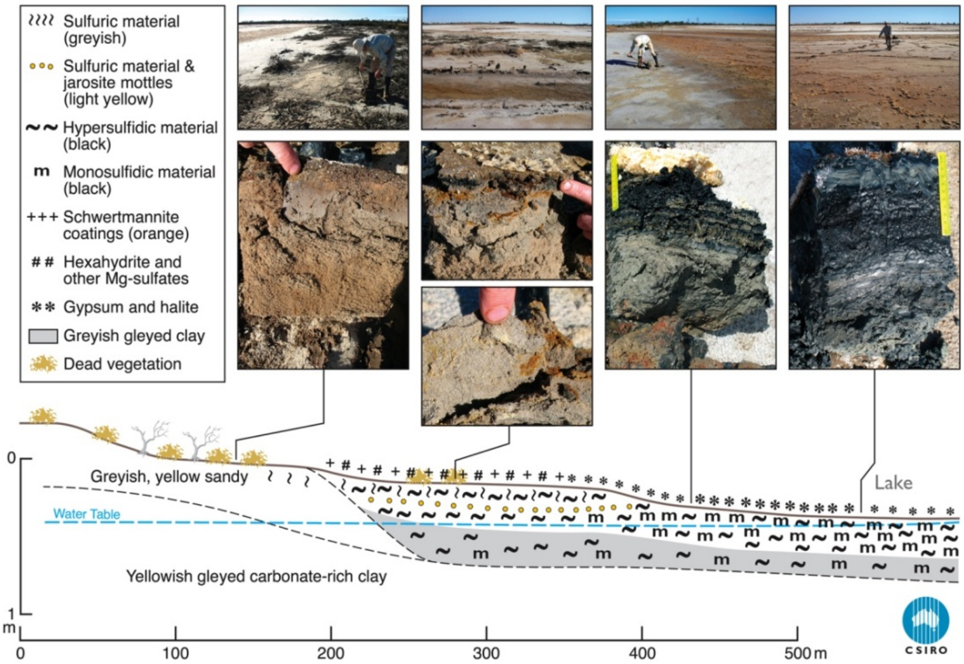


Figure 6-3 Descriptive soil-regolith toposequence model for transect across the Green Lake (or Wubin-Carter road Lake) (see site M2 in Figure 6-1) showing sequence of Inland ASS subtypes from lake lunette to the central basin. See Table 6-3 for profile descriptions of the lake margin dune (i.e. second row of photographs from left showing bright jarosite mottles in sulfuric material), lake shoreline and lakebed (right hand side row of photographs showing a mixture of hypersulfidic and monosulfidic materials).

Table 6-3 Summary descriptions of major horizons for Green Lake.

Depth (cm)	Horizon description
Lake margin dune – Green Lake	
0 - 0.2	Salt crust, very thin white, with slight yellow staining, very friable.
0.2 - 2	Olive-grey sandy loam with layers of black sulfidic material.
2 - 7	Jarosite mottles and bright orange (schwertmannite) mottles in pale grey sandy clay loam. Field pH 3.5.
7 - 30	Olive-grey sandy clay loam, sticky, gleyed. Lens of olive-grey clay with diffuse yellow mottles (15-20cm).
30 - 50	Pale olive-grey/green gley, sticky sandy clay with red and red-brown mottles (distinct).
Lake shoreline – Green Lake	
0 - 1	Tubular to needle gypsum, sticking out vertically, in red gel matrix.
1 - 5	Pale grey 'gel', very sticky silt.
5 - 15	Black sulfidic soft silty material; many organic fibres and gypsum crystals. Water-table at ~ 15 cm.
15 - 20	Pale grey, very soft with layers of sticky clay and gypsum (fine needles).
20 - 25	Olive-green gleyed sticky clay.
Lake bed – Green Lake	
0 - 4	Hard halite crust with some needle gypsum.
4 - 4.5	Bright orange gel with needles of gypsum (max. 2 mm)
4.5 - 10	Black sulfidic soft silt with many gypsum crystals. Water-table at ~ 10 cm.
10 - 13	Large tubular and needle (1 to 2 cm) gypsum in grey-olive, soft, sticky silt.
13 - 20	Grey-blue gleyed sticky clay with large needle-shaped gypsum.
20+	Olive-grey clay, gleyed with red and reddish-yellow mottles

Assessing the net acid generation potential (NAGP) of soils was carried out using the acid-base accounting is a technique commonly applied to acid sulfate soils which balances the potential amount of acid generation against the potential amount of neutralisation from minerals such as carbonates in the soils. This calculation gives an indication of acid generation if the soils are completely oxidised (dried out or drained) and all components react fully. Potential acid is estimated as that likely to be generated from oxidation of sulfide-S (determined by the chromium reducible S technique or S_{CR}) plus the total actual acidity (TAA) of the soil balanced by the total amount of potential neutralisation (or alkalinity as ANC) generated. Acid generation potential (AGP) is the sum of potential acidity from sulfides and total actual acidity whereas net acid generation potential (NAGP) is the potential acidity minus potential alkalinity or:

$$\text{NAGP} = \text{AGP} - \text{ANC}$$

A positive value indicates an excess of acid and the likelihood of sulfuric materials (or an actual acid sulfate soil material) forming in the soil when it is disturbed and oxidised.

A major assumption of these calculations is that the form of potential alkalinity (generally carbonates) may not be completely available to soil solutions (e.g. if it is coated and protected with organic material or iron oxides) or if it is in a form which is not particularly reactive (e.g. iron carbonates and dolomite ($CaMgCO_3$) have much slower reaction kinetics than calcite). Furthermore, fine grinding of soil materials during sample preparation may lead to an over-estimate of ANC when carbonates are present in the form of hard nodules or shells. A “fineness factor” is used to adjust for this possibility, whereby net acidity is calculated by dividing the ANC by a factor of 1.5.

6.3.3. Acid-base accounting results

Concentrations of acidity stored within sulfides (as indicated by S_{CR} analyses) varied widely across the different lakes as well as with the position in individual lakes and soil profiles (Table 6-4). Most of the potential acid generation capacity within the samples was due to sulfides, with little contribution from total actual acidity (TAA), except in the samples from the margins of the lakes (Table 4). Alkalinity, indicated by ANC, was also low across the samples, with greatest amounts occurring in samples with greatest sulfide content.

The soil sample from a 0.12–0.25 m soil horizon at the centre of MacPherson Lake had a high sulfide concentration (S_{CR} or RIS) at 0.935 % (Table 6-4) and a positive NAGP (Figure 6-4) confirming presence of hypersulfidic material, which poses an acidification risk if dried out or excavated, while the sample from the edge of the lake had a small but measurable sulfide concentration with sufficient ANC to give a small negative NAGP (Figure 4) posing no acidification risk.

All profiles sampled from Green Lake had at least one layer comprising hypersulfidic material at < 0.1 m depth with sulfide concentrations ranging from 0.006 to 0.719 %S. These horizons pose an acidification risk, should the soils dry out.

None of the results for sampled horizons had pH values < 4, based on pH_{KCl} (Table 6-4), however, field measurements of some horizons in Green Lake and MacPherson Lake indicated pH<4 (Table 6-2 and Table 6-3). These measurements also corresponded with minor levels of total actual acidity (Table 4), compared with that due to stored acidity in sulfides and also reflected in acid generation potential (AGP) in Figure 6-4.

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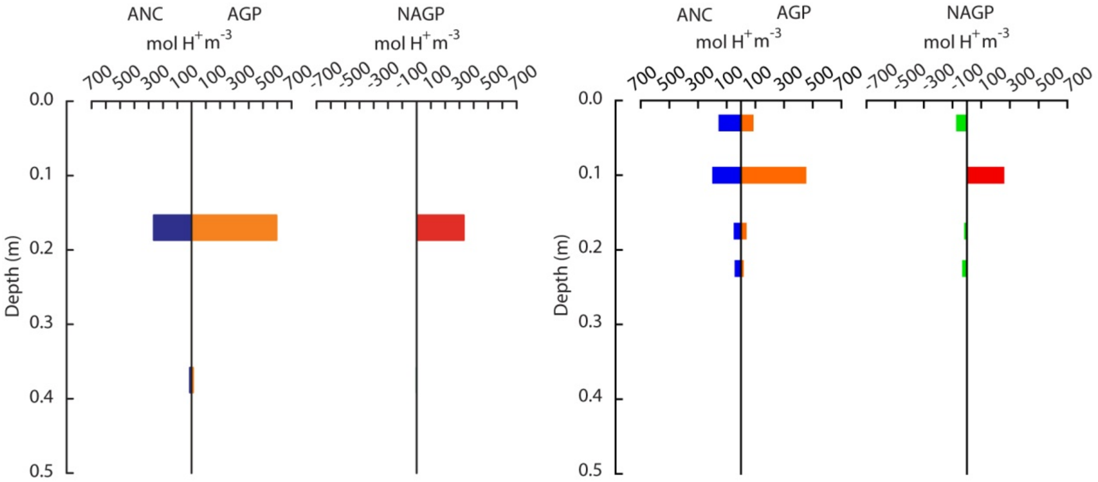
Table 6-4 Acid-base accounting data.

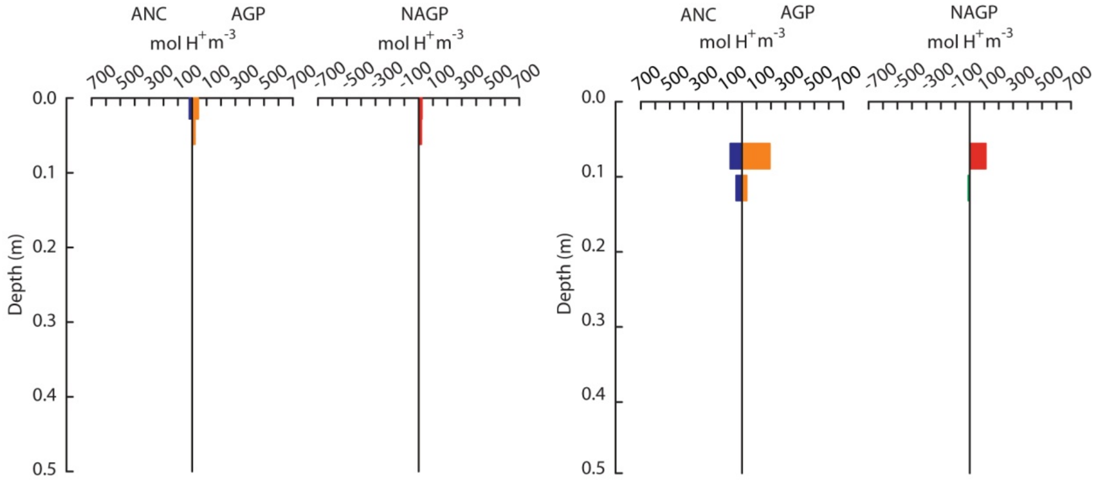
Location		Sample I.D.	Depth (cm)		ANC (Carbonates)		pH_{KCl}[§]	TAA	Reduced inorganic S (RIS)		Acid–Base calculations		Lime requirement[†]		
									S_{CR}	S_{CR}	AGP[1]	NAGP[1]	NAGP	TAA	RIS
			Upper	Lower	% $CaCO_3$	mol H^+/tonne		mol H^+/tonne	%	mol H^+/tonne	mol H^+/tonne		kg/tonne		
MacPherson Lake	Edge	MUG 2.4	25	50	0.05	11	5.2	7.6	0.004	2	10	–1	–0.1	0.57	0.19
	Centre	MUG 3.4	10	24	1.32	264	8.0	0.0	0.953	594	594	330	25	0.00	45
Green Lake	Beach	R8NM 4.2	0.2	2	0.10	19	5.5	3.8	0.060	37	41	22	1.7	0.28	2.8
		R8NM 4.3	2	7	0.00	0.0	4.8	14.2	0.006	4	18	18	1.3	1.07	0.28
	Margin	R8NM 5.2	1	5	0.75	150	7.5	0.0	0.130	81	81	–69	–5.2	0.00	6.1
		R8NM 5.3	5	15	0.97	194	7.5	0.0	0.719	448	448	254	19	0.00	34
		R8NM 5.4	15	20	0.22	44	6.8	0.0	0.051	32	31.8	–12	–0.9	0.00	2.39
		R8NM 5.5	20	25	0.19	38	6.9	0.0	0.019	12	12	–26	–2.0	0.00	0.89
	Centre	R8NM 6.3	4.5	10	0.40	81	6.6	0.0	0.307	191	191	110	8.3	0.00	14
		R8NM 6.4	10	13	0.20	40	6.7	0.0	0.050	31	31.2	–9	–0.7	0.00	2.3

[§] 1: 40 1M KCl; [¶] Includes 1.5 fineness factor to give a modified reduced ANC; [†] Including 1.5 safety factor to neutralise for all acid generation potential (NAGP), actual acidity (TAA) or stored sulfide acidity (RIS); [1] AGP = acid generation potential; NAGP = net acid generation potential (taking into account alkalinity).



(a) MacPherson Lake

(b) Green Lake - margin



(c) Green Lake - beach

(d) Green Lake - centre

Figure 6-4 Acid neutralising capacity, acid generating potential and net acid generating potential for soil samples from MacPherson Lake (top left) and Green Lake (margin (top right), beach (lower left) and centre (lower right). In the case of MacPherson Lake samples are from two profiles, the sample from 0.17 m is from the centre of the lake and the sample from 0.37 m from the edge of the lake. The samples from Green Lake are for individual profiles at the indicated position.

6.4. Discussion

Both lakes contained significant accumulation of hypersulfidic and monosulfidic materials in the central basin, although this had only occurred in thin (<15 cm thickness), shallow horizons. This store of potential acidity had probably formed as a result of microbial sulfate reduction, fuelled by organic materials in the lake bed, much of it containing discernable straw/pasture organic fragments probably washed in from surrounding landscapes. The source of sulfate and iron for this process may have been discharge of saline groundwater to the site, aided by rising saline water-tables (evident from seepages on the margin of the lakes) and persistent waterlogging. The conditions within the horizons, high water-tables (as determined by sampling at the end of summer) and analysis results suggest that these are not actively releasing acidity and would be unlikely to unless drained or excavated.

Despite the history of discharge of acidic saline waters to Green Lake, the sediments were not showing signs of significant widespread acidification (i.e. soils with layers or lenses containing sulfuric material were confined to narrow margins on the edges of lakes). At least 3 years of acidic drain discharge to the lake (Figure 6-5) had occurred prior to sediment sampling with the drain having been constructed in early 2003. Flow from the drain discharging to the lake on the southern side in October 2004 was pH 3.1 with an acidity of 202 mg $CaCO_3$/L (from Shand and Degens, 2008) and water within the lake has been at pH 3.3–3.7 between 2005 and 2006 with an acidity of between 220 and 2200 mg $CaCO_3$/L (depending on whether water was evaporating or flowing through). The lake was noted to be dry in summer 2006-07 with drain inflow having ceased during winter 2006 (Figure 6-3). Sediment analysis from a previous survey in February 2006 (Degens *et al.*, 2008) also indicated no evidence of significant actual acidity having accumulated within shallow sediments. It was possible that sampling missed the horizons in the centre of the lake affected by acidification, which may have been limited to the few millimetres of gels within the upper lake bed. This would indicate the highly spatially variable incidence of sediment acidification in these environments.

Figure 6-5 Green Lake after 2 years discharge, October 2005 (left) and on sampling in May 2007 (right).

Limited penetration of discharged acidic water had occurred into the sediments of Green Lake possibly because there was limited head pressure from ponded waters to cause downward seepage of water. The lake had not been filled to a depth of more than 0.3 m during any time since drain inflow occurred, which was partly because water levels were controlled by an exit drain flowing out on the north-eastern side of the lake. A further factor limiting acidification of the lake-bed sediments may have been the protective effect of sulfate reduction resulting in formation of hypersulfidic materials. The latter may have contributed to neutralisation of any acidity diffusing or seeping from the ponded water in the lake.

Alkalinity in the sediments of undisturbed MacPherson Lake was limited and the distribution appears to correspond with the accumulation of sulfides in the profiles sampled. Sulfate reduction can result in production of alkalinity, as is commonly exploited when treating acidic waters (e.g. Degens 2009). Enhancing biological activity within disposal lakes to increase organic matter assumulation may be a way of treating acidity in lakes and minimising down-stream impacts of water discharging from these lakes, providing that the sediments are protected from scouring during flooding. The formation of a thick halite crust on the lakes (as observed in MacPherson Lake) may assist with protection of sediments against scouring, however the barrier might limit the rate of neutralisation of acidity in ponded waters should this be dependent on microbial sulfate reduction in the underlying sediments.

There was no evidence of significant and widespread acidification or formation of sulfuric materials in soils occurring in the middle of lakes. The only indication of sulfuric materials is mostly confined to lake margins (Figure 6-2 and Figure 6-3; Table 6-2 and Table 6-3), as indicated in field pH measurements and the occurrence of bright yellow jarosite mottles. Both lakes are under the influence of acidic saline groundwater discharge, mainly evident on the margins of the lakes (as seeps and higher watertables than the basin; see Figure 6-2 and Figure 6-3). Sampling of shallow groundwater drainage up-catchment of Green Lake (reported in Chapter 2) and in groundwater sampling in the catchment in which MacPherson Lake occurs (Mongers 55, see Chapter 2) indicated that local groundwater up-catchment of both lakes was acidic. Despite the field evidence of acidity at the margins, measurements of none of the sampled horizons appeared to support the occurrence of sulfuric material because $pH_{KCl} > 4$ (Table 6-4). It is likely that drying and grinding of the soils for analysis may have partially neutralised any actual acidity (i.e. because as indicated in Table 6-4 all samples do contain ANC (i.e. carbonate), which indicates that perhaps the form of this acidity is not as extreme as commonly encountered with ASS that contain low ANC values, secondary mineral precipitates and on-going sulfide oxidation.

This survey documents the first occurrence of acid sulfate soils containing sulfuric material in secondary salinised lakes in the northern Wheatbelt of Western Australia. The surveys also highlight that spatial and temporal disconnection of acidity and alkalinity can occur in lakes across centimetre scales, which has implications for behaviour of acidity in these aquatic environments. While alkalinity (*c.f.* acid neutralising capacity) may be present or generated within lake environments, neutralisation of acidic discharge into lakes will only occur if the sediment alkalinity is in contact with acidic waters (occurs in the same spatial zone) and able to react fast enough to neutralise waters (temporally available). Slow reaction rates can result in lake conditions cycling between acidic and alkaline depending on rates of acidity loading from drainage waters. Further, work needs to be conducted to confirm the occurrence of hypersulfidic materials by re-sampling soils in the field or from samples stored in fridges and commencing incubations experiments using the chip tray method (Fitzpatrick et al. 2010). The chip tray field sampling incubation method is considered to represent a “realistic tool” for ASS testing based on allowing the soil to “speak for itself” (Dent 1986). The acid-base accounting method appears to underestimate the acidy risk because of the presence of ground carbonates (ANC), which are produced when the dried samples ground prior to analyses.

6.5. Management implications

- The central basins of Wheatbelt lakes may contain some capacity to neutralise acidic drain discharge, but this may be slow and spatially separated from where the acidity accumulates from discharge.
- Acidification of margin sediments may require active neutralisation to reduce risks of acidification to surrounding and down-stream environments.
- Enhancing natural microbiological activity in sediments (increasing bacterial sulfate reduction) by addition of organic materials may be a practical option of reducing acidic water impacts in some lakes.

- Assessing the behaviour of acidic waters in Wheatbelt lakes is complex and contains uncertainties due to the variation in geochemical reactions in space and over time.

7. CONCLUDING COMMENTS – REGIONAL PATTERNS IN ACIDIC SALINE WATER HAZARDS ACROSS THE WA WHEATBELT

Brad Degens[1] and Paul Shand[2]
[1] Salinity and Water Resource Recovery Branch, Water Resource Management Division Department of Water, P.O. Box K822 Perth WA 6892
[2] CSIRO Land and Water, PB 2, Glen Osmond, Adelaide SA 5064

7.1. Introduction

Prior to the inception of the Department of Water's Engineering Evaluation Initiative and complimentary Wheatbelt Drainage Evaluation, the threats posed by rising saline groundwater in the WA Wheatbelt were widely accepted to lie with increased salt accumulation and alteration surface water hydrology (Hatton et al., 2003). Little was known of underlying geochemical processes and hazards coupled with saline groundwater and the risks these posed to surface water resources and riparian environments (Dogramaci and Degens, 2003).

The area affected by shallow water-tables in the WA Wheatbelt is currently about 1 million hectares (Caccetta et al., 2010) and is expected to continue to expand over at least the next 25 years, particularly in inland parts of the Wheatbelt. Imbalance between groundwater recharge and discharge in the landscape (hydrological imbalance) created by clearing native vegetation some 30 to100 years ago (Hatton et al., 2003) still remains, with rising groundwater apparent across most of the Wheatbelt since before 1980 (George et al., 2008). This is occurring despite trends of falling autumn-spring rainfall across the Wheatbelt (since 1970), as summer rainfall appears to be increasing (Bureau of Meteorology, 2010). The latter indicates that rainfall events during the summer period (generally associated with thunderstorms and cyclonic systems) may play an expanded role in continued hydrological imbalance. Modelling indicates that hydrological imbalance in central parts of the Wheatbelt (Avon and Blackwood basins) will continue to occur for at least 20 years (Ali et al., 2008; Ali et al., 2009b). Even with climate change causing an overall decline in annual rainfall of up to 20% (across all rainfall events) this is expected to continue, although the rate of expansion in areas affected by shallow watertables is expected to slow and surface hydrological processes are expected to change significantly (Ali et al., 2009a; Ali et al., 2009b).

