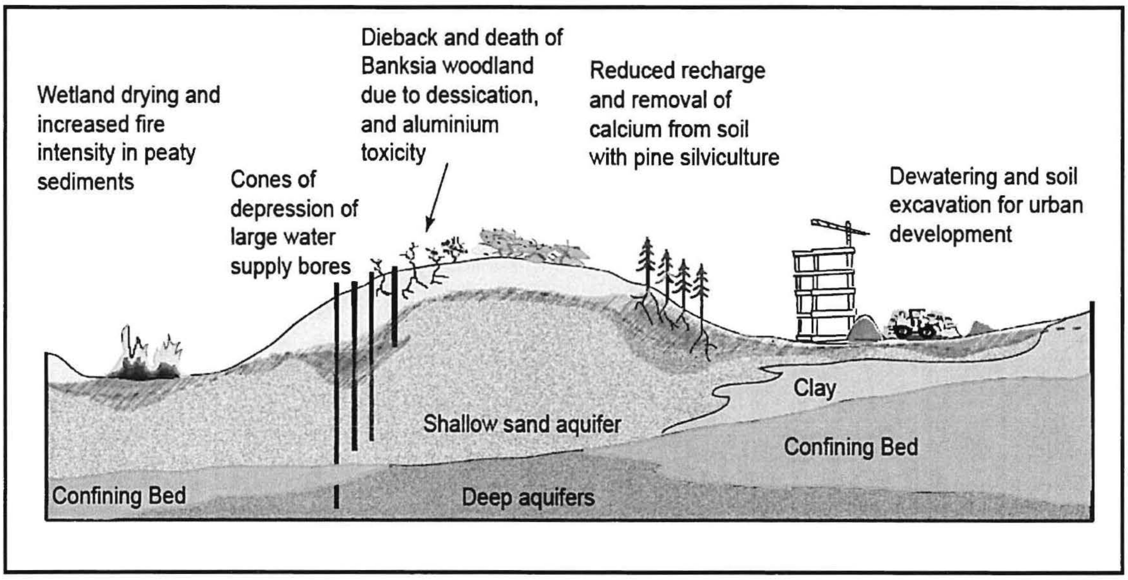
Department of
Environment and Conservation

AN INITIAL ASSESSMENT OF GROUNDWATER ACIDIFICATION ON THE GNANGARA MOUND



SUMMARY

Investigations carried out at eighteen sites on the Gnangara Mound have indicated that sediments in the unsaturated zone and groundwater near the water table are generally acidic with most groundwater pH values being less than 5.5, and values less than 4.5 being recorded at five sites. Groundwater pH profiles indicate that an acidification front is typically located at depths of 4 to 10 metres below the land surface. The level of acidity in shallow groundwater is particularly high near the Mirrabooka borefield where both the concentration of aluminium and the molar aluminium to calcium ratio indicate that groundwater quality poses a significant risk to the health of phreatophytic vegetation. Data from water supply bores indicate that calcium and magnesium have been progressively leaching from soils in this area over the last 20 years which is increasing the risk of vegetation dieback due to aluminium toxicity near the Mirrabooka borefield.

Geochemical modelling indicates that the pH of shallow groundwater prior to European settlement was likely to have been about 6.5, the current average pH of groundwater in the lower part of the superficial aquifer. The modelling suggests that acidification commenced about 100 years ago as a result of increasing air pollution on the Swan Coastal Plain, but it is likely that the combined effects of low rainfall and increasing groundwater use over the last 30 years have increased acidity levels through the oxidation of organic matter and sulphide minerals by the declining water table.

These data suggest that current groundwater management and land use practices on at least part of the Gnangara Mound are not sustainable and pose a threat to the continuing viability of both woodland and wetland ecosystems in the area. Further investigations and monitoring information are needed to enable the effective management of soil and groundwater acidification in the area.

1. INTRODUCTION

The use of groundwater resources is increasing in the Perth region due to rapid population growth and a prolonged period of low winter rainfall that may be associated with regional climate change. As a consequence of these factors, it is becoming increasingly important to understand what level of groundwater use is sustainable in the region and what the environmental consequences of excessive groundwater use are likely to be.

Typically, measures of the sustainability of groundwater use are developed using a purely hydraulic approach, particularly for sandy aquifers. That is, sediments in these aquifers are often viewed as chemically inert "glass-beads" through which groundwater flows, and the "sustainable yield" of groundwater is determined on the basis of the hydraulic properties of the aquifer and on changes in the overall water-balance of the system predicted to be caused by groundwater abstraction. This approach often ignores natural geochemical interactions between groundwater and aquifer sediments and between aquifers and overlying soils and vegetation. Adverse changes in groundwater quality are seen as being mostly caused by contaminants leached from poorly-managed surface land-use practices, and these are managed using a variety of land-use control measures implemented in water-source protection programs.

This approach to managing groundwater resources works well when groundwater use is relatively low and rainfall is high. However, management may become much less effective if declining rainfall and increasing groundwater withdrawal cause large regional declines in the elevation of the water table. Under these conditions, organic and inorganic chemical compounds containing reduced forms of iron, sulphur and nitrogen can be oxidised by exposure to atmospheric oxygen (Hartog et al. 2002), allowing acidity, nutrients and metals to be mobilised and cause environmental problems in groundwater-dependent wetlands and woodlands (van Tol et al. 1998).

Especially large changes in the acidity of soils and shallow groundwater can occur if soils and aquifer sediments are sandy and have little or no carbonate content to provide an acid buffering capacity. Water table decline under these conditions can lead to a suite of environmental problems similar to those caused by "acid rain". This process is often referred to as "drought induced acidification" or "desiccation" (Moss and Edmunds, 1992; Edmunds et al., 1992; van Tol et al. 1998; Laudon et al. 2004; Clarke et al. 2005; Smolders et al. 2006). As sandy soils progressively become more acidic, the base-cations calcium and magnesium can be leached from the soil and their exchange sites in the soil profile replaced by soluble and phytotoxic aluminium and hydrogen ions (Lawrence et al. 1995; Fenn et al. 2006). Loss of calcium from soils in particular can lead to a progressive decline in the health of both woodland and wetland ecosystems and the loss of both plant and animal species (Dudley and Stolton 1996; van Tol et al. 1998; Hames et al. 2001; Fenn et al. 2006). Geochemical changes in soil and groundwater caused by falling water tables are often the most significant causes of biodiversity loss in areas with large rates of groundwater use under conditions of low rainfall. For example, these factors are estimated to account for about 60% of the loss of biodiversity in the Netherlands (Netherlands Environmental Assessment Agency, 2006).

There is increasing evidence that acidification and base-cation depletion are taking place in soils, wetlands and shallow groundwater on the Gnangara Mound, one of the most important and intensively used groundwater resources in Western Australia. This region also contains a large number of groundwater dependent wetlands of significant conservation value and biologically rich *Banksia* woodlands which are at risk of being harmed by changes in soil and groundwater geochemistry.

This study was commissioned to determine the sources, extent and severity of soil and shallow groundwater acidity on part of the Gnangara Mound. This report presents results of soil and groundwater investigations that indicate that the combined effects of low rainfall, groundwater abstraction and land management practices are playing significant roles in exacerbating acidification and base-