Whilst hydrological imbalance is inadvertently creating new shallow saline groundwater resources, the challenge is to provide clear planning guidance to assist with management of impacts on infrastructure, waterways and lakes, land and biodiversity assets.

Investigations in the Avon Basin have indicated the presence of extensive risks posed by acidic saline groundwater (Shand & Degens 2008; Shand et al. 2008), however the nature of these risks in catchments adjoining the Avon was unclear. The discussion above highlights that rising watertables and increased discharge of groundwater to landscapes continues to occur, thereby indicating that where groundwater is acidic, the discharge of this will continue to influence valley floors and expand across the Wheatbelt. The acidic nature of saline waters in the WA Wheatbelt has implications for both active management of groundwater discharge (using deep drainage) as well as management of areas where groundwater discharge is expected to occur to landscapes.

The comments in the following section present a broad summary of the regional patterns in acidic groundwater hazards that are apparent from the data collected during this and the previous Avon Basin project (Shand and Degens, 2008).

7.2. pH of groundwater and waters in groundwater drains

The distribution of groundwater pH (irrespective of depth) for data aggregated across the Wheatbelt (Figure 7-1) reflects the bimodal distributions reported in Section 3 of this report and in Lillicrap and George (2008). This dataset comprised pH measurements taken in the field from a mix of bailed and pumped samples (51% were pumped samples) from 435 bores, the majority of these (60%) being in the Avon catchment, with 16% from the Yarra Yarra, 16% from the South Coast (Esperance and Albany Coastal basins) and the remainder from the Blackwood catchment (Figure 7-1). The data represents sampling of groundwater near the top of the watertable, mostly being within 1 to 7 m of the watertable. It is possible that the range of sampling methods has distorted the distribution contributing to lower pH waters reported at some sites than existed in the aquifer, but unlikely as pH of the drain waters shows a similar distribution.

The drain waters generally exhibit a pH distribution similar to that of groundwaters across the WA Wheatbelt, although skewed slightly downwards at pH <3.5 and upwards at pH >7. This is probably mainly due to evaporation of water within drains resulting in concentration of H^+ and OH^- (resulting in a fall or rise in pH depending on initial pH). Greater concentrations of CO_2, and therefore carbonic acid, in some groundwater that is most likely absent in drain waters in contact with the atmosphere may also contribute to differences in pH (as reported in Section 3 of this report), particularly in the mid-pH range where there were few drains with water pH between 5 and 6.5 (less than 5%).

Summary pH data for 82 drain systems of which most were in the Avon (57%) showed that 45% of drains had a pH of less than 4.5, although 41% had a pH of >7. It is important to bear in mind that this data reflects drains where baseflow (from groundwater discharge) could be sampled, and that this may not reflect some drains where flow was intermittent or for those which have subsequently ceased to flow. This may be common in western areas of the Wheatbelt where more dissected landscapes occur, and large valley floor aquifers do not occur that would feed extended baseflow in groundwater drains.

Aggregation of drain and groundwater pH data from the present and the previous Avon survey indicate that low pH groundwater mostly occurs within broad valley floors of the south-western Yarra Yarra basin, southern Ninghan basin, north-eastern Blackwood basin and northern parts of the South Coast and Esperance Coast basins (Figure 7-2). Consistent with the distribution reported in earlier collated data by Lillicrap and George (2008), this area is broadly defined by the agricultural zone south of a line from Perenjori to Three Springs, east of a line from Three Springs to Katanning and north of a line from near Cranbrook through Ravensthorpe to just north of Esperance (Figure 7-2). Notably, the occurrence of low pH groundwater broadly conforms to being south of the Menzies line (after Butt et al., 1973) as previously cited by Gray (2001) and east of the Meckering line (after Mulcahy 1973). Interestingly, low pH groundwater occurs generally, but not exclusively, within the south-western part of the zone of ancient drainage (after Bettenay, 1962).

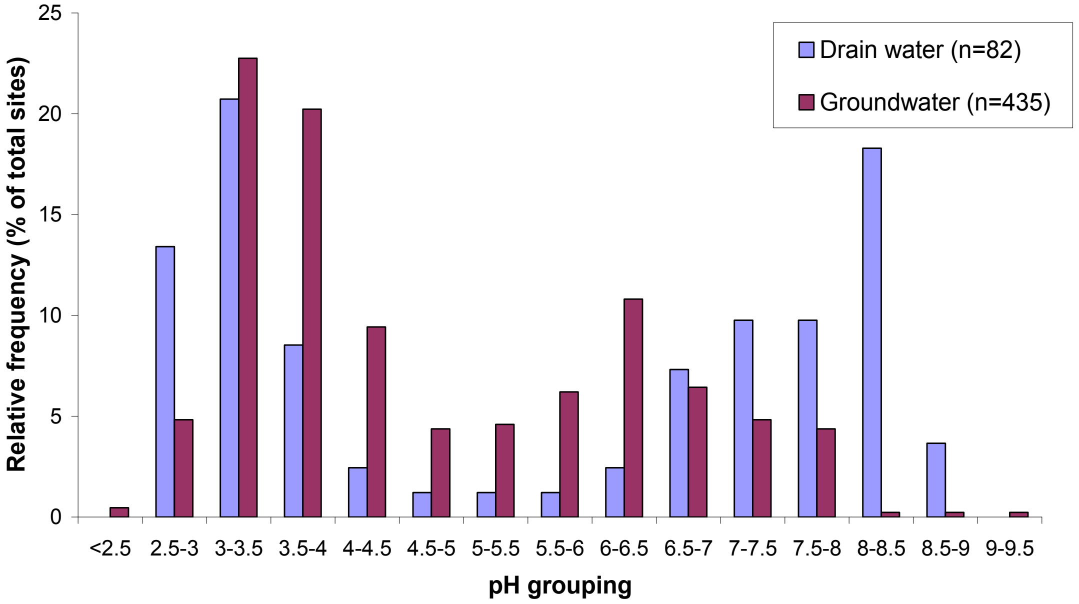


Figure 7-1 Summary data for groundwater and drain water pH (median of sites and sampling times when more than one) across the WA Wheatbelt.

7.3. Acidity of groundwater and waters in groundwater drains

The distribution of acidity levels in drain water across the Wheatbelt was skewed downwards (tendency to be more alkaline) slightly more than that of groundwater (Figure 7-3). This might be due to changes in water chemistry on discharge that would contribute to increased alkalinity (e.g. interaction with drain sediments containing carbonates eroded from drain walls), particularly mildly acidic drain waters. In a general sense, acidity in groundwater indicated by this regional level sampling presents a reasonable reflection of acidity likely to occur in drain waters.

Over 45% of drains and 75% of groundwater sample sites (Figure 7-3) contained water with net acidity exceeding 40 mg $CaCO_3$/L, which is the Department of Environment and Conservation (WA) acidity threshold limit (DEC 2009). This indicates that discharge of groundwater to surface waterways via drains or diffuse discharge has the potential to acidify surface environments, although the extent to which this will occur will depend on discharge volumes, neutralising processes in receiving environments and the relative timing of each. The neutralising processes in receiving environments include mixing with alkalinity in receiving waters (see Chapter 6) and neutralisation by carbonates or alkalinity generation during microbial sulfate reduction in surface sediments (see Chapter 5). The median acidity for those drain waters with net acidity greater than the DEC limit of 40 mg $CaCO_3$/L was 569 mg $CaCO_3$/L and broadly corresponds with what has been reported elsewhere (Degens, 2009a). Notably, up to 10% of these drainage systems contained extremely acidic water (>1000 mg $CaCO_3$/L) and has similarly been found to occur in groundwater samples from across the Wheatbelt (Figure 7-3).

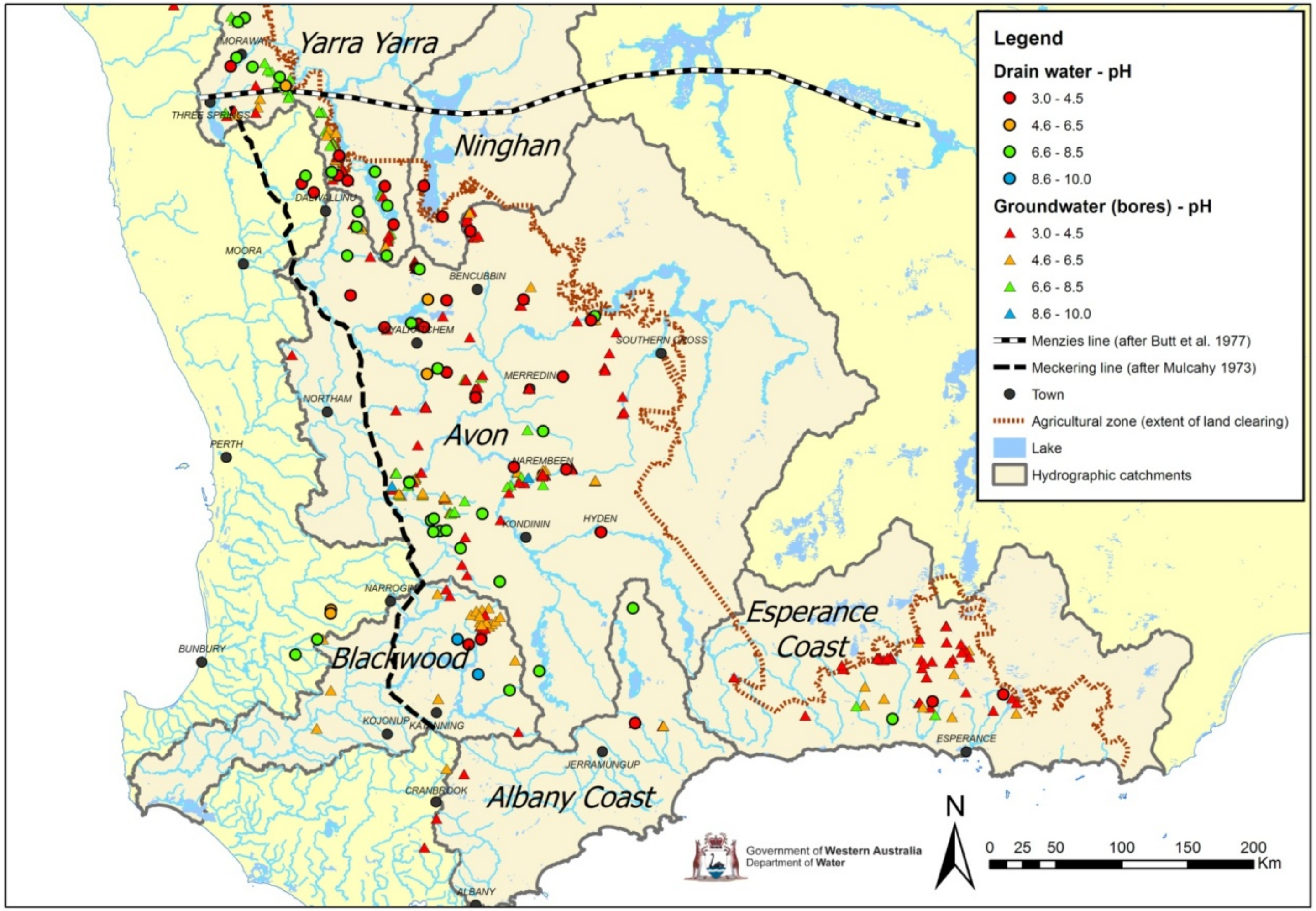


Figure 7-2 Spatial distribution of groundwater pH across the WA Wheatbelt as indicated by field pH in bores and groundwater drains.

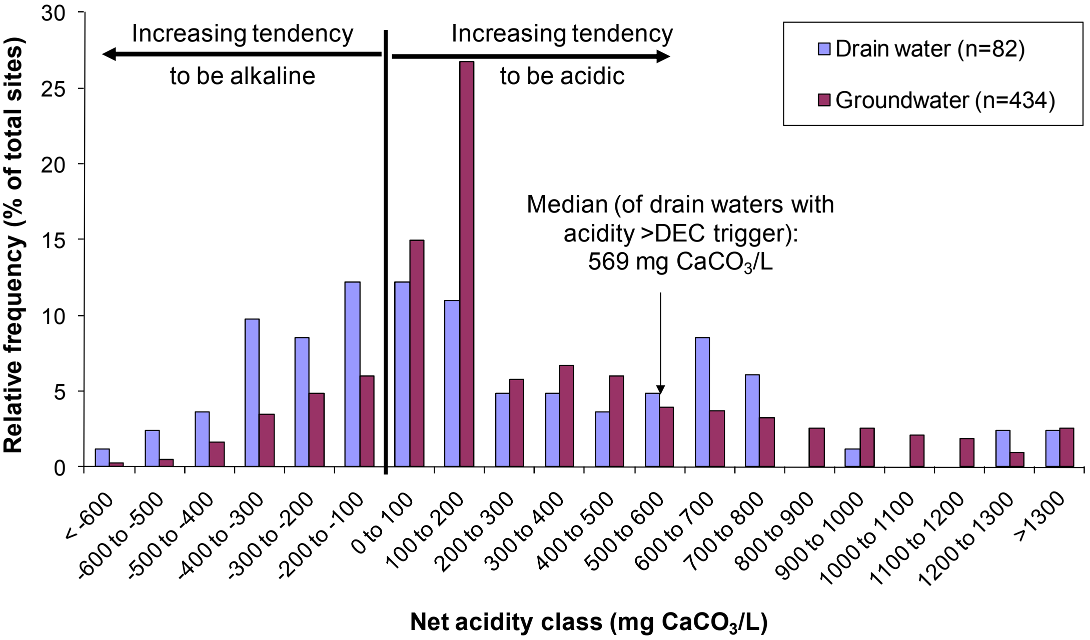


Figure 7-3 Distribution of net acidity (calculated) for groundwater and drain water (median of sites and sampling times when more than one) across the WA Wheatbelt. Note: net acidity calculated as per Section 5 where net acidity = alkalinity–acidity (see also Degens, 2009a). Data for drains represent summary data of sites within a drainage system.

The distribution of pH and net acidity in shallow groundwater (within 6 m of the water-table) did not appear to greatly differ from that of deeper groundwater (Figure 7-4). The only trend was that net acidity was skewed upwards and pH skewed downwards in shallower groundwater. This contrasts with significant trends in groundwater pH found to occur in earlier work (using data from a different source) where lowest groundwater pH was found with bores screened between 5 and 10 m depth, presumably below surface (Lillicrap and George, 2008). The present result is not surprising with such broad-scale comparisons, however local scale investigations in the Blackwood catchment have identified that significant variation in water chemistry can occur with depth (see Section 3 of this report).

Broad spatial patterns were apparent in the net acidity data indicating that low pH saline groundwater in the Wheatbelt contain varying capacity to acidify surface environments (Figure 7-5). The areas with highest acidity in groundwater and drains occurred in the central and south-eastern Wheatbelt (in the east Avon Basin and northern part of Esperance Coast Basin). Localised occurrences of highly acidic groundwater also occurred in the upper Blackwood Basin (see also Section 3 of this report) and northern Albany Coast Basin. Classification of net acidity for this mapping was undertaken using the acidity within drains and groundwater: highly acidic waters contained net acidity exceeding 700 mg $CaCO_3$/L (approximating the net acidity of the top 25% of drain water and groundwater being 677 mg $CaCO_3$/L and 708 mg $CaCO_3$/L, respectively) and mid-range acidity of 300–700 mg $CaCO_3$/L representing the middle 50% of all drain and groundwater net acidity.

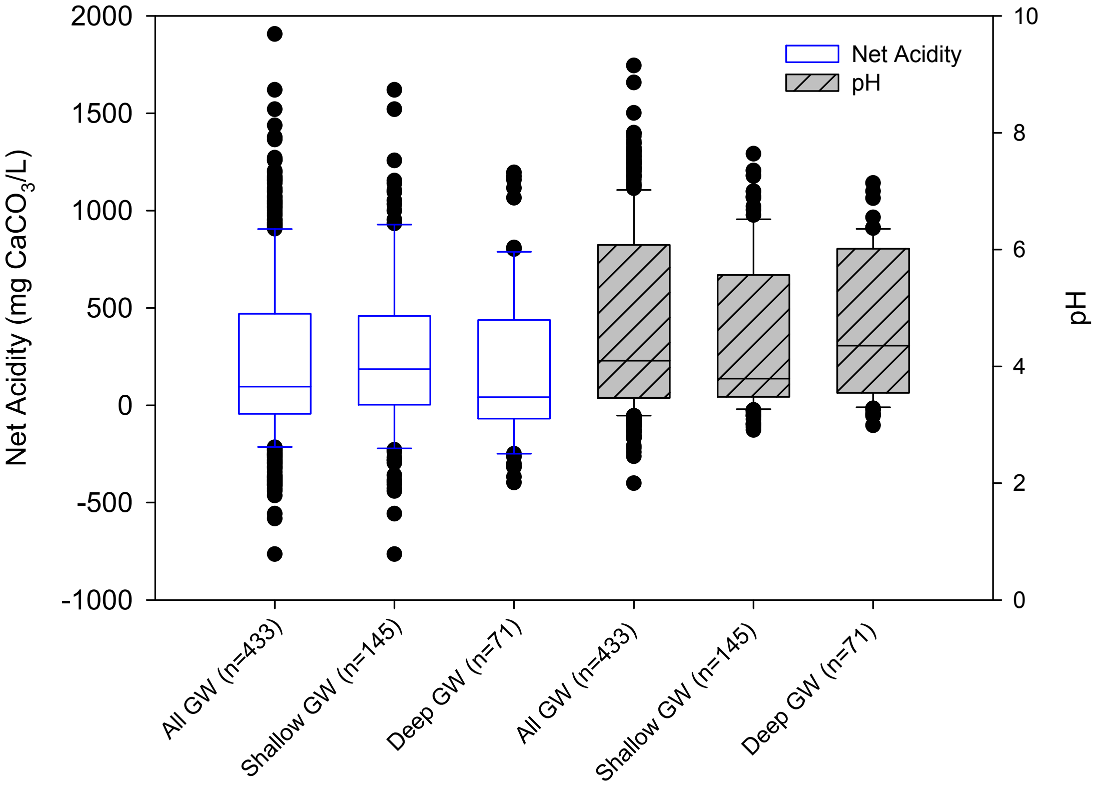


Figure 7-4 Distribution of net acidity (calculated) and pH for all groundwater sampling points across the WA Wheatbelt and the subset distribution of net acidity in shallow groundwater (< 6 m below water-table) and deep groundwater (>6 m below water-table). Note: net acidity calculated as for Figure 7-3 and box-plots show median, interquartile ranges (25% and 75%) and 5% and 95% limits.

The risk posed by this acidity is framed by the volumes of water likely to be discharged by drains, with net acidity varying independently to baseflow (Figure 7-6). Flow estimates for drainage systems in this and previous investigations (where available, Shand and Degens 2008) indicate that whilst over 75% of base flows in drains in these surveys were less than 1.5 L/s, these can sometimes be highly acidic (net acidity >600 mg $CaCO_3$/L). Furthermore, some drainage systems contain average baseflow exceeding more than 5 L/s and contain similarly high levels of acidity (Figure 7-6). Baseflow in deep drains is dependent on design of drainage systems (e.g. length of channel) and the properties of shallow aquifers into which these are frequently constructed to drain groundwater (Cox and Tetlow, 2010). The data here consist of snapshot estimates of flows, and a more expanded estimation of the range of baseflow discharge is required to enable a more complete assessment of the risks posed by acidic drain discharge in the WA Wheatbelt. In particular, the question of longevity of flows is required, considering there is evidence of some drains flowing continuously for over a decade.

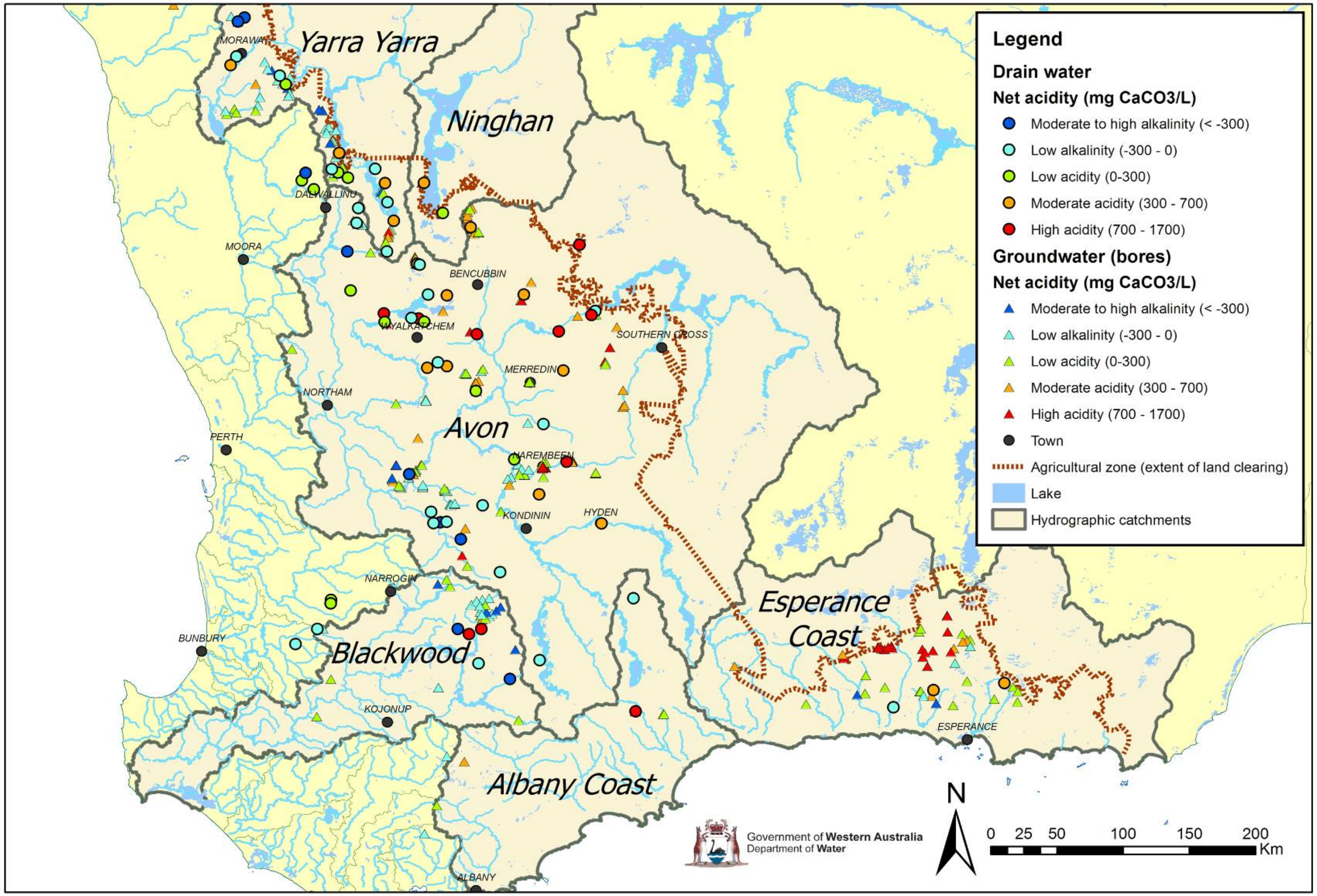


Figure 7-5 Spatial distribution of groundwater acidity across the WA Wheatbelt as indicated by water chemistry in bores and groundwater drains.

In summary, acidic groundwater is a hazard extending across the Wheatbelt, with some regional variations in the level of risk, but with much of this dependent on whether groundwater discharge occurs to surface environments by either land management (deep drainage) or driven by on-going hydrological imbalance in landscapes. Risk management will also depend on whether the discharge is managed to treat or contain acidity. Recent guidelines for treating acidic drain waters highlight a number of practical ways in which this might be achieved (Degens, 2009a). While there is evidence that neutralisation might be achieved by mixing with alkaline surface waters during floods (see Chapter 6) this is highly dependent on spatial and temporal alignment of processes generating acidity with processes neutralising acidity. Indications of lake and river water alkalinity from snapshot sampling are that surface waters contain limited capacity to neutralise drainage waters (Figure 7-7; lake median 99 mg $CaCO_3$/L; river median 44 mg $CaCO_3$/L) and would need to be continuously replenished at rates several times more than that of the rate of drain discharge (see Chapter 6). Where acidic drain waters are not immediately neutralised by alkaline surface waters on discharge, the main result in the WA Wheatbelt is acidification of sediments (see Chapter 5). This is likely to result in intermittent, but recurrent acidification of surface waters for many years (e.g. Degens, 2009b).

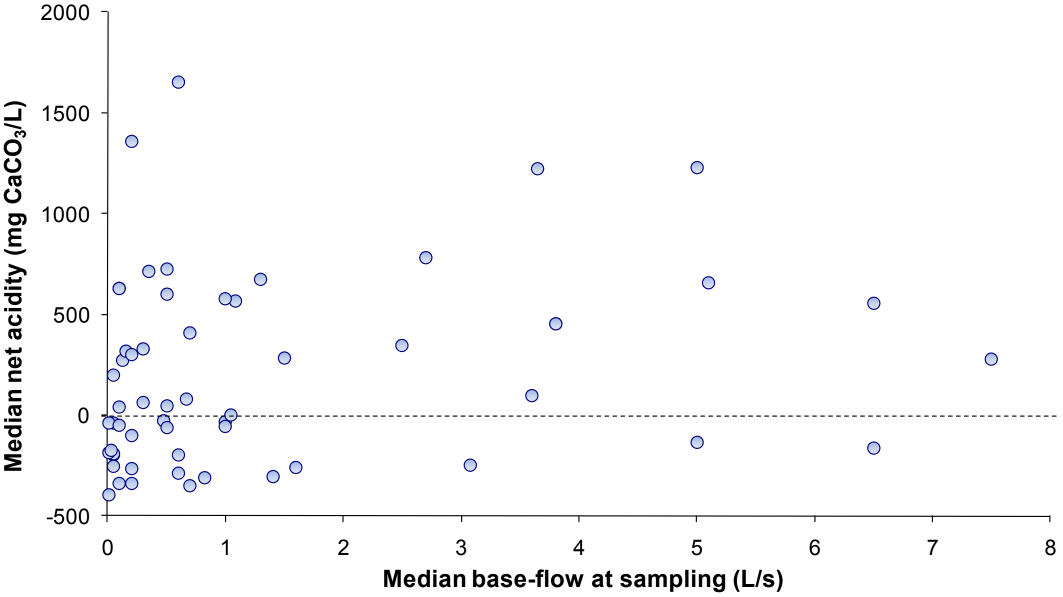


Figure 7-6 Median net acidity (mg $CaCO_3$/L) in relation to median base-flows at time of sampling for drainage systems in the WA Wheatbelt.

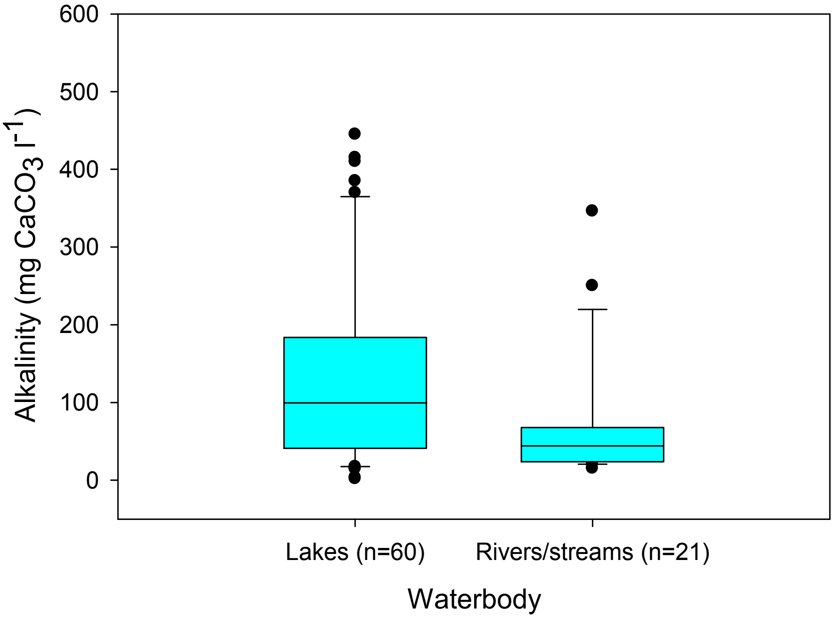


Figure 7-7 Indicative distribution of alkalinity of lake water (mostly following flood filling) and rivers or streams from snapshot sampling across the Wheatbelt (box plots displaying median, interquartile ranges (25% and 75%) and 5% and 95% boundaries).

7.4. Trace elements in groundwater and groundwater drains

Concentrations of trace elements in drain waters have been frequently highlighted in this and other reports as posing short term toxicity and longer-term bioaccumulation risks to aquatic ecosystems (Degens et al., 2008; Degens 2009a; Jones et al., 2009). This risk is in addition to that posed by net acidity, which is predominantly borne by the concentrations of iron and aluminium in waters.

Concentrations of metals such as lead, nickel, copper and zinc in drains exhibited a range and distribution similar to that of groundwater across the Wheatbelt. As indicated previously (Sections 2, 3 and 4 of this report), high concentrations of these metals are generally associated with acidic drains and groundwater.

Some trace metals such as lead, copper and zinc in some drains and groundwater may pose significant risks to many aquatic species in inland ecosystems. The comparative risks of trace metals to aquatic ecosystems can be assessed by comparison with national water quality guideline limits for the protection of aquatic species (Table 7-1; ANZECC&ARMCANZ, 2000a), although there are no specific limits applicable to mostly highly seasonal and ephemeral inland aquatic saline ecosystems. The risks of lead, copper and zinc would apply when water reaches aquatic ecosystems and would only be apparent when water conditions favoured establishment of aquatic organisms (i.e. when sufficient water with low enough salinity to support life occurs). There is no locally relevant information to assess whether elements such as cerium and lanthanum pose a risk to saline aquatic ecosystems. Median and 75th percentile concentrations of cerium were 98 µg/L and 272 µg/L in groundwater and for lanthanum were 41 µg/L and 109 µg/L in groundwater.

Factors associated with the salinity of the waters are likely to off-set some of the potential toxicity of trace elements in the acidic waters. Interactions between trace elements and other ions in saline waters (e.g. chloride, calcium and magnesium) are widely known to modify toxicity (ANZECC & ARMCANZ, 2000b). This suggests that toxicity of at least trace metals in waters more saline than seawater is likely to be less than indicated here. An indication of the effect of this on aquatic ecosystem risk is reflected in Table 7-1 as the number of sites with concentrations of trace elements more the 10 times that of the existing marine guideline limits (which is the same as the number of sites exceeding the limits if these were 10 times greater). The presence of dissolved organic matter in some drains and groundwaters exceeding tens of mg/L will also likely reduce the toxicity of some metals (e.g. lead; ANZECC & ARMCANZ, 2000b).

Bioaccumulation risks may exist for trace metals such as lead and cadmium where these accumulate in lakes and pools (Degens et al., 2008; Degens 2009a). It is not certain how salinity or other water quality components would affect this risk.

Although all waters sampled in these investigations were saline, there are potential risks of trace metals affecting ephemeral fresh-water ecosystems, particularly after filling of lakes and water-courses during flooding (and freshening of these systems). The dilution occurring during such events (if metals are not flushed) may not be sufficient to reduce concentrations of some metals to a point where risks are reduced for aquatic life in transient fresh-water ecosystems. Remobilisation may also occur from metals concentrated in sediments by evaporation, although is not considered here. Copper, lead and zinc concentrations in more than 15% of groundwaters and 5% of existing drains exceeded fresh water ecosystem trigger limits by more than 10 times (Table 7-1). This indicated that conservative dilution of the saline waters by 10 times, as would be common during flooding (e.g. from seawater salinities of 35 000 mg TDS/L to 3500 mg/L), could result in the trace metals remaining at concentrations that might pose a risk to fresh-water aquatic ecosystems estabilishing after floods. This worse-case-scenario effect, however, assumes that the metals would not precipitate with rising pH and that water hardness does not affect metal toxicity. Estimates of hardness remaining in saline groundwater diluted to less than 2500 mg/L TDS (approximately 300–400 mg $CaCO_3$/L) indicate that this can increase trigger limits for some metals by at least 10 fold for some species (ANZECC & ARMCANZ, 2000a). This may result in the concentrations of copper, zinc and lead in many waters being potentially non-toxic for most aquatic species.

At a regional level, there are no patterns apparent in the occurrence of high concentrations of trace metals of concern such as lead (Figure 7-8) and copper in groundwater or groundwater drains, aside from the underlying pattern determined by low pH. This suggests that high concentrations of trace metals in low pH waters are probably localised and due to variations in the geochemistry of the local regolith and geology as has been reported elsewhere in the adjoining Goldfields region (Gray 2001).

Table 7-1 Summary of potential trace metal toxicity for aquatic ecosystems by comparison with ANZECC&ARMCANZ (2000a) fresh water (<2500 mg/L TDS) and marine aquatic ecosystem guideline limits (for conservative protection of 80% of species).

Metal/ metalloid	Fresh water ecosystem guidelines				Marine ecosystem guidelines			
	% sites exceeding protection limits[1]		% sites exceeding protection limits[1] by more than x10[a]		% sites exceeding protection limits[1]		% sites exceeding protection limits[1] by more than x10	
	GW[2]	Drain[2]	GW	Drain	GW	Drain	GW	Drain
Arsenic[3]	0	0	0	0	N/A	N/A	N/A	N/A
Cadmium	44	15	1.5	0	0.2	0	0	0
Copper	72	65	34	4	62	53	16	1
Lead	50	47	15	12	48	43	12	11
Nickel	65	53	5	1.2	0.2	0	0	0
Selenium	2	0	0	0	N/A	N/A	N/A	N/A
Zinc	70	65	24	5	63	60	18	2

[1] Ecosystem protection limit of 80% of aquatic species.

[2] GW = groundwater sampling sites with water chemistry data (433 for copper, zinc, lead and nickel; 410 for arsenic and cadmium), drain = drain system summary with water chemistry data (81 for arsenic, copper, zinc, lead and nickel and 52 for cadmium).

[3] Assumed As (V) given most drains and groundwaters were oxidising (see section 2, 3 and 4).

[a] Note: the toxicity of elements in fresh-water ecosystems decreases with increasing water hardness (mainly due to calcium and magnesium). Estimates of hardness remaining in saline groundwater diluted to less than 2500 mg/L TDS (approximately 300–400 mg $CaCO_3$/L) indicate that this can significantly increase trigger limits.

N/A: no guideline limit has been derived.

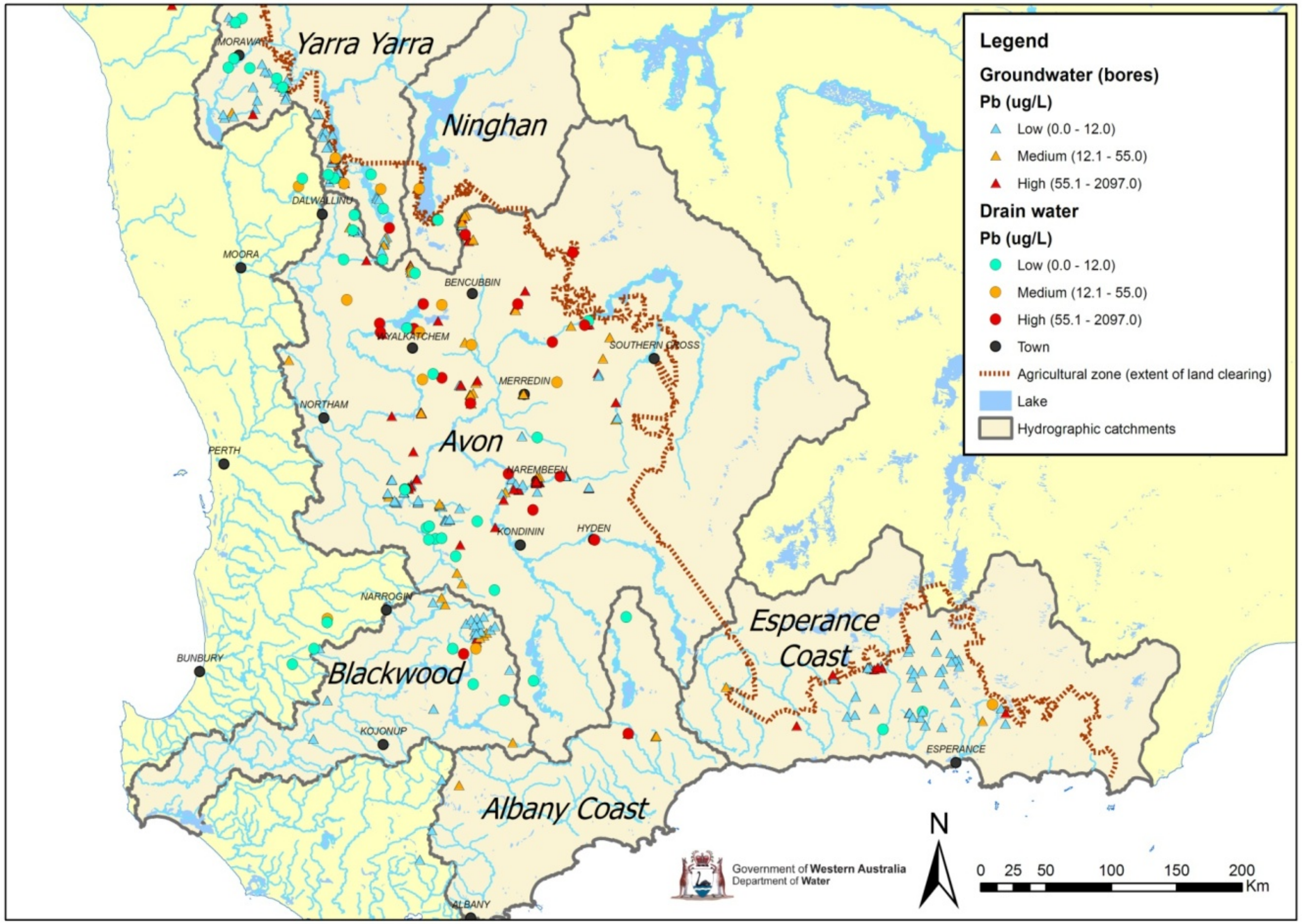


Figure 7-8 Spatial distribution of lead in groundwater across the WA Wheatbelt as indicated by water chemistry in bores and groundwater drains. Low classification limit based on 80% marine species protection limit (ANZECC&ARMCANZ 2000a), with high deemed as above median percentile of dataset

7.5. Nutrients in groundwater and groundwater drains.

Nutrients in groundwater and groundwater drains across the WA Wheatbelt are generally low. Median total nitrogen (TN) concentrations for 46 drainage systems (Shand and Degens, 2008 and the present investigation) were 0.6 mg/L with 75% being less than 3 mg/L, with most of this being dominated by inorganic nitrogen (a mix of nitrate and ammonia). Whilst median TN concentrations in groundwater were 1.6 mg/L, this was generally due to greater concentrations of ammonia. Concentrations of phosphate in drain waters were much less with a median of 0.08 mg/L and 75% being less than 0.13 mg/L, and reflected the concentrations found in groundwater. These nutrient concentrations do not represent a significant threat to aquatic ecosystems, particularly when compared with concentrations occurring in surface water flows across the Avon Basin each winter. Annual median TN concentrations for almost half of waterways exceeded 1.6 mg/L, whereas annual median total phosphorus concentrations of almost a quarter of waterways exceeded 0.08 mg/L (Department of Water, 2009a,b). This contrasts with previous assessments (Jones et al. 2009), although it is acknowledged that with **unleveed** drains, nutrient concentrations may increase during rainfall events as a result of surface runoff transporting nutrients from surrounding catchments.

7.6. Summary outcomes

- Groundwater drain water pH distribution across the Wheatbelt reflects that of groundwater.
- The distribution of acidity in groundwater is similar to that occurring in drain waters, reflecting that drain water acidity is sourced primarily from groundwater.
- Over 45% of groundwater drainage systems surveyed across the Wheatbelt (with flowing water) contained acidic water with the median acidity of these being 569 mg $CaCO_3$/L.
- Up to 10% of groundwater drainage systems contained **very** acidic waters (>1000 $CaCO_3$/L) and similarly reflected in sampling of groundwater acidity across the Wheatbelt. This indicates that shallow saline groundwater in some areas of the Wheatbelt will be extremely acidic.
- Areas of the central and eastern Wheatbelt and northern South Coast are likely to contain groundwater with high acidity (>700 mg $CaCO_3$/L).
- Trace metals such as lead, copper and zinc in some drains and groundwater pose risks to many aquatic species in inland ecosystems, although the risks may be slightly lessened due to the high salinity of the water and ephemeral nature of aquatic ecosystems (possibly reducing likely exposure to the metals).
- Nutrients in groundwater and groundwater drains across the WA Wheatbelt are generally low and comparable with concentrations occurring in surface waters (at least during baseflow periods).
- Acidic groundwater is a hazard extending across the Wheatbelt with some regional variations in the magnitude of the hazard. The risks posed by this acidic groundwater depends on whether discharge occurs to surface environments by either land management (deep drainage) or driven by on-

going hydrological imbalance in landscapes and whether the discharge is managed to treat or contain acidity.

REFERENCES

ABCB (Australian Buildings Code Board). 2004. Buildings subject to attack from salt and acid sulphate soils: Discussion paper. August 2004. Government of Australia. Accessed at: <http://www.abcb.gov.au/index.cfm?objectid=E8F81A35-92DB-55CE-FD2AAA1E63C15908>

Affek, H.P., Ronen, D. & Yakir, D. 1998. Production of CO_2 in the capillary fringe of a deep phreatic aquifer. *Water Resources Research* 34, pp. 989-996.

Ahern CR, Sullivan LA, McElnea AE 2004. Laboratory Methods Guidelines 2004 – Acid Sulfate Soils. In: 'Queensland Acid Sulfate Soil Technical Manual'. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

Ali, R., Viney, N., Hodgson, G., Aryal, S., George. R., Dawes, W., & McIntosh, K. (2008). Predicting impacts of current and future salinity on hydrology of major river systems of the Avon Basin of Western Australia. Proceedings: "2nd International Salinity Forum", Adelaide 31st March - 3rd April, 2008. Available at: <http://www.internationalsalinityforum.org/Final%20Papers/ali,%20riasat_C3.pdf>

Ali, R., Viney, N., Hodgson, G., Aryal, S. & Dawes, W. (2009a). Wheatbelt Drainage Evaluation – Avon River Basin. CSIRO: Water for a Healthy Country National Research Flagship (Better Basin Futures).

Ali, R., Viney, N., Hodgson, G., Smart, N., Dawes, W., Aryal, S. & John, M. (2009b). Wheatbelt Drainage Evaluation – Blackwood River Basin, Western Australia. CSIRO: Water for a Healthy Country National Research Flagship (Better Basin Futures).

Anand, R.R. & Paine, M. 2002. Regolith geology of the Yilgarn Craton, Western Australia: implications for exploration. *Australian Journal of Earth Sciences* 49, pp. 3-162.

Anand, R.R., Paine, M.D. & Smith, R.E. 2002. Genesis, classification and atlas of ferruginous materials, Yilgarn Craton. *CRC LEME Open File Report* 73, 87 pp.

ANZECC (Australia and New Zealand Environment and Conservation Council) & ARMCANZ (Agriculture and Resource Management Council of Australia and New Zealand) 2000a. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Agriculture and Resource Management Council of Australia and New Zealand, Canberra.

Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand 2000b. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality Volume2 Aquatic Ecosystems – Rationale and Background Information*, Canberra.

Appelo, C.A.J. & Postma, D. 2005. *Geochemistry, Groundwater and Pollution* (2^{nd} edn.). A.A. Balkema Publishers, Leiden, London, New York, 649 pp.

ASTM (American Society for Testing and Materials). 2002. *Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations*. ASTM D6771-02. ASTM International, Pasadena, USA, 7 p.

Australian Bureau of Statistics (ABS) 2002 Salinity of Australian Farms. Bulletin No. 4615. Australian Bureau of Statistics, Canberra.

Ali, R & Coles, N 2002 Drainage options and their use in Wheatbelt landscapes in WA. In: Dealing with salinity in Wheatbelt valley floors conference, Merredin 30th July – 1st August 2002, WA Salinity Research and Development Technical Committee, 8pp, accessible at: <www.water.wa.gov.au>.

Barnes, C.J., Jacobson, G. & Smith, G.D. 1992. The origin of high-nitrate ground waters in the Australian arid zone. *Journal of Hydrology* 137, pp. 181-197.

Baxter, J.L. & Lipple, S.L. 1985. Perenjori, Western Australia (Sheet SH 50-6). 1:250,000 geological series – explanatory notes. Geological Survey of Western Australia, Perth.

Beard, J.S. 2000. Drainage evolution in the Moore-Monger System, Western Australia. *Journal of the Royal Society of Western Australia,* 83, 29-38.

Bennett, A. 2009. Greenhouse gas emissions from agriculture. *Factsheet* 366. Department of Agriculture & Food Western Australia, South Perth, 2 p.

Blight, D.F., Chin, R.J. & Smith, R.A. 1984. Bencubbin, Western Australia (Sheet SH 50-11). 1:250,000 geological series – explanatory notes. Geological Survey of Western Australia, Perth.

Boggs, D.A., Boggs, G.S., Eliot, I. & Knott, B. 2006. Regional patterns of salt lake morphology in the lower Yarra Yarra drainage system of Western Australia. *Journal of Arid Environments* 64, 97–115.

Boggs, D.A., Boggs, G.S., Knott, B. & Eliot, I. 2007a. The hydrology and hydrochemistry of six small playas in the Yarra Yarra drainage system of Western Australia. *Journal of the Royal Society of Western Australia* 90, 15–32.

Boggs, D.A., Eliot, B. & Knott, B. 2007b. Salt lakes of the northern agricultural region, Western Australia. *Hydrobiologia* 576, 49–59.

Boggs, D.A, Gell, P., Eliot, I. & Knott, B. 2008. Distribution of modern diatom assemblages among small playas. *Australian Journal of Botany* 56, 131–143.

Bowen, B.B. & Benison, K.C. 2009. Geochemical characteristics of naturally acid and alkaline saline lakes in southern Western Australia. *Applied Geochemistry* 24, pp. 268-284.

Bureau of Meteorology 2009, Australian climate variability and change – trend maps for Western Australia. Bureau of Meteorology, Commonwealth of Australia, accessible at: <www.bom.gov.au/climate/climatechange/trendmaps/>.

Bureau of Meteorology (2010). Australian climate variability & change - trend maps. Bureau of Meteorology , Commonwealth of Australia. Accessed at: <http://www.bom.gov.au/cgi-bin/climate/change/trendmaps.cgi>

Butt, C.R.M., Horowitz, R.C.H. & Mann, A.W. 1977. Uranium occurrences in calcrete and associated sediments in Western Australia. , Report FP16. CSIRO Division of Mineralogy, Perth.

Caccetta, P., Dunne, R., George, R., & McFarlane, D. (2010) A Methodology to Estimate the Future Extent of Dryland Salinity in the Southwest of Western Australia. *Journal of Environmental Quality* 39, 26–34.
Cattle, S. & Elias, S. 2003. Dust deposition across the central wheat/sheep belt of NSW. *Agricultural Science* 16, pp. 42-46.

Chin, R.J. & Brakel, A.T. 1986. Dumbleyung, Western Australia, Sheet SI/50-07 International Index. *1:250 000 Geological Series – Explanatory Notes*, Geological Survey of Western Australia, Perth, 21 p.

Clarke, M. 2001. Yarra Yarra Catchment Rapid Catchment Appraisal. Resource Management Technical Report No. 230. Western Australian Department of Agriculture, South Perth.

Commander, D.P. & McGowan, R.J. 1991. Explanatory notes on the Perenjori 1:250 000 hydrogeological sheet. Hydrogeological Series – Explanatory Notes. Geological Survey of Western Australia, Perth, Western Australia.

Commander, P., Schoknecht, N., Verboom, B. & Caccetta, P. 2002 The geology, physiography and soils of Wheatbelt valleys. In "Dealing with salinity in Wheatbelt valley floors conference", Merredin 30th July – 1st August 2001, WA Salinity Research and Development Technical Committee. 27p, Accessed at: http://www.water.wa.gov.au.

Coudrain-Ribstein, A., Gouze, P. & de Marsily, G. 1998. Temperature-carbon dioxide partial pressure trends in confined aquifers. *Chemical Geology* 145, pp. 73-89.

Cox, N.M .& Tetlow, S.F. (2010) Drainage in the Dumbleyung catchment, Western Australia, Salinity and land use impacts series, Report no. SLUI 43, Department of Water, Government of Western Australia.

Davis, S.N., Whittenmore, D.O. & Fabryka-Martin, J. 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water* 36, pp. 338-350.

Degens, B., Fitzpatrick, R. & Hicks, W. 2008. Avon basin, WA Wheatbelt: Acidification and formation of inland ASS materials in salt lakes by acid drainage and regional groundwater discharge. In: 'Inland Acid Sulfate Soil Systems Across Australia' R. Fitzpatrick & P. Shand (Eds.). CRC LEME. Special Volume Open File Report No. 249 (Thematic Volume). CRC LEME, Perth, Australia. pp 176–188. Accessed at <http://www.clw.csiro.au/acidsulfatesoils/ass-book.html>

Degens, B, Fitzpatrick, R, Douglas, G & Hicks, W 2008, Geochemical risks associated with disposal of acidic waters to lakes, In: P Shand & B Degens (eds.), Avon catchment acid ground-water: geochemical risk assessment, CRC-LEME Open File Report 191, CSIRO Exploration and Mining, Bentley, WA, pp. 35–44.

Degens B.P., Fitzpatrick RW, & Raven MD 2010. Hydric halitic sulfuric soils in secondary salinised landscapes of Southwest Western Australia. 19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia, pp. 56–59.

Degens, B.P., Shand, P., Fitzpatrick, R.W., George, R.G., Rogers, S.L. & Smith, M. 2008. Avon basin, WA Wheatbelt: An overview of geochemical risks of saline acidic discharge from deep drains used to manage dryland salinity in Western Australia. In:

Inland acid sulfate soil systems across Australia, R Fitzpatrick and P Shand (eds.), *CRC LEME Open File Report No. 249* (Thematic Volume), CRC LEME, Perth, Australia, pp. 169–175.

Degens, B 2009a Proposed guidelines for treating acidic drain water in the Avon catchment: adapting acid mine drainage treatment systems for saline acidic drains, Salinity and land use impacts series, SLUI 54, Department of Water, Government of Western Australia. Accessed at: <www.water.wa.gov.au/PublicationStore/first/91346.pdf>

Degens, B. 2009b Treating acidity in saline water and sediments in the Wallatin Creek catchment using a hydrated lime dosing unit. Department of Water, Government of Western Australia. 8pp. Accessed at: <www.water.wa.gov.au/PublicationStore/first/90783.pdf>

Dentith, M.C. & Featherstone, W.E. 2003. Controls on intra-plate seismicity in southwestern Australia. *Tectonophysics* 376, pp. 167-184.

Department of Environment and Conservation (2009) Draft treatment and management of acid sulfate soils and water in acid sulfate soil landscapes, Department of Environment and Conservation, Government of Western Australia, Acid Sulfate Soil Guideline Series, January 2009.

Department of Water. 2008. Review of water quality downstream of the Fence Road Drainage Scheme, Dumbleyung, 24 October 2008. Department of Water, Perth, unpublished report, 15 p.

Department of Water 2009a. Avon River catchment water quality and nutrient monitoring program for 2007. Department of Water, Government of Western Australia.

Department of Water 2009b. Avon River catchment water quality and nutrient monitoring program for 2008. Department of Water, Government of Western Australia.

Dickson, A.G. 1993. The measurement of sea water pH. *Marine Chemistry* 44, pp. 131-142.

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

Douglas, G. and Degens, B., 2008. Case Study Assessment of Regional Drainage Geochemical Risks using Geochemical Modelling. Chapter 7 In: Avon Catchment Acidic Groundwater Geochemical Risk Assessment, P.Shand and B. Degens (eds.). *CRC LEME Open File Report* 191, 98 pp.

Driscoll, C.T., Lambert, K.F. & Chen, L. 2007. Acidic deposition: sources and ecological effects. In: G.R. Visgilio & D.M. Whitelaw (Eds.) 'Acid in the environment: lessons learnt and future prospects', Springer, New York, pp. 27–58.

Eugster, H.P. & Jones, B.F. 1979. Behaviour of major solutes during closed-basin brine evolution. *American Journal of Science* 279, pp. 609-631.

Fitzpatrick, R., Degens, B., Baker, A., Raven, M., Smith, M., Rogers, S., George, R. & Shand, P. 2008. Geochemical and hydrochemical processes occurring within drain environments in the Avon basin. In: P. Shand & B. Degens (Eds.). 'Avon catchment acid ground-water: geochemical risk assessment'. CRC-LEME Open File Report 191, CSIRO Exploration and Mining, Bentley, WA, pp. 20–34.

Fitzpatrick R, Grealish G, Shand P, Merry P, Creeper N, Thomas M, Baker A, Thomas B, Hicks W and Jayalath N 2010. Chip-tray incubation – a new field and laboratory method to support Acid Sulfate Soil Hazard Assessment, Classification and Communication. 19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia. Published on CDROM (In press).

Fitzpatrick R, Shand P 2008. Inland Acid Sulfate Soils: Overview and conceptual models. In 'Inland Acid Sulfate Soil Systems Across Australia'. (Eds. R. Fitzpatrick, P Shand) pp 6-74. CRC LEME Open File Report No. 249 Thematic Volume. (CRC LEME: Perth, Australia.

Fordyce, I. & Hudson, M. 2007. Deep drains in the Yarra Yarra catchment: what we've learned to date and our proposal for the future. Report prepared for the Northern Agricultural Catchments Council by the Yarra Yarra Catchment Management Group Inc. Accessed at <http://www.yarrayarracatchment.asn.au/index_files/Page819.htm>

Geological Survey of Western Australia. 1990. Geology and mineral resources of Western Australia. *Western Australia Geological Survey Memoir* 3, 827 p.

George, R., Kingwell, R., Hill-Tonkin, J. and Nulsen, R. 2005. Salinity investment framework: Agricultural land and infrastructure. Resource Management Technical Report 270. Department of Agriculture Western Australia.

George. R.G., Speed, R.J., Simons J.A., Smith. R.H., Ferdowsian, R., Raper G.P. and Bennett D.L. 2008a Long-term groundwater trends and their impact on the future extent of dryland salinity in Western Australia in a variable climate. Proceedings: "2nd International Salinity Forum", Adelaide 31st March - 3rd April, 2008.

George, R., Clarke, J. & English, P. 2008b Modern and palaeogeographic trends in the salinisation of the Western Australian wheatbelt: a review. *Australian Journal of Soil Research* 46, pp. 751-767.

GHD 2006. Yarra Yarra catchment regional drainage waters management evaluation. Report for the Western Australian Department of Water, October 2006.

Gray DJ, 2001. Hydrogeochemistry in the Yilgarn Craton. Geochemistry: Exploration, Environment, Analysis 1, 253–264.

Gray, D.J. & Lillicrap, A.M. 2008. The top down paradigm – do plants control groundwater and weathering in semi-arid Australia? In: 'Australian Earth Sciences Convention 2008. New Generation Advances in Geoscience' Abstracts No. 89 of the 19th Australian Geological Convention. Perth Convention and Exhibition Centre, Perth WA, 20-24 July. Pp 117–118.

Grey, N.F. 1997 Environmental impact and remediation of acid mine drainage: a management problem. *Environmental Geology* **30**, 62-71

Halse, S.A., Pearson, G.B. & Kay, W.R. 1998. Arid zone networks in time and space: Waterbird use of Lake Gregory in North-Western Australia. *International Journal of Ecological and Environmental Science,* 24, 207–222.

Halse, S.A., Pearson, G.B., McRae, J.M. & Shiel, R.J. 2000 Monitoring aquatic invertebrates and waterbirds at Toolibin and Walbyring Lakes in the Western Australian wheatbelt. *Journal of the Royal Society of Western Australia* 83, pp. 17-28.

Hardie, L.A. & Eugster, H.P. 1970. The evolution of closed-basin brines. *Mineralogical Society of America Special Paper* 3, pp. 273-290.

Hare, L. 1992. Aquatic insects and trace metals: bioavailability, bioaccumulation, and toxicity. *Critical Reviews in Toxicology* 22 *(5&6)*, 327–369.

Harrington, G.A. 1999. *Recharge Mechanisms and Chemical Evolution in an Arid Groundwater System, Central Australia*. PhD thesis, Flinders University of South Australia (unpubl.), 293 p.

Hatton, T.J. Ruprecht, J. & George, R.J. (2003). Pre-clearing hydrology of the Western Australian Wheatbelt: Target for the future ? *Plant and Soil* 257, 341–356.

Hedin, R.S., Nairn, R.W. and Kleinmann, R.L.P., (1994). Passive treatment of coal mine drainage. United States Bureau of Mines Information Circular, No. 9389. *United States Department of the Interior*.

Henschke, C.J. 1989. Catchment Salinity: Report on a Study of the East Perenjori Catchment. Resource Management Technical Report No.85. Western Australian Department of Agriculture, South Perth.

Hiemstra, T., Barnett, M.O. & van Riemsdijk, W.H. 2007. Interaction of silicic acid with goethite. *Journal of Colloid and Interface Science* 310, pp. 8-17.

Hingston, F.J. & Gailitis, V. 1976. The geographic variation of salt precipitated over Western Australia. *Australian Journal of Soil Research* 14, pp. 319-335.

Isbell RF 1996. The Australian soil classification system. CSIRO, Publishing, Melbourne.

Jones S.M., Francis C.J., Halliday D.L., Leung A.E. (2009). The potential effects of groundwater disposal on the biota of wetlands in the Wheatbelt, Western Australia. Prepared for the Avon Catchment Council by the Department of Environment and Conservation, Perth.

Keywood, M.D., Chivas, A.R., Fifield, L.K., Cresswell, R.G. & Ayers, G.P. 1997. The accession of chloride to the western half of the Australian continent. *Australian Journal of Soil Research* 35, pp. 1177-1189.

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

Kirby, C.S. and Cravotta, C.A., 2005. Net alkalinity and net acidity 1: theoretical considerations. *Applied Geochemistry*, 20, 1920-1940.

Kirby, C.S. & Cravotta, C.A. 2005. Net alkalinity and net acidity 2: practical considerations. *Applied Geochemistry* 20, pp. 1941-1964.

Kirby, C.S., Dennis, A. & Kahler, A. 2009. Aeration to degas CO_2, increase pH, and increase iron oxidation rates for efficient treatment of net alkaline mine drainage. *Applied Geochemistry* 24, pp. 1175-1184.

Komarzynski, M. (2000) Surface and sub-surface water management in Dalyup Catchment 2000, Misc. Publication No. 005/2001 Agriculture Western Australia

Kortatsi, B.K., Tay, C.K., Anornu, G., Hayford, E. & Dartey, G.A. 2008. Hydrogeochemical evaluation of groundwater in the lower Offin Basin, Ghana. *Environmental Geology* 53, pp. 1651-1662.

Land Monitor 2000. Land monitor salinity mapping mosaic for the Western Australian Wheatbelt – GIS dataset. Land Landgate, Department of Land Information, Government of Western Australia, Perth.

Lee, S.Y. and Gilkes, R.J. 2005 Ground-water geochemistry and composition of hardpans in southwestern Australian regolith. Geoderma 126, 59-84.

Lewis, M.E. 2006. Dissolved Oxygen (Version 2.1). In: Radtke, D.B., White, A.F., Davis, J.V. & Wilde, F.D. National Field Manual for the Collection of Water-Quality Data. *U.S. Geological Survey Techniques of Water-Resources Investigations Book* 9, Chapter A6, Section 6.2, 48 p. Available online on 22nd May 2009: <http://water.usgs.gov/owq/FieldManual/Chapter6/6.2_contents.html>.

Leys, J.F. & McTainsh, G.H. 1999. Dust and nutrient deposition to riverine environments of south-eastern Australia. *Zeitschrift für Geomorphologie* 116, pp. 59-76.

Lillicrap, A (2004) *Groundwater tends in the Fitzgerald Biosphere sub-region*. Department of Agriculture Miscellaneous Publication 13/2004. Perth

Lillicrap, A. & George, R (2008) Acidic groundwater in the south west of Western Australia: distribution and geospatial relationships. In: P.Shand & B Degens (Eds.) 'Avon Catchment acidic groundwater – geochemical risk assessment'. Pp 12–15. CRC LEME Open File Report 191.

Lindberg, R.D. & Runnells, D.D. 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modelling. *Science* 225, pp. 925-927.

Lipple, S.L., Baxter, J.L. & Marston, R.J. 1983. Ninghan, Western Australia (Sheet SH 50-7). 1:250,000 geological series – explanatory notes. Geological Survey of Western Australia, Perth.

Lizamore J.M., Cale D., Mudgway L., Prideaux C. (2008) Notice of Intent to Drain: Field manual for Rapid Assessment or Initial Inspections for the Department of Environment and Conservation of Western Australia, Department of Environment and Conservation, Perth.

Long, D.T., Lyons, W.B. & Hines, M.E. 2009. Influence of hydrogeology, microbiology and landscape history on the geochemistry of acid hypersaline waters, N.W. Victoria. *Applied Geochemistry* 24, pp. 285-296.

Luke, G.J., Burke, K.L. & O'Brien, T.M. 2003. Evaporation data for Western Australia. *Resource Management Technical Report* 65. Department of Agriculture Western Australia, South Perth, 32 p.

LWRRDC (Land and Water Resources Research and Development Corporation). 1999. Contamination of Australian Groundwater Systems with Nitrate. *Land and Water Resources Research and Development Corporation Occasional Paper* 03/99, Canberra, 134 p.

Mann, A.W., 1983 Hydrogeochemistry and weathering on the Yilgarn Block, Western Australia - ferrolysis and heavy metals in continental brines. Geochimica et Cosmochimica Acta 47, 181-190.

Mayer, X., Ruprecht, J. & Bari, M. 2005. Stream salinity status and trends in south-west Western Australia. *Salinity and Land Use Impacts Series* 38. Department of Environment, Perth, 176 p.

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

McArthur, J.M., Turner, J.V., Lyons, W.B., & Thirlwall, M.F. 1989. Salt sources and water-rock interaction on the Yilgarn Block, Australia: isotopic and major element tracers. *Applied Geochemistry* 4, pp. 79-92.

McElnea, A.E., Ahern, C.R.. and Menzies, N.W., (2002). The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research*, 40, 1133-1157.

McFarlane, DJ, George, RJ & Caccetta, PA 2004 'The extent and potential area of salt-affected land in Western Australia estimated using remote sensing and digital terrain models', in: S Dogramaci & A Waterhouse (eds.), 1st National salinity engineering conference, November 2004, Perth, Western Australia, Institution of Engineers, Australia, pp. 55–60.

Millero, F.J., Zhang, J-Z., Fiol, S., Sotolongo, S., Roy, R.N., Lee, K. & Mane, S. 1993. The use of buffers to measure the pH of seawater. *Marine Chemistry* 44, pp. 143-152.

Morgan, B. 2005. The corrosion of infrastructure by acid sulfate soils at Yunderup, Western Australia. Honours Thesis. School of Earth and Geographical Sciences, University of Western Australia, Perth.

Morrissy, N.M. 1974. Reversed longitudinal salinity profile of a major river in the south-west of Western Australia. *Australian Journal of Marine & Freshwater Research* 25, pp. 327-335.

Mulcahy, M. J. 1967. Landscapes, laterites and soils in southwestern Australia. In: Jennings, J.N. & Mabbutt, J. A. (eds.). *Landform Studies from Australia and New Guinea*, Cambridge University Press, Cambridge, pp. 211–230.

Mulcahy, M.J. 1973. Landforms and soils of southwestern Australia. *Journal of the Royal Society of Western Australia*, 56,16–22.

Parkhurst, D.L. & Appelo, C.A.J. 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U.S. Geological Survey Water-Resources Investigations Report* 99-4259, 310 p.

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

Percy, H. 2000. Katanning area land resources survey. *Land Resources Series* 16. Department of Agriculture Western Australia, South Perth, 244 p.

Percy, H. 2003. Nyabing-Kukerin area land resources survey. *Land Resources Series* 18. Department of Agriculture Western Australia, South Perth, 72 p.

Pinder, A. M., S. A. Halse, J. M. McRae, and R. J. Shiel. 2005. Occurrence of aquatic invertebrates of the Wheatbelt region of Western Australia in relation to salinity. *Hydrobiologia* **543**:1-24.

Playford, P.E., Cockbain, A.E. & Low, G.H. 1976. Geology of the Perth Basin, Western Australia. Bulletin 124. Geological Survey of Western Australia, Perth.

Post, V., Kooi, H. & Simmons, C. 2007. Using hydraulic head measurements in variable-density ground water flow analyses. *Ground Water* 45, pp. 664-671.

Rasmussen, T.C. & Crawford, L.A. 1997. Identifying and removing barometric pressure effects in confined and unconfined aquifers. *Ground Water* 35, pp. 502-511.

Regeneration Technology, 2002. Ecological assessment of the Yarra Yarra catchment. A report prepared for the Yarra Yarra Catchment Management Group. February 2002. Accessed at http://www.yarrayarracatchment.asn.au/index_files/Page819.htm.

Ridley, J. & Hagemann, S.G. 1999. Interpretation of post-entrapment fluid-inclusion re-equilibration at the Three Mile Hill, Marvel Loch and Griffins Find high-temperature lode-gold deposits, Yilgarn Craton, Western Australia. *Chemical Geology* 154, pp. 257-278.

Rose, A.W. and Cravotta, C.A., (1998). Geochemistry of coalmine drainage. In Brady, K.B.C., Smith, M.W. and Shueck, J. (Eds.). Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, Harrisburg, PA, pp. 1.1-1.22.

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

Stewart, B, Strehlow, K & Davis, J 2009 'Impacts of deep open drains on water quality and biodiversity of receiving waterways in the wheatbelt of Western Australia', Hydrobiologia, 619, no. 1, pp. 103–118.

Salama, R.B., Otto, C.J., Bartle, G.A. & Watson G.D. 1994. Management of saline groundwater discharge by long term pumping in the wheatbelt of Western Australia. *Hydrogeology Journal* 2, 19–33.

Salama, R.B., Otto, C.J. & Fitzpatrick, R.W. 1999. Contributions of groundwater conditions to soil and water salinization. *Hydrogeology Journal* 7, pp. 46-64.

Salama, R.B., Wells, A.S.M., Farrington, P. & Bartle, G.A. 1993. The chemical evolution of groundwater in the aquifer systems of the Yilgarn Craton of Western Australia. IAH XXIVth Congress. Hydrogeology of Hard Rocks Conference. Oslo 1993.

Sammut, J. 2000. An introduction to acid sulfate soils. 2nd Ed. Environment Australia and Agriculture, Fisheries and Forestry – Australia <http://www.deh.gov.au/coasts/cass/pubs/acidsulfate.pdf>.

Shand, P (2008) Hydrogeochemical characteristics of groundwaters and surface waters in the WA wheatbelt *in* Shand, P. & Degens, B (*Eds.*) *Avon Catchment acidic groundwater – geochemical risk assessment*. CRC LEME Open File Report 191.

Shand, P. & Degens, B. 2008 Avon catchment acid ground-water: geochemical risk assessment, CRC LEME Open File Report 191, CSIRO Exploration and Mining, Bentley, WA. Accessible at: http://crcleme.org.au/Pubs/

Shand, P., Degens, B. & Rogers, S. 2008 The geochemistry of acid-saline waters and drainage sediments in the Avon Catchment, Western Australian Wheatbelt. Explore, 140, 1-11.

Shepherd, D.P., Beeston, G.R. & Hopkins, A.J.M. 2002. Native vegetation in Western Australia; extent, type and status. Resource Management Technical Report no. 249. Western Australian Department of Agriculture & Food, Perth.

Simons, J (2000) Groundwater and Salinity in Dalyup Catchment 2000, Misc. Publication No. 005/2001 Agriculture Western Australia

Simons, J (2004) *Groundwater tends in the Esperance Sandplain and Mallee sub-regions*. Department of Agriculture Miscellaneous Publication 13/2004. Perth

Smith, M.S. 2009. *The Geochemistry of Alkaline Salt-Affected Soils*. Ph.D. thesis. Research School of Earth Sciences, The Australian National University (unpubl.), 343 p.

Spane, F.A. 2002. Considering barometric pressure in groundwater flow investigations. *Water Resources Research* 38, pp. 14.1-14.18.

Stewart B, Strehlow K, Davis J 2009, Impacts of deep open drains on water quality and biodiversity of receiving waterways in the wheatbelt of Western Australia. Hydrobiologia, 619, 103–118.

Stuart-Street, A. 2003. Natural resource management issues: south west region. *Resource Management Technical Report* 244. Department of Agriculture Western Australia, South Perth, 55 p.

Stumm, W. & Morgan, J.J. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters* (3rd edn). John Wiley & Sons, Brisbane, Chichester, New York, 1022 p.

Sullivan LA, Fitzpatrick RW, Bush, RT, Burton ED, Shand P, Ward NJ 2010 Modifications to the classification of acid sulfate soil materials. Southern Cross GeoScience Tech Report 309. pp. 11.

Tille, P.J., Mathwin, T.W. & George, R.J. 2001. The south-west hydrological information package: understanding and managing hydrological issues on agricultural land in the south-west of Western Australia. *Bulletin* 4488. Department of Agriculture Western Australia, South Perth, 284 p.

Totsche, O., Pothig, R., Uhlmann, W., Buttcher, H. and Steinberg, C.E.W., (2003). Buffering mechanisms in acidic mining lakes – a model-based analysis. *Aquatic Geochemistry*, 9, 343-359.

Toll, N.J. & Rasmussen, T.C. 2007. Removal of barometric pressure effects and Earth tides from observed water levels. *Ground Water* 45, pp. 101-105.

Vance, G.F. 2006. Acid rain and N deposition. In : L. Rattan (Ed.), 'Encyclopedia of Soil Science'. Pp. 5–10. 2nd edition, Taylor and Francis.

Yarra Yarra Catchment Management Group 2007. Establishing priorities for deep drainage in the Yarra Yarra catchment. Yarra Yarra Catchment Management Group Inc. Accessed at <http://www.yarrayarracatchment.asn.au/index_files/Page819.htm>

Yarra Yarra Catchment Management Group 2008. Progress report of the Yarra Yarra regional drainage and research project. June 2008. Yarra Yarra Catchment Management Group Inc. Accessed at <http://www.yarrayarracatchment.asn.au/index_files/Page819.htm>

Whitfield, B. 1999. Salinity and hydrology of the Fence Road catchment: a focus catchment of the Blackwood Basin. *Resource Management Technical Report* 189. Department of Agriculture Western Australia, South Perth, 47 p.

Wilde, S.A., Middleton, M.F. & Evans, B.J. 1996. Terrane accretion in the southwestern Yilgarn Craton: evidence from a deep seismic crustal profile. *Precambrian Research* 78, pp. 179-196.

Williams, W.D. & Buckney, R.T. 1976. Chemical composition of some inland surface waters in south, western and northern Australia. *Australian Journal of Marine & Freshwater Research* 27, pp. 379-397.

Wood, B.D., Keller, C.K. & Johnstone, D.L. 1993. In situ measurement of microbial activity and controls on microbial CO_2 production in the unsaturated zone. *Water Resources Research* 29, pp. 647-659.

WRM (Wetlands Research and Management) 2008. Yarra Yarra Aquatic Monitoring: Assessing the Effect of Deep Drains on the Ecological Health of the Yarra Yarra Playas and Wetlands. Unpublished report by Wetland Research & Management, University of Western Australia, for the Yarra Yarra Catchment Management Group. December 2008.

Yeats, C.J. & Vanderhor, F. 1998. Archaean lode-gold deposits. *AGSO Journal of Australian Geology & Geophysics* 17, pp. 253-258.

Zhu, C., Hu, F.Q. & Burden, D.S. 2001. Multi-component reactive transport modelling of natural attenuation of an acid groundwater plume at a uranium mill tailings site. *Journal of Contaminant Hydrology* 52, pp. 85-108.

APPENDIX 2.1 SAMPLING SITES – YARRA YARRA AND NINGHAN BASINS.

Yarra Yarra basin sites. Note: sample data available on request from the Department of Water (WA).

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Bore Depth (mbgl.)	Flow at sampling (L/s)
D1	WADGC 01-A	D	Jibberding	484212	6673020	N/A[3]	0.05
D93	WB037	D	Morowa drain, Holder Rd	406083	6795698	N/A	
D94	WB038	D	Morowa drain evaporation basin inflow	404260	6794560	N/A	
BAT1D1	BAT1D1	D	Goodlands Rd, East Lake DeCourcy	514164	6654137	N/A	6.5
BG4D	BG4D1	D	Bowgada drain at Malcolm Rd crossing	412000	6758793	N/A	
CG45D	CG45D1	D	Canna Gutha drain flume, Gutha East Rd	401096	6792661	N/A	
GO20D1	GO20D1-2	D	Youangarra Drain, Glamoff Rd crossing	512219	6668927	N/A	0.1
GO20D1	GO20D1	D	Youangarra Drain, Glamoff Rd crossing	512219	6668927	N/A	
K41D	MK41D1	D	Meerkanooka drain flume (Morawa-Three Springs Rd)	399950	6766020	N/A	
MU 55 D1	MU 55 D1	D	Mongers 55 Drain, approx. 50 m upstream flume	477569	6691884	N/A	
MU 55 D4	MU55D9	D	Mongers 55 Drain, flume	477728	6692175	N/A	
MU 55 D4	MU55 D10	D	Mongers 55 Drain, flume	477728	6692175	N/A	
MU 55 D4	MU55 D11	D	Mongers 55 Drain, flume	477728	6692175	N/A	
MU 55 D4	MU55D8	D	Mongers 55 Drain, flume	477728	6692175	N/A	
MU 55 D4	MU55D.2	D	Mongers 55 Drain, flume	477728	6692175	N/A	1.1
MU 55 D4	MU55	D	Mongers 55 Drain, flume	477728	6692175	N/A	2
MU 55 D4	MU 55 D4	D	Mongers 55 Drain, flume	477728	6692175	N/A	
MU55D2	MU55D2	D	Mongers 55 Drain, Wasley Rd Crossing	476228	6689901	N/A	0.3
MU55D2	MU55D2.2	D	Mongers 55 Drain, Wasley Rd Crossing	476228	6689901	N/A	0.2
MU55D3	MU55D5	D	Mongers 55 Drain, conveyance channel	479684	6695766	N/A	

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Bore Depth (mbgl.)	Flow at sampling (L/s)
MU55D4	MU55D6	D	Mongers 55 Drain, flume	477728	6692175	N/A	
NIX1D1	NIX1D1	D	Nixons drain, Kalannie-Kulja Rd	518893	6639864	N/A	6.5
PJ13D1	PJD1	D	Perenjori Drain, Solomon Rd flume	437213	6744429	N/A	
YYD20A	YYD202304	D	Jibberding drain, Woolf Rd Xing, Jibberding	476681	6676790	N/A	3.6
YYD20B	YYD20B2304	D	Jibberding drain, Walsey Rd Xing, Jibberding	479214	6681158	N/A	14.5
YYD20C	YYD20C2304	D	Jibberding drain, Rabbitproof Fence Rd, Jibberding	481816	6682407	N/A	
YYD3	YYD3.1	D	Sanderson Rd	504872	6679669	N/A	0.5
YYD4	YYD4.1	D	Great Northern Highway, Jibberding Drain Outlet	481584	6679482	N/A	0.2
YYD5	YYD5.1	D	Richards Rd	471982	6679451	N/A	1.6
YYD6	YYD6.1	D	Perenjori Drain, Norrish Rd	432539	6751058	N/A	0.2
YYD7	YYD7.1	D	Morowa-Three Springs Rd	399899	6765844	N/A	0.6
YYD8	YYD8.1	D	Morowa-Three Springs Rd, Merkanooka Drain	395389	6759081	N/A	2.5
BU10	BU10	GW-B	Bunketch	515301	6629568	2.36	N/A
BU17	BU17	GW-B	Bunketch	516960	6633091	2.9	N/A
BU19	BU19	GW-B	Bunketch	515838	6632486	3.77	N/A
BU34	BU34	GW-B	Larry Mincherton Bunketch	514418	6627380	4.15	N/A
BU39	BU39	GW-B	Burakin	512785	6623514	4.13	N/A
BU5A	BU5A	GW-B	West Kirwan	513872	6616595	3.44	N/A
CA12 (D)	CA12 (D)	GW-B	North Carnamah	392501	6721748	24.6	N/A
CA12- OB	CA12- OB	GW-B	North Carnamah	392501	6721748	5.3	N/A
CA6 (D)	CA6 (D)	GW-B	North Carnamah	398326	6725722	11.35	N/A
CA6-OB	CA6-OB	GW-B	North Carnamah	398326	6725722	5.27	N/A
DC102	DC102	GW-B	North Carnamah	399819	6722773	2.96	N/A
DC11	DC11	GW-B	North East Carnamah	417812	6734798	2.17	N/A
DC57	DC57	GW-B	North East Carnamah	416170	6728459	3.1	N/A

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Bore Depth (mbgl.)	Flow at sampling (L/s)
DC77	DC77	GW-B	East Carnamah	414508	6724228	3.67	N/A
DC86	DC86	GW-B	North East Carnamah	414537	6744801	2.43	N/A
DC92/ DC91	DC92/ DC91	GW-B	North Carnamah	391514	6724256	4.49	N/A
MU130	MU130	GW-B	Lussick, East Latham	467262	6710505	4.01	N/A
MU215	MU215	GW-B	Macpherson	476363	6689817	4.4	N/A
MU215	MU 215	GW-B	Macpherson	476362	6689817		N/A
MU222	MU222	GW-B	Shaw, East Buntine	474639	6688682	4.85	N/A
MU222	MU 222	GW-B	Shaw, East Buntine	474639	6688682		N/A
MU232	MU232	GW-B	Macpherson	477795	6692123	4.63	N/A
MU232	MU 232	GW-B	Macpherson	477795	6692123		N/A
MU237	MU237	GW-B	Shaw, East Buntine	475655	6689419	4.33	N/A
MU237	MU 237	GW-B	Macpherson	475655	6689419		N/A
MU241	MU 241	GW-B	Macpherson	478726	6693695		N/A
MU26	MU26	GW-B	East Latham	469763	6711691	5.14	N/A
MU34	MU34	GW-B	Paul Parnham, East Maya	468121	6707373	5.14	N/A
MU40	MU40	GW-B	Macpherson	476766	6690280	3.79	N/A
MU40	MU 40	GW-B	Macpherson	476903	6690431	4	N/A
MU41	MU 41	GW-B	Macpherson	477282	6691013	4	N/A
MU41	MU41	GW-B	Macpherson	477282	6691013	5.14	N/A
MU44	MU 44	GW-B	Macpherson	477397	6691567	4	N/A
MU44	MU44	GW-B	Macpherson	477397	6691567	5.12	N/A
MU46	MU46	GW-B	Macpherson	477298	6692362	5.18	N/A
MU47	MU47	GW-B	Macpherson	478160	6693144	5.04	N/A
MU47	MU 47	GW-B	Macpherson	478160	6693144	4	N/A
MU5	MU5	GW-B	Mongers Lake	475381	6709340	4.99	N/A
MU55	MU55	GW-B	Shaw, East Buntine	474963	6688973	4.87	N/A
MU55	MU 55	GW-B	Macpherson	474963	6688973	4	N/A
MU76	MU76	GW-B	Jibberding	472850	6673882	4.1	N/A

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Bore Depth (mbgl.)	Flow at sampling (L/s)
MU83	MU83	GW-B	Jibberding	473910	6676713	3.85	N/A
MU85	MU85	GW-B	Moroni, Jibberding	477245	6677792	4.64	N/A
MU87	MU87	GW-B	Moroni, Jibberding	476526	6676545	5.06	N/A
PJ13 DENE	PJDENE	GW-B	Windmill, ~20 m	440547	6749816	20	N/A
PJ201	PJ201	GW-B	East Perenjori	434871	6745004	4.51	N/A
PJ31	PJ31	GW-B	North Perenjori	430960	6747517	5.14	N/A
PJ40	PJ40	GW-B	East Perenjori	437694	6744308	5.25	N/A
PJ41	PJ41	GW-B	East Perenjori	438101	6744545	6.96	N/A
PJ43	PJ43	GW-B	East Perenjori	439009	6744702	5.26	N/A
PJ44	PJ44	GW-B	East Perenjori	439395	6745032	5.28	N/A
PJ49	PJ49	GW-B	East Perenjori	437623	6744881	3.3	N/A
SG089i04	SG089	GW-B	Carter	484566	6673061	5.2	N/A
BG3P1	WB120	GW-P	Bowgada	426615	6755175	N/A	N/A
BG3P4	WB121	GW-P	Bowgada	423623	6756466	N/A	N/A
BG3P7	WB122	GW-P	Bowgada	421257	6761836	N/A	N/A
BU27P1	WB117	GW-P	Burakin	514619	6627686	N/A	N/A
BU27P12	WB118	GW-P	Burakin	512696	6623384	N/A	N/A
BU27P6	WB119	GW-P	Burakin	514832	6631235	N/A	N/A
CG45P1	WB123	GW-P	Canna-Gutha	401068	6792462	N/A	N/A
CG45P5	WB124	GW-P	Canna-Gutha	398076	6793953	N/A	N/A
CG45P6	WB125	GW-P	Canna-Gutha	395920	6796756	N/A	N/A
GO33P1	WB114	GW-P	Goodlands	509135	6663616	N/A	N/A
GO33P3	WB115	GW-P	Goodlands	509274	6662061	N/A	N/A
GO33P5	WB116	GW-P	Goodlands	510985	6661115	N/A	N/A
JB19P2	WB111	GW-P	Jibberding	480683	6681057	N/A	N/A
JB19P3	WB112	GW-P	Jibberding	479994	6681108	N/A	N/A
JB19P5	WB113	GW-P	Jibberding	477856	6679706	N/A	N/A
MU17P2	WB105	GW-P	Mongers Lake West	472905	6701160	N/A	N/A

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Bore Depth (mbgl.)	Flow at sampling (L/s)
MU17P4	WB106	GW-P	Mongers Lake West	471353	6700103	N/A	N/A
MU17P5	WB107	GW-P	Mongers Lake West	470861	6699506	N/A	N/A
MU29P11	WB102	GW-P	Mongers Lake West	464300	6724350	N/A	N/A
MU29P12	WB103	GW-P	Mongers Lake West	464947	6724424	N/A	N/A
MU29P18	WB104	GW-P	Mongers Lake West	462389	6725382	N/A	N/A
MU55P1	WB108	GW-P	Mongers Lake West	475907	6691770	N/A	N/A
MU55P3	WB109	GW-P	Mongers Lake West	477461	6692016	N/A	N/A
MU55P4	WB110	GW-P	Mongers Lake West	476856	6690906	N/A	N/A
PJ13 P4	WB099	GW-P	Perenjori	438612	6741472	N/A	N/A
PJ13P6	WB100	GW-P	Perenjori	440048	6738000	N/A	N/A
PJ13P8	WB101	GW-P	Perenjori	439182	6735657	N/A	N/A
YYD8Ref	YYD8Ref.1	Ref.L	Morowa-Three Springs Rd, Merkanooka Ref Playa	395300	6758850	N/A	N/A
RMOF	RMOF2705	Ref.L	East Boundary Rd, Mollerin	557988	6619947	N/A	N/A
MU55 L2	MU55 L2	Ref.L	MacPherson Lake, MU55	478259	6691495	N/A	N/A
YYL01	YYL01	Ref.L	Lake DeCourcy -- northern end	507758	6656802	N/A	N/A
YYL02	YYL02	Ref.L	Lake Hilman, W side of gypsum island	515710	6647329	N/A	N/A
MU55 L1	MU55 L1	Ref.L	Boat Lake, MU55	478006	6693158	N/A	N/A
RMGB	RMGB2204	Ref.L	Mongers Lake North, Wannara Rd, Perenjori	471661	6731868	N/A	N/A
RMGA	RMGA2204	Ref.L	Mongers Lake North, Wannara Station track	471755	6733304	N/A	N/A
YYL04	YYL04	Ref.L	Lake DeCourcy -- southern end	510303	6647967	N/A	N/A
RMOE	RMOE2805	Ref.L	Mollerin Lake South, Off Kulja-Mollerin Rock Rd	555951	6623914	N/A	N/A
YYL03	YYL03	Ref.L	Lake Goorly near Glamoff Rd crossing	503740	6665331	N/A	N/A
MU55 L3	MU55 L3	Ref.L	Small playa, Mongers 55	477290	6692240	N/A	N/A
MU 55 D2	MU55D7	Rec.L	15 ha Lake, Mongers 55	478747	6694014	N/A	N/A
MU 55 D2	MU 55 D2	Rec.L	15 ha Lake, Mongers 55	478747	6694014	N/A	N/A
MU 55 D3	MU 55 D3	Rec.L	15 ha Lake, Mongers 55	479684	6695766	N/A	N/A

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Bore Depth (mbgl.)	Flow at sampling (L/s)
MU55LAKE	MU55RE.2	Rec.L	15 ha Lake, Mongers 55	478419	6693879	N/A	N/A
MU55LAKE	MU55LAKE	Rec.L	15 ha Lake, Mongers 55	478419	6693879	N/A	N/A
R10YY	R10 YY	Rec.L	Nixon Evaporation Basin	521570	6637276	N/A	N/A
R8NMA	R8NMA.1	Rec.L	Jibberding Hall Rd (east side of Green Lake)	483932	6674124	N/A	N/A
R8NMA	R8NMA-2	Rec.L	Jibberding Hall Rd (east side of Green Lake)	483932	6674124	N/A	N/A
R9YY	R9 YY	Rec.L	Nixon Evaporation Basin	517945	6637590	N/A	N/A
YYD8RE	YYD8RE.1	Rec.L	Morowa-Three Springs Rd, Merkanooka Rec Playa	395300	6758160	N/A	N/A
YYL07	YYL07	Rec.L	Perenjori Drain receiving lake	441076	6746723	N/A	N/A
JB19	JB19 C1	SW	Mouth of Jibberding Creek	481221	6688815	N/A	N/A
MU16	MU16 C1	SW	Mouth of MU16 Creek, off Simpson Rd	472310	6719510	N/A	N/A
RMGC	RMGC2204	SW	Mongers Lake floodway, Warreidar Copper Mine Rd	469468	6751916	N/A	N/A

[1] Site type: D – drain, GW-B – groundwater sampled from monitoring bore, GW-P – groundwater sampled from shallow pit, Ref.L – reference lake, Rec.L – lake receiving drain waters, SW – surface water in floodway.

[2] Easting and northing values are for the GDA94 co-ordinate system and are in MGA94 units for zone 50.

[3] N/A : Not applicable

Ninghan basin sites. Note: sample data available on request from the Department of Water (WA).

Site Code	Sample ID	Site Type[1]	Location	Easting[2]	Northing[2]	Flow at sampling (L/s)
YYD2	YYD2-1	D	Glamoff Rd (Eastern End)	541771	6669040	0.7
YYD1	YYD1-1	D	North off Scotsman Rd, NE Mollerin	555991	6645945	0.3
YYL05	YYL05	Ref.L	Lake Harvey	555010	6644574	N/A
RMOH	RMOH2808	Ref.L	Longmuir Rd, Mollerin East	563940	6620853	N/A
RMOB	RMOB1903	Ref.L	Gooder Rd, Mollerin East	565932	6620861	N/A
RLH	RLH270906	Ref.L	Samphire Rd, Lake Harvey	552550	6647826	N/A
RMLP	RMLP1201	Ref.L	Kurrangin Lake (margin), Black Rd, Mollerin North	539570	6649037	N/A
YYL06	YYL06	Ref.L	Lake Moore, SE corner	547662	6644216	N/A
RMOE	RMOE1104	Ref.L	Mollerin Lake South, Off Kulja-Mollerin Rock Rd	555951	6623914	N/A
RMOG	RMOG1706	Ref.L	Mollerin Lake South, Off Kulja-Mollerin Rock Rd	557475	6620600	N/A
RLMA	RLMA1509	Ref.L	Samphire Lake, Mollerin North Road	548633	6631046	N/A
RMOD	RMOD1104	Rec.L	Longmuir Rd, Mollerin East	558505	6620428	N/A
RMOC	RMOC12805	Rec.L	Longmuir Rd, Mollerin East	558495	6620938	N/A
RMOC	RMOC1104	Rec.L	Longmuir Rd, Mollerin East	558495	6620938	N/A
YYRE1	YYRE1-1	Rec.L	North off Scotsman Rd, NE Mollerin	555850	6645945	N/A
RMOA	RMOA1903	SW	Longmuir Rd, floodway, Mollerin East	558240	6620755	850

[1] Site type: D – drain, GW-B – groundwater sampled from monitoring bore, GW-P – groundwater sampled from shallow pit (during pit filling), Ref.L – reference lake, Rec.L –lake receiving drain waters, SW – surface water in floodway.

[2] Easting and northing values are for the GDA94 co-ordinate system and are in MGA94 units for zone 50.

APPENDIX 3.1 SAMPLING SITES AND WATER CHEMISTRY – UPPER BLACKWOOD BASIN

Sample ID	Site Type	Location/Bore	Easting (m)	Northing (m)	Elevation (mAHD)	Sample date	Sample depth (mbgl)	Flow rate (L/s)	Groundwater level (mbgl)
SW1	Lake	Lake Parkeyerring	532610	6308476		16/05/2007	0		
SW2	Lake	Lake Queerearrup	520907	6291727		17/05/2007	0		
SW3	Lake	Lake Norring	526633	6299023		16/05/2007	0		
SW4	Drain	Douglas Rd, Woodanilling	525210	6288314		17/05/2007	0	0.1	
SW5	Drain	Robson Rd, Datatine	583037	6300772		18/05/2007	0	0.1	
SW6	River	Doradine Gully	571416	6324551		18/05/2007	0	1	
SW7	River	Blackwood R., Nannup	385639	6239955		22/05/2007	0	300	
SW8	River	Blackwood R., Bridgetown	414778	6239561		22/05/2007	0	50	
SW9	River	Blackwood R., Boyup Brook	444393	6255351		22/05/2007	0		
SW10	River	Blackwood R., Asplin Bridge, Condinup	452622	6259082		22/05/2007	0		
SW11	River	Blackwood R., Condinup Crossing Rd	455202	6262960		23/05/2007	0		
SW12	River	Blackwood R., Condinup Crossing Rd	455514	6263037		23/05/2007	0		
SW13	River	Blackwood R., Eulin Crossing Rd	470726	6271107		23/05/2007	0	100	
SW14	Lake	Lake Towerinning	480674	6283931		23/05/2007	0		
SW15	River	Arthur R., Moodiarrup Bridge	482680	6282344		24/05/2007	0		
SW16	Drain	Darkan	464680	6310850		25/05/2007	0	9	
SW17	Lake	Lake Qualeup	477653	6255350		25/05/2007	0		
SW18	Drain	Uannup	517013	6228720		25/05/2007	0	3	
SW19	Drain	Uannup	515782	6228925		25/05/2007	0	0.02	
SW20	Drain	Nyabing	588841	6286754		23/01/2008	0	0.24	
SW21	Drain	Gnowangerup	600610	6248715		23/01/2008	0	0.004	
SW22	Drain	Broomehill	560917	6247925		23/01/2008	0	1.56	
SW23	Drain	Treloars Rd, Nth Moulyinning	587227	6332244	278	24/01/2008	0	0.81	0

Sample ID	Site Type	Location/Bore	Easting (m)	Northing (m)	Elevation (mAHD)	Sample date	Sample depth (mbgl)	Flow rate (L/s)	Groundwater level (mbgl)
SW24	Drain	Lake Grace-Dumbleyung. Rd, Nth Moulyinning	585168	6327439	274	24/01/2008	0	3.56	0
SW25	Groundwater	Bore 07FR04	584364	6337420	285	14/02/2008	10.3		-0.785
SW26	Groundwater	Bore 07FR02I	591222	6337123	291.5	15/02/2008	10.8		-3.755
SW27	Groundwater	Bore 07FR02D	591221	6337121	291.5	15/02/2008	39.8		-3.72
SW28	Groundwater	Bore 07FR03I	585747	6332168	278	18/02/2008	22.4		-1.24
SW29	Groundwater	Bore 07FR03D	585747	6332169	278	18/02/2008	42.8		-1
SW30	Groundwater	Bore 07FR03S	585748	6332166	278	19/02/2008	10.8		-1.26
SW31	Groundwater	Bore 07FR01	593394	6339027	299	20/02/2008	22.9		-12.32
SW32	Groundwater	Bore priv.	596367	6341260	307	22/02/2008	28.2		-23.16
SW33	Groundwater	Bore 20061594	599617	6344240	324	21/02/2008	36.8		-31.24
SW34	Groundwater	Bore 85FR53D	585617	6334453	280.5	26/02/2008	21.7		-0.9
SW35	Groundwater	Bore 85FR53I	585617	6334453	280.5	26/02/2008	12.8		-0.95
SW36	Groundwater	Bore 85FR53S	585617	6334453	280.5	26/02/2008	6.3		-1.18
SW37	Groundwater	Bore 85FR90I	588176	6335462	286	27/02/2008	9.2		-1.455
SW38	Groundwater	Bore 98FR107I	584286	6340416	297	28/02/2008	21.0		-5.44
SW39	Groundwater	Bore 98FR106D	585906	6343439	294	29/02/2008	39.8		-3.615
SW40	Groundwater	Bore 98FR105I	588980	6340131	298	5/03/2008	19.0		-12.775
SW41	Groundwater	Bore 98FR104I	585386	6338418	287	5/03/2008	28.2		-1.565
SW42	Groundwater	Bore 98FR109D	591111	6350974	316	6/03/2008	36.0		-26.3
SW43	Groundwater	Bore 98FR108I	585875	6349901	309.5	6/03/2008	21.9		-15.7
SW44	Groundwater	Bore 98FR113D	588181	6345628	299	10/03/2008	10.0		-6.25
SW45	Groundwater	Bore 98FR111D	577627	6346074	330	11/03/2008	38.5		-29.31
SW46	Groundwater	Bore 98FR110D	581571	6348931	307.5	11/03/2008	17.8		-14.87
SW47	Groundwater	Bore 98FR112S	584070	6345042	296	12/03/2008	6.5		-3.54
SW48	Groundwater	Bore 08UC12	613244	6257545		13/03/2008	8.5		-1.07
SW49	Groundwater	Bore DC34I	471335	6288921		14/03/2008	7.7		-1.02
SW50	Groundwater	Bore 07DP08S	552638	6282409		17/03/2008	4.5		0.775
SW51	Groundwater	Bore 07DP08I	552635	6282412		17/03/2008	12.6		0.7
SW52	Groundwater	Bore SS9719	552242	6361795		20/03/2008	10.7		-1.7
SW53	Groundwater	Bore RS02D	465319	6327353		25/03/2008	8.0		>>+1 m (artesian)
SW54	Groundwater	Bore DW16I	460684	6260176		25/03/2008	10.8		-7.43

Sample ID	Site Type	Location/Bore	Easting (m)	Northing (m)	Elevation (mAHD)	Sample date	Sample depth (mbgl)	Flow rate (L/s)	Groundwater level (mbgl)
SW55	Groundwater	Bore TL7	561611	6360123		26/03/2008	30.4		-1.295
SW56	Groundwater	Bore LT29	558923	6365173		26/03/2008	12.5		-2.355
SW57	Groundwater	Bore 07SK03D	610782	6311510		27/03/2008	22.4		-16.56
SW58	Drain	Fence Rd, Nth Moulyinning	583505	6336469	283	3/04/2008	0	1.66	0
SW59	Groundwater	Bore 98FR112I	584072	6345042	296	29/04/2008	18.5		-3.5
C1	Lake	Gnowangerup Rd	593512	6267603		5/10/2005	0		
C2	Lake	Wagel Rd, Kwobrup Swamp	588147	6271891		5/10/2005	0		
C3	Lake	Lk Coyrecup outflow	576142	6269089		5/10/2005	0		
C4	Lake	Lk Ewlymartup	568151	6271281		5/10/2005	0		
C5	Lake	Nth of Coblinine R., Bibkin Bridge	567858	6304716		5/10/2005	0		
C6	Lake	Lk Dumbleyung	562182	6313966		5/10/2005	0		
C7	Lake	Lk Coomelburrup	573165	6303458		5/10/2005	0		
C8	Lake	Lk Dongolocking	574071	6308646		23/11/2005	0		
C9	Drain	Beynon Rd, Dumbleyung	575973	6322970		23/11/2005	0		
S1	Lake	Lk Muir	471707	6183451		18/01/2007	1		
S2	Lake	Lk Unicup	475491	6198547		15/01/2007	0.3		

Sample name	EC (dS/m)	pH	Temp (°C)	Eh (mV SHE)	DO (mg/L)	Field Alk (meq/L)	Lab EC (dS/m)	Lab pH	Lab Alk (meq/L)	Lab Acy (meq/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Al (mg/L)	Si (mg/L)
SW1	227	7.77	15.3				150.0	7.54	5.8		104300	560	10700	770	<10	<10
SW2	215	7.44	13.3				150.2	7.30	6.1		86600	1100	16220	470	<10	<10
SW3	216	7.58	15.8				155.8	7.48	4.9		73900	560	8260	790	<10	<10
SW4	31.0	9.11	20.2				25.07	8.91	4.4		6000	44	600	140	<1	<1
SW5	82.9	4.32	13.0				69.29	4.20		7.2	18400	132	2150	300	56	25
SW6	39.0	8.41	16.4				31.54	7.96	3.8		7130	64	880	670	<1	8
SW7	7.89	7.96	13.2				6.642	7.86	3.2		1200	9	240	84	<1	<1
SW8	9.22	8.29	14.3				8.340	7.72	3.1		1400	10	300	104	<1	2
SW9	16.30	8.52	13.9				14.29	8.06	4.6		2500	14	510	178	<1	5
SW10	25.6	8.46	14.6				21.04	7.95	5.2		3800	18	960	310	<1	5
SW11	19.51	8.79	13.3				16.63	8.31	4.8		3000	16	620	210	<1	3
SW12	25.10	8.81	12.5				20.93	8.29	4.8		4000	20	840	230	<1	4
SW13	19.34	8.44	13.9				16.76	7.97	4.4		2900	16	640	220	<1	3
SW14	18.25	8.67	15.7				16.03	8.24	3.9		2700	16	630	240	<1	10
SW15	19.23	8.52	14.4				17.00	8.12	3.9		3000	20	610	220	<1	<1
SW16	17.35	8.27	16.7				15.59	7.53	2.0		2400	13	680	320	<1	15
SW17	5.93	7.26	13.3				5.201	7.63	4.3		840	26	150	125	<1	5
SW18	21.6	7.91	16.6				18.83	7.68	3.5		3000	17	910	260	<1	23
SW19	29.9	6.14	17.9				26.63	7.00	2.6		4900	25	1060	310	<1	21
SW20	11.54	7.13	19.4				10.97	7.92	4.7		1800	28	297	122	<0.01	33.5
SW21	84	6.45	30.1				65.23	7.28	3.0		16000	74	1959	353	<0.05	11.6
SW22	43.1	8.44	34.8				34.28	8.46	5.5		8250	42	776	160	<0.05	7.8
SW23	72.2	2.67	19.8	636			55.79	2.78		32.4	12500	98	1870	185	133	55.8
SW24	79.7	2.5	34.3	636			63.36	2.52		38.3	15750	108	2312	230	142	60.6
SW25	57.1	4.34	30.7	378	0.6		47.31	5.72	0.1	0.9	9750	110	1287	165	0.55	44.4
SW26	39.7	4.37	26.8	463	0.8		33.52	4.83	0.0	2.0	7000	60	748	52	9.2	40.6
SW27	42.6	5.32	38.6	411	1.0	1.25	36.50	7.18	1.0	0.3	8000	92	994	239	<0.05	34.5
SW28	82.0	4.41	25.2	436	0.6		65.68	4.70		4.3	14250	120	2457	472	1.0	27.7
SW29	98.8	6.37	25.4	161	0.7	2.77	89.10	6.76	1.1	0.7	16500	158	2930	729	<0.1	13.0
SW30	71.4	4.27	23.2	464	1.4		59.12	4.30		3.7	12000	104	1806	301	0.55	32.7
SW31	47.8	4.67	22.7	510	2.1		40.15	6.32	0.2	0.3	8500	82	886	138	0.45	39.8
SW32	17.97	6.32	21.3	340	3.4	9.24	16.33	7.73	7.9		3050	34	221	62	0.07	30.1
SW33	11.43	6.48	28.4	-78	0.2	9.99	10.46	7.52	8.6		1750	26	247	70	<0.01	33.0

Sample name	EC (dS/m)	pH	Temp (°C)	Eh (mV SHE)	DO (mg/L)	Field Alk (meq/L)	Lab EC (dS/m)	Lab pH	Lab Alk (meq/L)	Lab Acy (meq/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Al (mg/L)	Si (mg/L)
SW34	59.6	4.81	29.9	353	0.4	0.60	50.24	5.36	0.0	1.0	10500	108	1468	279	0.65	37.5
SW35	58.5	3.83	29.2	353	0.2		49.49	4.11		3.7	10250	104	1423	180	12	39.8
SW36	53.8	3.77	33.3	405	0.3		46.43	4.10		8.7	9500	86	1204	102	46	36.7
SW37	36.0	4.44	29.7	345	0.5		31.76	4.71		1.6	6500	76	718	53	4.2	44.6
SW38	43.3	6.02	32.8	266	0.5	5.95	36.41	7.00	5.0		7750	102	1106	325	<0.05	28.1
SW39	42.5	5.33	37.1	355	1.1	1.07	37.55	6.59	0.9	0.5	6750	80	830	222	<0.05	28.5
SW40	26.5	6.29	26.4	309	1.6	7.58	23.32	7.28	6.3		4530	50	534	158	<0.05	25.8
SW41	63.9	5.64	36.8	262	1.1	1.80	54.68	6.82	1.2	0.5	11000	102	1628	419	<0.05	21.4
SW42	17.03	6.37	28.3	19	0.9	6.50	16.73	7.31	5.3		3100	30	141	21	<0.01	29.5
SW43	22.6	6.01	29.5	359	1.6	5.38	21.37	7.02	4.4		4150	52	294	32	<0.05	33.0
SW44	33.1	4.42	29.7	145	0.8		29.47	5.06	0.1	1.2	6250	74	574	32	3.8	38.4
SW45	9.49	6.33	27.4	239	1.9	3.42	9.05	7.17	2.7		1150	22	338	109	<0.01	23.9
SW46	22.4	6.00	32.5	375	2.6	5.72	21.48	7.07	4.8		4240	28	318	45	<0.05	30.3
SW47	35.3	4.47	29.0	187	0.3		31.81	5.56	0.2	0.6	6250	42	635	39	1.0	51.0
SW48	53.9	3.93	20.5	567	0.9		46.05	4.12		6.4	9250	38	1425	38	40	40.0
SW49	7.19	4.95	28.2	378	1.7	0.48	6.61	5.13	0.0	2.0	1050	1.2	232	37	0.07	6.2
SW50	9.43	4.25	22.9	529	0.7		9.12	4.73		1.0	1650	1.2	142	3.0	3.6	46.1
SW51	7.63	6.03	21.2	355	2.8	1.54	6.29	6.80	1.3		700	12	371	164	<0.01	27.2
SW52	22.3	6.30	24.3	380	2.4	7.88	21.33	7.15	6.4		3690	30	281	34	<0.05	29.1
SW53	10.38	5.76	18.6	363	0.2	2.31	9.78	6.52	2.0		1350	2.0	322	181	<0.01	22.5
SW54	10.91	5.44	21.9	118	0.4	1.42	9.99	5.75	0.5	3.8	1550	0.8	343	15	0.03	5.0
SW55	90.7	3.82	22.6	452	0.3		71.64	4.03		2.5	15750	80	2994	754	9.6	30.5
SW56	39.9	3.85	25.4	548	0.5		34.03	4.19		2.4	7250	20	813	24	9.1	48.6
SW57	31.6	6.22	20.9	383	1.9	7.32	28.20	6.99	6.0		5500	50	498	51	<0.05	29.5
SW58	39.8	7.53	20.8	309		4.78	32.77	7.68	4.5		6750	62	765	127	0.15	12.6
SW59	39.0	6.08	20.2	291	0.4	5.16	33.28	6.75	4.3		6750	50	960	364	<0.05	24.7
C1	1010	8.31	19.5				12	8.2	3.6		2013	28	260	192	1.2	1.7
C2	890	8.64	17.8				11	8.3	2.3		1764	20	269	200	0.5	0.6
C3	710	7.88	17.5				9	7.5	2		1377	15	204	160	0.5	0.9
C4	3360	8.84	18.4				34	8.4	3.3		7788	46	1039	327	0.9	0.7
C5	2020	9.98	20.1				21	9.3	0.9		4115	30	612	421	0.9	0.9
C6	3320	8.35	18.9				34	8.1	2.3		8190	48	650	391	0.9	0.7
C7	3640	9.51	23.2				30	8.9	2		7650	51	948	453	<1	<2

Sample name	EC (dS/m)	pH	Temp (°C)	Eh (mV SHE)	DO (mg/L)	Field Alk (meq/L)	Lab EC (dS/m)	Lab pH	Lab Alk (meq/L)	Lab Acy (meq/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Al (mg/L)	Si (mg/L)
C8	10330	4.6	23.2				90	5.3		0.8	28200	295	1771	1394	5.2	<2
C9	8140	2.87	31.5				60	3.0		20.9	16630	254	1925	195	105	38
S1	93.9	7.45	20.1			7.10					19200	400	3260	1510	<0.5	6
S2	26.7	8.3	22.2			4.85					4930	95	856	452	<0.5	10

Sample name	Fe (mg/L)	Mn (mg/L)	B (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	PO_4^{3-} (mg/L)	Br (mg/L)	F (mg/L)	I (mg/L)	TN (mg/L)	P (mg/L)	S (mg/L)	TOC (mg/L)	NPOC (mg/L)
SW1	<10	<10	<10	186000	10950	0.1	0.8	0.036	305			17.0	<10	3770		245
SW2	<10	<10	11	184000	13500	<0.1	<0.1	0.025	523			21.9	<10	4730		392
SW3	<10	<10	<10	142000	11400	<0.1	0.3	0.014	324			17.3	<10	3470		289
SW4	<1	<1	1	10400	1140	<0.1	<0.1	0.006	29			0.5	<1	390		21
SW5	<5	13	<5	32600	3870	<0.1	0.6	0.012	93			0.8	<5	1330		12
SW6	<1	<1	1	13500	1370	<0.1	<0.1	0.007	37			0.6	<1	460		22
SW7	<1	<1	<1	2370	122	0.1	<0.1	0.008	6			0.0	<1	41		10
SW8	<1	<1	<1	2810	193	<0.1	<0.1	0.005	7			0.2	<1	67		9
SW9	<1	<1	<1	5270	277	<0.1	<0.1	0.005	14			0.6	<1	94		17
SW10	<1	<1	<1	8720	481	0.1	<0.1	0.009	21			1.3	<1	163		25
SW11	<1	<1	<1	6460	345	0.1	<0.1	0.005	17			1.3	<1	117		23
SW12	<1	<1	<1	8540	360	0.2	<0.1	0.004	24			2.0	<1	126		33
SW13	<1	<1	<1	6390	400	<0.1	<0.1	0.015	17			0.8	<1	140		20
SW14	<1	<1	<1	6090	349	0.1	0.2	0.015	16			1.6	<1	118		30
SW15	<1	<1	<1	6430	444	<0.1	<0.1	0.006	17			0.9	<1	151		21
SW16	<1	<1	<1	5870	371	0.6	0.3	0.005	14			0.3	<1	125		8
SW17	<1	<1	<1	1750	8	<0.1	<0.1	0.002	4			2.0	<1	2.3		45
SW18	<1	<1	<1	7440	528	<0.1	<0.1	0.008	21			0.0	<1	180		10
SW19	2	<1	<1	10400	918	<0.1	<0.1	0.008	30			0.0	<1	310		1
SW20	0.08	0.36	0.76	3380	352	0.43	0.44	<0.02	10			2.1	<0.2	112		20
SW21	22	8.2	6.6	29000	4040	0.01	1.26	<0.02	95			1.9	<0.8	1102		24
SW22	<0.1	<0.2	2.8	13500	1970	-0.01	0.14	<0.02	46			0.9	<0.8	565		16
SW23	195	1.0	1.9	25000	3520	0.12	2.91	<0.02	80			3.1	<0.8	946		17
SW24	282	1.4	2.7	28500	4260	0.11	3.12	0.03	92			3.4	<0.8	1219		19
SW25	9.4	1.8	1.2	19200	2960	0.03	1.02	0.02	55			1.2	0.8	794		7

Sample name	Fe (mg/L)	Mn (mg/L)	B (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	PO_4^{3-} (mg/L)	Br (mg/L)	F (mg/L)	I (mg/L)	TN (mg/L)	P (mg/L)	S (mg/L)	TOC (mg/L)	NPOC (mg/L)
SW26	9.3	7.0	2.4	12400	1460	0.04	1.18	<0.02	36			1.3	<0.8	418		18
SW27	<0.1	3.0	1.4	13300	2230	0.01	0.23	0.03	44			0.3	<0.8	682		7
SW28	67	12	0.7	28300	4500	0.05	0.97	<0.02	87			1.1	<0.8	1253		18
SW29	32	3.3	0.6	34700	5510	0.03	0.59	<0.02	123			0.8	<2	1344		9
SW30	55	3.6	0.8	24500	3660	0.08	0.85	<0.02	73			1.0	<0.8	952		9
SW31	<0.1	2.6	1.6	14600	2340	0.07	0.12	<0.02	49			0.2	<0.8	647		5
SW32	0.08	<0.03	0.92	4890	580	0.03	0.11	0.08	17			0.0	0.8	164		2
SW33	0.44	0.24	0.38	3140	280	0.01	19.41	1.0	11			22	1.6	81		12
SW34	18	2.4	1.3	20300	3020	0.05	0.58	0.03	59			0.7	<0.8	853		7
SW35	24	1.0	1.3	19800	2790	0.06	0.61	0.04	62			0.8	<0.8	762		8
SW36	25	0.6	1.5	18500	2520	0.16	1.77	0.02	55			2.1	<0.8	692		10
SW37	11	1.2	2.2	11500	1330	0.13	0.99	<0.02	33			1.4	<0.8	382		8
SW38	0.3	<0.2	1.0	13600	2020	0.05	0.18	<0.02	46			0.2	<0.8	589		3
SW39	0.9	6.4	1.2	13500	2200	0.04	0.42	<0.02	45			0.5	<0.8	523		4
SW40	<0.1	0.2	1.4	8210	1010	0.11	0.24	0.05	27			0.4	<0.8	282		2
SW41	3.0	2.6	0.6	22100	3510	0.04	1.05	<0.02	67			1.3	<0.8	957		4
SW42	0.54	0.18	1.0	4670	609	0.04	0.22	0.08	17			0.2	<0.2	177		2
SW43	<0.1	<0.2	1.0	6390	857	0.06	0.13	0.13	23			0.2	<0.8	243		2
SW44	2.7	0.8	1.4	10300	1590	0.08	1.33	0.02	31			1.7	<0.8	482		9
SW45	0.58	0.48	0.12	2630	157	0.04	0.20	<0.02	9			0.2	<0.2	46		3
SW46	<0.1	<0.2	0.6	6920	814	0.17	0.14	0.16	21			0.3	<0.8	238		2
SW47	2.6	<0.2	0.8	11100	1630	0.04	0.72	0.06	35			0.9	<0.8	441		8
SW48	0.9	0.8	4.8	16700	2970	0.02	1.05	<0.02	55			0.8	<0.8	821		16
SW49	45	0.30	0.04	2140	146	0.09	1.30	<0.02	7			1.4	<0.2	46		5
SW50	0.18	0.18	<0.02	2550	233	0.32	0.18	<0.02	8			0.5	<0.2	75		7
SW51	<0.02	<0.03	<0.02	2170	90	2.35	0.14	<0.02	7			3.4	<0.2	27		2
SW52	<0.1	<0.2	0.4	6350	714	0.15	0.12	0.09	22			0.2	<0.8	179		3
SW53	<0.02	0.63	0.04	3060	188	0.03	0.13	<0.02	8			0.0	<0.2	59		5
SW54	107	0.03	<0.02	3190	253	0.11	0.26	<0.02	10			0.4	<0.2	81		9
SW55	74	7.2	0.6	37100	8051	0.06	1.60	0.03	86			1.6	3.2	1950		8
SW56	2.1	0.6	1.9	12500	1320	0.02	0.82	0.03	38			0.8	<0.8	390		5
SW57	<0.1	0.4	1.0	9680	978	0.04	0.14	0.06	27			0.0	<0.8	270		3
SW58	0.3	0.6	0.9	12300	1580	2.38	0.47	<0.02	40			3.3	<0.8	420		12
SW59	2.3	0.4	0.4	12000	1870	0.02	0.52	0.03	39			1.0	<0.8	548		9

Sample name	Fe (mg/L)	Mn (mg/L)	B (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	PO_4^{3-} (mg/L)	Br (mg/L)	F (mg/L)	I (mg/L)	TN (mg/L)	P (mg/L)	S (mg/L)	TOC (mg/L)	NPOC (mg/L)
C1	0.3	<0.01	0.6	3990		0.01	0.33	0.029	8	<0.5				116	70	
C2	<0.05	<0.01	0.5	3640		0.03	0.47	0.017	8	<0.5				158	55	
C3	0.1	<0.01	0.4	2780		0.23	0.11	0.025	6	<0.5				135	55	
C4	<0.05	<0.01	1.3	14600		0.2	0.86	0.071	34	<0.5				514	114	
C5	<0.05	<0.01	0.8	8150		0.01	0.08	0.017	18	<0.5				472	31	
C6	<0.05	<0.01	1.1	14300		0.32	0.04	0.018	17	<0.5				512	52	
C7	<1	0.1	2.4	13550		0.02	0.19	<0.002	38	<1				683	41	
C8	<1	4.9	3.3	48940		0.05	4.6	0.01	62	<1				1470	11	
C9	86	1.4	3.8	29140		0.49	3.5	0.03	91	2				1230	20	
S1	0.1	1.1	1.2	38960	6185				36				<2	2180		
S2	0.1	<0.1	0.6	10110	507	5.35			13	0.5	5.4		<2	190		

Sample name	Li (mg/L)	Be (µg/L)	V (µg/L)	Cr (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Se (µg/L)	Rb (µg/L)	Sr (mg/L)	Y (µg/L)	Mo (µg/L)	Ru (µg/L)	Pd (µg/L)	Ag (µg/L)	Cd (µg/L)
SW1		<0.4	1.3	<2	2.2	4	<0.8	4	5	<1		24	<0.4	<2	<0.4	2	<0.4	<0.8
SW2		<0.4	<0.8	<2	<0.4	<2	<0.8	<4	3	<1		50	<0.4	<2	<0.4	<1	<0.4	<0.8
SW3		<0.4	<0.8	<2	<0.4	<2	<0.8	4	4	<1		40	<0.4	<2	<0.4	1	<0.4	<0.8
SW4		<0.4	5.8	<1	1.1	<0.4	0.9	2	<0.7	<0.4		2	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW5		11	<0.4	8	513	316	13	73	9	<0.6		5	167	<1	<0.4	<0.6	<0.4	<0.4
SW6		<0.4	3.6	<1	0.5	<0.4	4.5	4	<0.7	<0.4		6	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW7		<0.4	<0.4	<1	<0.4	<0.4	<0.4	10	<0.7	<0.4		<1	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW8		<0.4	<0.4	<1	<0.4	<0.4	<0.4	5	<0.7	<0.4		1	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW9		<0.4	0.5	<1	<0.4	<0.4	<0.4	5	<0.7	<0.4		2	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW10		<0.4	<0.4	<1	0.4	<0.4	0.7	10	<0.7	<0.4		3	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW11		<0.4	0.9	<1	<0.4	<0.4	0.6	6	<0.7	<0.4		2	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW12		<0.4	1.5	<1	<0.4	<0.4	<0.4	5	<0.7	<0.4		3	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW13		<0.4	0.6	<1	0.6	<0.4	<0.4	6	<0.7	<0.4		2	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW14		<0.4	3.8	<1	<0.4	<0.4	<0.4	4	<0.7	<0.4		3	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW15		<0.4	<0.4	<1	<0.4	<0.4	<0.4	3	<0.7	<0.4		3	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW16		<0.4	<0.4	<1	1.7	<0.4	<0.4	6	<0.7	<0.4		2	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW17		<0.4	<0.4	<1	<0.4	<0.4	<0.4	21	0.8	<0.4		1	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW18		<0.4	0.5	<1	1.6	1.9	<0.4	3	<0.7	<0.4		2	<0.4	<0.5	<0.4	<0.4	<0.4	<0.4
SW19		1.5	<0.4	<1	4.8	0.8	<0.4	4	<0.7	<0.4		4	13	<0.5	<0.4	<0.4	<0.4	<0.4

Sample name	Li (mg/L)	Be (µg/L)	V (µg/L)	Cr (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Se (µg/L)	Rb (µg/L)	Sr (mg/L)	Y (µg/L)	Mo (µg/L)	Ru (µg/L)	Pd (µg/L)	Ag (µg/L)	Cd (µg/L)
SW20		<0.1	<2	<0.3	1.6	0.8	<20	<8	<1	0.6		1.3	<0.1	<5	<0.1	<0.4		
SW21		<0.2	<5	<0.8	319	179	<50	<20	<3	<0.5		6.5	11	<10	<0.2	<1		
SW22		<0.2	<5	<0.8	1.5	<0.5	<50	<20	<3	<0.5		2.5	<0.1	<10	<0.2	<1		
SW23		5.0	<5	7.2	146	91	<50	<20	<3	<0.5		7.0	46	<10	<0.2	<1		
SW24		12	<5	10	298	171	<50	<20	<3	<0.5		7.3	113	<10	<0.2	<1		
SW25		4.6	<5	<0.8	83	69	<50	<20	<3	<0.5		5.8	11	<10	<0.2	<1		
SW26		4.8	<5	1.6	147	149	100	60	<3	<0.5		0.8	17	<10	<0.2	<1		
SW27		0.4	<5	<0.8	88	180	<50	120	<3	3.0		3.1	2.5	<10	<0.2	<1		
SW28		1.6	<5	<0.8	148	214	<50	60	<3	1.5		10.9	82	<10	<0.2	<1		
SW29		<0.4	<8	<1	1.0	20	<80	<30	<4	<0.8		17.0	1.2	<20	<0.3	<2		
SW30		1.2	<5	<0.8	55	107	<50	60	<3	<0.5		8.7	48	<10	<0.2	<1		
SW31		5.2	<5	<0.8	178	149	<50	80	<3	<0.5		2.3	37	<10	<0.2	<1		
SW32		<0.1	<2	<0.3	0.2	76	<20	36	<1	2.6		0.7	<0.1	<5	<0.1	<0.4		
SW33		<0.1	<2	2.7	0.3	12	<20	<8	<1	0.8		0.6	<0.1	<5	<0.1	<0.4		
SW34		1.4	<5	<0.8	58	101	<50	100	<3	<0.5		6.0	9.1	<10	<0.2	<1		
SW35		3.6	<5	0.8	93	180	<50	100	<3	<0.5		6.0	41	<10	<0.2	<1		
SW36		12	10	8.0	130	163	<50	140	<3	<0.5		4.3	50	<10	<0.2	<1		
SW37		7.2	<5	4.8	108	128	<50	260	<3	<0.5		1.2	25	<10	<0.2	<1		
SW38		<0.2	<5	<0.8	0.7	50	<50	<20	<3	10		6.2	<0.1	<10	<0.2	<1		
SW39		<0.2	<5	<0.8	80	74	<50	140	<3	<0.5		4.4	<0.1	<10	<0.2	<1		
SW40		<0.2	<5	<0.8	1.9	79	<50	220	<3	5.5		1.8	<0.1	<10	<0.2	<1		
SW41		<0.2	<5	<0.8	75	217	<50	180	<3	1.0		10.2	1.5	<10	<0.2	<1		
SW42		<0.1	<2	0.3	6.1	107	<20	<8	<1	<0.2		<0.5	<0.1	<5	<0.1	<0.4		
SW43		<0.2	<5	<0.8	0.6	141	<50	300	<3	2.5		1.1	<0.1	<10	<0.2	<1		
SW44		4.0	<5	6.4	71	102	<50	320	<3	<0.5		1.0	9.6	<10	<0.2	<1		
SW45		<0.1	<2	<0.3	6.5	32	<20	24	<1	<0.2		1.2	<0.1	<5	<0.1	<0.4		
SW46		<0.1	<2	<0.3	8.7	41	80	400	<1	2.0		1.5	<0.1	<5	<0.1	<0.4		
SW47		0.4	<5	<0.8	19	19	<50	80	<3	<0.5		3.1	1.7	<10	<0.2	<1		
SW48		11.8	<5	4.0	40	62	200	460	<3	<0.5		3.9	698	<10	<0.2	<1		
SW49		0.1	<2	<0.3	19	37	<20	552	<1	<0.2		0.9	7.7	<5	<0.1	<0.4		
SW50		2.9	<2	1.8	81	102	<20	120	<1	<0.2		<0.5	14	<5	<0.1	<0.4		
SW51		<0.1	<2	2.1	2.5	63	<20	24	<1	0.4		0.8	7.1	<5	<0.1	<0.4		
SW52		<0.2	<5	<0.8	0.3	130	<50	120	<3	16		0.6	<0.1	<10	<0.2	<1		
SW53		<0.1	<2	<0.3	17	16	<20	<8	<1	<0.2		0.8	2.1	<5	<0.1	<0.4		

Sample name	Li (mg/L)	Be (µg/L)	V (µg/L)	Cr (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Se (µg/L)	Rb (µg/L)	Sr (mg/L)	Y (µg/L)	Mo (µg/L)	Ru (µg/L)	Pd (µg/L)	Ag (µg/L)	Cd (µg/L)
SW54		<0.1	<2	<0.3	3.7	6.2	<20	72	<1	<0.2		<0.5	5.0	<5	<0.1	<0.4		
SW55		4.8	<5	7.2	161	171	<50	280	<3	<0.5		14.9	233	<10	0.8	<1		
SW56		2.2	<5	2.4	38	28	<50	240	<3	<0.5		1.4	15	<10	<0.2	<1		
SW57		0.2	<5	<0.8	24	47	<50	60	<3	15		1.2	1.5	<10	0.2	<1		
SW58		0.2	<5	<0.8	20	8	<50	<20	<3	1.5		5.0	1.3	<10	<0.2	<1		
SW59		<0.2	<5	<0.8	22	30	<50	20	<3	5.5		9.8	<0.1	<10	<0.2	<1		
C1			8.9	1.5	0.89	4.2	8.9	6.1	<0.35	17			<0.4	1.5	<0.5	2.9	<0.4	<0.2
C2			5.8	<1	1.1	2.6	3.3	2.9	1	8.7			<0.4	<1	<0.5	2.7	<0.4	<0.2
C3			6.8	1.6	1.3	3.9	4.7	4.8	1	7.5			0.65	2.9	<0.5	3.5	<0.4	<0.2
C4			9.4	2.1	1.4	3.7	12	3.2	0.7	8.9			<0.4	2.6	<0.5	6.2	<0.4	<0.2
C5			9.1	1.5	1.1	4.5	9.1	6.1	<0.35	8.5			<0.4	3.7	<0.5	6.6	<0.4	<0.2
C6			9.5	2	1.1	4.4	19	3.7	<0.35	12			<0.4	3.6	<0.5	7.8	<0.4	<0.2
C7			12	<1	0.2	6.6	14	<0.35	<0.35	3.1			<0.4	1.7	<0.4	7.7	<0.4	<0.2
C8			32	1.5	83	68	52	14	<0.35	9.4			299	0.87	<0.4	28	<0.4	<0.2
C9			17	6.2	154	78	51	25	<0.35	11			118	<0.8	<0.4	9.2	<0.4	<0.2
S1	0.12	<0.001	<200	<100	0.005	<0.1	<100	<100	0.03	80	160	39.6	3	0.018		1	<1	-0.002
S2	0.02	<0.001	<200	<100	<0.005	<0.1	<100	<100	0.02	30	80	5.62	<1	0.01		<0.5	<1	-0.002

Sample name	Sn (µg/L)	Sb (µg/L)	Ba (mg/L)	La (µg/L)	Ce (µg/L)	Pr (µg/L)	Nd (µg/L)	Sm (µg/L)	Eu (µg/L)	Gd (µg/L)	Tb (µg/L)	Dy (µg/L)	Ho (µg/L)	Er (µg/L)	Tm (µg/L)	Yb (µg/L)	Lu (µg/L)	Hf (µg/L)
SW1	8	20		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	7
SW2	6	13		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	7
SW3	4	11		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	5
SW4	1	2		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.8
SW5	<2	3		537	1057	87	290	41	9.9	39	5.2	28	5.4	14	1.7	9.2	1.3	<0.8
SW6	1	1		<0.4	0.9	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	2.6
SW7	<1	<1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.4
SW8	<1	<1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.4
SW9	<1	<1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.6
SW10	<1	<1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.6
SW11	2	1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.5
SW12	1	1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.9
SW13	1	1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.1

Sample name	Sn (µg/L)	Sb (µg/L)	Ba (mg/L)	La (µg/L)	Ce (µg/L)	Pr (µg/L)	Nd (µg/L)	Sm (µg/L)	Eu (µg/L)	Gd (µg/L)	Tb (µg/L)	Dy (µg/L)	Ho (µg/L)	Er (µg/L)	Tm (µg/L)	Yb (µg/L)	Lu (µg/L)	Hf (µg/L)
SW14	1	1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.2
SW15	1	1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.1
SW16	<1	<1		0.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.5
SW17	<1	<1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.2
SW18	<1	<1		0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.5
SW19	<1	<1		37	52	4.9	15	1.8	0.4	2.0	<0.4	1.5	<0.4	0.8	<0.4	0.5	<0.4	0.4
SW20	<0.6	<2	0.852	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW21	<2	<5	0.296	31	27	1.5	4.8	<0.5	0.2	1.0	<0.1	0.6	0.2	0.4	<0.1	0.2	<0.1	<1
SW22	<2	<5	0.124	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW23	<2	<5	0.016	69	186	17	64	12	2.5	11	1.7	9.4	1.9	5.6	0.7	4.9	0.7	<1
SW24	<2	<5	0.016	183	525	48	180	34	8.3	30	4.5	24	4.8	14	1.8	12	1.7	<1
SW25	<2	<5	0.032	8.0	19	1.9	6.0	1.0	0.3	1.2	0.3	1.5	0.4	1.0	0.2	0.9	0.2	<1
SW26	<2	<5	0.076	24	73	4.3	14	2.0	0.4	2.3	0.3	2.1	0.4	1.3	0.1	0.8	0.1	<1
SW27	<2	<5	0.032	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<1
SW28	<2	<5	0.088	180	341	30	110	17	3.7	18	2.3	13	2.6	6.7	0.8	4.7	0.7	<1
SW29	<2	<8	0.056	<0.2	<0.4	<0.2	<0.4	<0.8	<0.1	<0.2	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<2
SW30	<2	<5	0.072	102	208	19	70	11	2.3	11	1.4	8.1	1.6	4.2	0.5	3.1	0.4	<1
SW31	<2	<5	0.028	6.8	194	1.1	4.8	0.5	0.3	2.0	0.3	2.9	0.7	2.4	0.3	2.1	0.3	<1
SW32	<0.6	<2	0.028	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW33	<0.6	<2	0.084	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW34	<2	<5	0.048	8.0	18	1.7	6.3	<0.5	0.1	1.2	0.1	1.0	0.2	0.6	<0.1	0.4	<0.1	<1
SW35	<2	<5	0.028	36	93	11	44	8.5	2.1	8.8	1.5	8.0	1.8	4.8	0.9	4.7	1.0	<1
SW36	<2	<5	0.04	49	140	15	62	13	2.7	12	1.9	11	2.4	6.7	1.1	6.7	1.1	<1
SW37	<2	<5	0.032	23	110	6.5	24	3.0	0.7	3.6	0.4	3.0	0.7	1.9	0.3	1.6	0.2	<1
SW38	<2	<5	0.048	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW39	<2	<5	0.04	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW40	<2	<5	0.076	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW41	<2	<5	0.032	2.2	1.5	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW42	<0.6	<2	0.026	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW43	<2	<5	0.06	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW44	<2	<5	0.036	26	47	3.0	9.3	0.5	0.2	1.1	<0.1	0.9	0.2	0.5	<0.1	0.2	<0.1	<1
SW45	<0.6	<2	0.23	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW46	<0.6	<2	0.024	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW47	<2	<5	0.048	5.8	7.8	0.6	1.2	<0.5	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<1

Sample name	Sn (µg/L)	Sb (µg/L)	Ba (mg/L)	La (µg/L)	Ce (µg/L)	Pr (µg/L)	Nd (µg/L)	Sm (µg/L)	Eu (µg/L)	Gd (µg/L)	Tb (µg/L)	Dy (µg/L)	Ho (µg/L)	Er (µg/L)	Tm (µg/L)	Yb (µg/L)	Lu (µg/L)	Hf (µg/L)
SW48	<2	<5	0.1	355	542	85	331	69	11	89	16	107	24	69	8.7	47	7.1	<1
SW49	<0.6	<2	0.242	17	23	2.0	6.8	0.8	0.1	1.0	0.1	0.9	0.2	0.5	<0.1	0.3	<0.1	<0.4
SW50	<0.6	<2	0.096	11	16	1.5	5.7	0.8	0.2	1.5	0.3	2.0	0.4	1.3	0.2	1.2	0.2	<0.4
SW51	<0.6	<2	0.188	4.8	4.4	0.4	1.5	<0.2	<0.1	0.3	<0.1	0.4	0.1	0.3	<0.1	0.2	<0.1	<0.4
SW52	<2	<5	0.028	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW53	<0.6	<2	0.094	0.4	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4
SW54	<0.6	<2	0.17	17	24	2.0	6.9	0.8	0.1	0.8	<0.1	0.5	<0.1	0.2	<0.1	0.1	<0.1	<0.4
SW55	<2	<5	0.032	523	982	85	293	44	11	45	7.0	37	8.3	22	3.6	16	3.3	<1
SW56	<2	<5	0.064	27	53	4.6	17	2.5	0.6	3.4	0.6	3.0	0.6	1.5	0.3	1.1	0.2	<1
SW57	<2	<5	0.112	2.2	3.0	1.3	0.9	1.0	1.0	1.1	1.0	1.1	1.0	0.9	1.0	1.1	1.0	<1
SW58	<2	<5	0.228	1.2	3.6	0.3	1.2	<0.5	<0.1	0.3	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<1
SW59	<2	<5	0.092	<0.2	<0.3	<0.1	<0.3	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1
C1	0.58	2.6		0.63	1	<0.4	0.47	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	4.3
C2	0.56	2.3		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	3.2
C3	2	3		0.6	0.98	<0.4	0.67	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	3.7
C4	0.93	3.1		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	3.7
C5	0.7	2.9		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	2.6
C6	0.65	2.8		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	2.7
C7	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.7
C8	<0.4	<0.4		665	1145	130	459	71	17	80		47	8.9	23	2.6	14	1.9	0.89
C9	<0.4	<0.4		237	576	48	172	30	7.1	31		21	4.1	11	1.4	8.5	1.2	0.55
S1	<1	<2	0.17	<1	1	<1	<1	<1	<1	<0.001	<1	<1	<1	<1	<1	<1	<1	
S2	<1	<2	0.78	<1	<1	<1	<1	<1	<1	<0.001	<1	<1	<1	<1	<1	<1	<1	

Sample name	Pt (µg/L)	Au (µg/L)	Tl (µg/L)	Pb (µg/L)	Th (µg/L)	U (µg/L)
SW1	<0.4	6.1	<0.4	<2	141	19
SW2	<0.4	3.2	<0.4	<2	159	1.4
SW3	<0.4	2.2	<0.4	4	82	14
SW4	<0.4	<0.4	<0.4	<0.6	3	26
SW5	<0.4	0.6	<0.4	73	4	3.5
SW6	<0.4	<0.4	<0.4	<0.6	8	20
SW7	<0.4	<0.4	<0.4	<0.6	2	<0.4
SW8	<0.4	<0.4	<0.4	<0.6	2	0.6
SW9	<0.4	<0.4	<0.4	<0.6	3	1.4
SW10	<0.4	<0.4	<0.4	<0.6	4	2.3
SW11	<0.4	<0.4	<0.4	<0.6	12	2.4
SW12	<0.4	<0.4	<0.4	<0.6	16	2.2
SW13	<0.4	<0.4	<0.4	<0.6	8	4.3
SW14	<0.4	<0.4	<0.4	<0.6	7	0.6
SW15	<0.4	<0.4	<0.4	<0.6	6	3.3
SW16	<0.4	<0.4	<0.4	<0.6	2	0.9
SW17	<0.4	<0.4	<0.4	<0.6	5	<0.4
SW18	<0.4	<0.4	<0.4	1.3	3	0.5
SW19	<0.4	<0.4	<0.4	<0.6	2	<0.4
SW20	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW21	<2	<0.5	<0.3	<2	<0.5	<3
SW22	<2	<0.5	<0.3	<2	<0.5	<3
SW23	<2	<0.5	<0.3	56	6.0	<3
SW24	<2	<0.5	<0.3	74	19	<3
SW25	<2	0.5	0.3	<2	<0.5	<3
SW26	<2	<0.5	<0.3	4	<0.5	<3
SW27	<2	<0.5	0.3	20	<0.5	<3
SW28	<2	<0.5	<0.3	14	<0.5	<3
SW29	<2	<0.8	<0.4	<2	<0.8	<4
SW30	<2	<0.5	<0.3	38	<0.5	<3
SW31	<2	<0.5	<0.3	36	<0.5	<3
SW32	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW33	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW36	<2	<0.5	<0.3	58	<0.5	<3
SW37	<2	<0.5	<0.3	20	<0.5	<3
SW38	<2	<0.5	<0.3	<2	<0.5	6
SW39	<2	<0.5	<0.3	<2	<0.5	<3
SW40	<2	<0.5	<0.3	<2	<0.5	<3
SW41	<2	<0.5	<0.3	<2	<0.5	<3
SW42	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW43	<2	<0.5	<0.3	<2	<0.5	<3
SW44	<2	<0.5	<0.3	2	<0.5	<3
SW45	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW46	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW47	<2	<0.5	<0.3	<2	<0.5	<3
SW48	<2	<0.5	<0.3	50	<0.5	<3
SW49	<0.6	<0.2	<0.1	9.6	<0.2	<1
SW50	<0.6	<0.2	<0.1	17.4	<0.2	<1
SW51	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW52	<2	<0.5	<0.3	<2	<0.5	<3
SW53	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW54	<0.6	<0.2	<0.1	<0.6	<0.2	<1
SW55	<2	2.0	0.6	54	2.0	<3
SW56	<2	<0.5	<0.3	16	<0.5	<3
SW57	<2	0.5	<0.3	<2	<0.5	<3
SW58	<2	<0.5	<0.3	<2	<0.5	30
SW59	<2	<0.5	<0.3	<2	<0.5	<3
C1	<0.4	<0.4	<0.4	<0.5	1.9	1.2
C2	<0.4	<0.4	<0.4	<0.5	1.4	1.3
C3	<0.4	<0.4	<0.4	<0.5	7.3	1.7
C4	<0.4	<0.4	<0.4	<0.5	4.3	1.7
C5	<0.4	<0.4	<0.4	<0.5	1.9	1.1
C6	<0.4	<0.4	<0.4	<0.5	1.8	2.9
C7	<0.4	<0.4	<0.4	0.2	0.47	9.22
C8	<0.4	<0.4	<0.4	135	<0.4	<0.2
C9	<0.4	<0.4	<0.4	98	10	16

Sample name	Pt (µg/L)	Au (µg/L)	Tl (µg/L)	Pb (µg/L)	Th (µg/L)	U (µg/L)
SW34	<2	<0.5	<0.3	12	<0.5	<3
SW35	<2	<0.5	<0.3	42	<0.5	<3

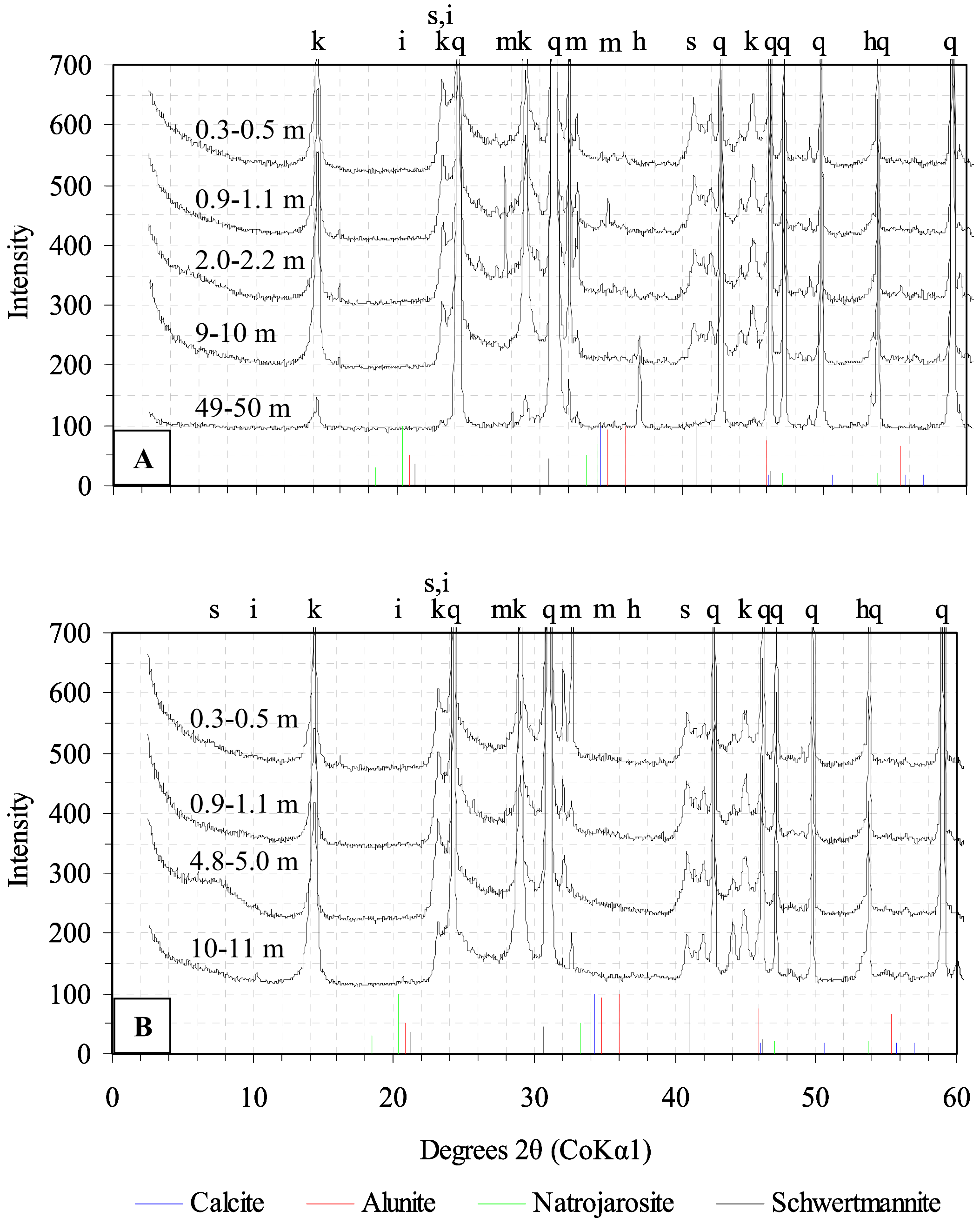
Sample name	Pt (µg/L)	Au (µg/L)	Tl (µg/L)	Pb (µg/L)	Th (µg/L)	U (µg/L)
S1	<0.1	<0.05	<1	<0.01	<1	8
S2	<0.1	<0.05	<1	<0.01	<1	4

APPENDIX 3.2 REGOLITH MINEROLOGY – FENCE RD CATCHMENT

Determined by the WA Chemistry Centre via the X-ray powder diffraction ($\mathrm{CoK}_{\alpha}1$, 40 kV/30 mA; autodivergence slits and exit-beam monochromation) of (1) bulk samples ground under alcohol and randomly back-packed (0.06° step size, 2 sec/step) and (2), following dispersion in water in an ultrasonic bath, -20 µm subsamples oriented on low-background quartz plates (0.05° step size, 4 s/step). Aquifer depths are 13-51 m at site 07FR03 and 8-10 m at site 07FR04. See Appendix 3.1 for site co-ordinates.

Sample site	Depth interval (m)	Bulk or -20 µm	Mineral concentration (wt. %)									
			Quartz	Microcline	Plagioclase	Muscovite/ illite	Kaolinite	Smectite	Interstratified clay mineral	Haematite	Anatase	Halite
07FR03	0.3-0.5	Bulk	Dominant	Minor	n.d.	n.d.	Major	n.d.	n.d.	n.d.	n.d.	n.d.
		-20 µm	Major	Trace	n.d.	n.d.	Dominant	n.d.	n.d.	n.d.	n.d.	n.d.
	0.9-1.1	Bulk	Dominant	Minor	Trace?	n.d.	Major	n.d.	n.d.	n.d.	n.d.	n.d.
		-20 µm	Major	Trace	Trace	n.d.	Dominant	n.d.	n.d.	n.d.	n.d.	n.d.
	2.05-2.2	Bulk	Dominant	Minor	n.d.	n.d.	Minor	n.d.	n.d.	n.d.	n.d.	n.d.
		-20 µm	Major	Minor	n.d.	n.d.	Dominant	Minor	n.d.	n.d.	n.d.	n.d.
	9.0-10.0	Bulk	Dominant	Minor	n.d.	Trace	Minor	n.d.	n.d.	n.d.	Trace	Trace
		-20 µm	Minor	Trace	n.d.	Trace	Dominant	?	Major?	Trace	n.d.	n.d.
	49.0-50.0	Bulk	Dominant	Trace	n.d.	n.d.	Minor[1]	Minor?	n.d.	n.d.	n.d.	Trace
		-20 µm	Minor	Trace	n.d.	Trace	Dominant	Major?	n.d.	n.d.	n.d.	Minor
	Lamellae at 39+ m	Bulk	Subdominant	Trace	n.d.	Trace	Subdominant	Minor	n.d.	n.d.	Trace	Trace
		-20 µm	Minor	Trace	n.d.	Trace	Dominant	Major	n.d.	n.d.	n.d.	n.d.
07FR04	0.3-0.5	Bulk	Dominant	Trace	Minor	n.d.	Minor	n.d.	n.d.	n.d.	n.d.	n.d.
		-20 µm	Minor	Trace	n.d.	Trace	Dominant	Major	n.d.	n.d.	n.d.	n.d.
	0.9-1.1	Bulk	Dominant	Trace	n.d.	n.d.	Minor	n.d.	Trace?[2]	n.d.	n.d.	n.d.
		-20 µm	Minor	Trace	n.d.	Trace	Dominant	Minor	n.d.	n.d.	n.d.	n.d.
	4.8-5.0	Bulk	Dominant	Trace	n.d.	Trace?	Minor	Major	n.d.	n.d.	n.d.	n.d.
		-20 µm	Major	Trace	n.d.	Trace?	Dominant	Major	n.d.	n.d.	n.d.	n.d.
	10.0-11.0	Bulk	Subdominant	Trace	Trace?	Trace	Subdominant	Minor?	n.d.	n.d.	n.d.	Trace
		-20 µm	Minor	Trace	n.d.	Trace	Dominant	Major	n.d.	n.d.	n.d.	n.d.

NOTES: Concentrations were estimated from diffraction peak intensities and are given as dominant >50 wt. %, subdominant 40-50 wt. %, major 10-40 wt. %, minor 2-10 wt. %, trace <2 wt. %, n.d. not detected. Plagioclase is generally a minor phase exsolved within microcline and is reported only where present in sufficient abundance to signify a separate phase. Halite likely precipitated during sample drying. [1] Includes some metahalloysite. [2] Tentative identification based on a single weak diffraction peak at 11.2Å. Alunite, calcite, natrojarosite and schwertmannite were not detected in any sample.



Appendix 3.2, continued. X-ray diffractograms (CoK$_{\alpha}$1, 40 kV/30 mA; 0.06° steps at 2 sec/step) of bulk regolith from piezometer sites (A) 07FR03 and (B) 07FR04 with sample depths labelled in metres. Selected peak positions are labelled above the diffractograms for the minerals smectite (s), illite (i), kaolinite (k), quartz (q), microcline (m) and halite (h), and peak positions and intensities are shown as vertical colour-coded lines beneath the diffractograms for calcite, alunite, natrojarosite and schwertmannite.

APPENDIX 4.1 WATER SAMPLING SITES – SOUTH COAST

Note: sample data available on request from the Department of Water (WA).

Site ID code	Location	Site type	Zone	Easting (m)	Northing (m)	Bore depth (mbgl)
AG22	Groundwater Bore AG22	Groundwater	51	368531	6284417	11.17
FF01D	Groundwater Bore FF01D	Groundwater	51	359590	6287485	24.21
FF01I	Groundwater Bore FF01I	Groundwater	51	359590	6287485	11.76
FF01S	Groundwater Bore FF01S	Groundwater	51	359590	6287485	3.70
FF03I	Groundwater Bore FF03I	Groundwater	51	360055	6287640	17.98
CA10	Groundwater Bore CA10	Groundwater	51	331194	6318042	N/A
CA13D	Groundwater Bore CA13D	Groundwater	51	326133	6319081	15.94
CA13OB	Groundwater Bore CA13OB	Groundwater	51	326133	6319081	5.82
CA7	Groundwater Bore CA7	Groundwater	51	336131	6321011	26.97
CA8	Groundwater Bore CA8	Groundwater	51	336805	6319270	13.34
CA8OB	Groundwater Bore CA8OB	Groundwater	51	336805	6319270	4.20
CA9D	Groundwater Bore CA9D	Groundwater	51	333637	6319931	15.14
GS8A	Groundwater Bore GS8A	Groundwater	51	372453	6279142	23.20
GS8B	Groundwater Bore GS8B	Groundwater	51	372453	6279142	7.76
GS8OB	Groundwater Bore GS8OB	Groundwater	51	372453	6279142	5.71
GS9A	Groundwater Bore GS9A	Groundwater	51	362545	6284384	N/A
GS9B	Groundwater Bore GS9B	Groundwater	51	362545	6284384	9.23
GS9OB	Groundwater Bore GS9OB	Groundwater	51	362545	6284384	5.56
PD1	Groundwater Bore PD1	Groundwater	51	274240	6272887	22.90
CA2D	Groundwater Bore CA2D	Groundwater	51	300666	6309499	17.80
CA3D	Groundwater Bore CA3D	Groundwater	51	299775	6312499	13.55
AG30	Groundwater Bore AG30	Groundwater	51	318205	6283486	24.54
AG30OB	Groundwater Bore AG30OB	Groundwater	51	318205	6283486	11.74
EWD5	Groundwater Bore EWD5	Groundwater	51	312300	6282230	15.46
AG12	Groundwater Bore AG12	Groundwater	51	429645	6294926	23.33
AG12S	Groundwater Bore AG12S	Groundwater	51	429645	6294926	5.59
AG13D	Groundwater Bore AG13D	Groundwater	51	433237	6291685	26.21
AG13S	Groundwater Bore AG13S	Groundwater	51	433237	6291685	10.88

Site ID code	Location	Site type	Zone	Easting (m)	Northing (m)	Bore depth (mbgl)
GS10	Groundwater Bore GS10	Groundwater	51	415939	6284870	11.86
GS11	Groundwater Bore GS11	Groundwater	51	433612	6283888	13.38
RS17D	Groundwater Bore RS17D	Groundwater	51	385166	6278270	8.64
BDR1	Tributary A	Surface waters	51	366029	6284412	
BDR2	Dalyup R Boydell Rd	Surface waters	51	375112	6284555	
SPW1	West Dalyup R Speddingup Rd	Surface waters	51	362515	6290347	
LRV1	Lort R Rolland Rd	Surface waters	51	341678	6324781	
LRV2	Lort R Grass Patch Rd	Surface waters	51	346407	6315893	
WDR1	West Dalyup R Boydells Rd	Surface waters	51	364738	6284399	
NWB1	Groundwater Bore NWB	Surface waters	51	369750	6289000	
NWD1	Drain E of Dalyup Rd	Surface waters	51	369703	6288976	
CO1	Drain Ashdale Rd	Surface waters	51	340265	6274200	
DRV1	Dalyup R Pioneer Reserve	Surface waters	51	366365	6262890	
LR3	Lort R crossing	Surface waters	51	337935	6274815	
WDR2	West Dalyup R South Coast Hwy	Surface waters	51	367191	6270120	
YR1	Young R Mills Rd	Surface waters	51	312329	6282096	
YR2	Yerritup Ck Neds Corner Rd	Surface waters	51	320947	6264446	
YR3	Young R	Surface waters	51	328865	6275787	
ARD1	Drain Upper Neridup	Surface waters	51	422862	6297553	
cdiDD07	Groundwater Bore cdiDD07	Groundwater	50	701670	6264192	4.80
cdiDD08	Groundwater Bore cdiDD08	Groundwater	50	701673	6264227	4.70
cdiDD09	Groundwater Bore cdiDD09	Groundwater	50	701661	6264260	4.75
cdiDD10	Groundwater Bore cdiDD10	Groundwater	50	701606	6264211	4.80
cdiDD11	Groundwater Bore cdiDD11	Groundwater	50	701642	6264193	3.50
cdiDD12	Groundwater Bore cdiDD12	Groundwater	50	701617	6264194	4.75
DSED	Big Pond East drain	Surface waters	50	701730	6264094	
CCB	Cameron Ck - Bees	Surface waters	50	700759	6263460	
RCS	Spring Robbies Ck	Surface waters	50	712274	6259879	
F30i00	Groundwater Bore F30i00	Groundwater	50	723171	6262258	5.63

Contact Us

Phone: 1300 363 400
+61 3 9545 2176

Email: enquiries@csiro.au

Web: www.csiro.au

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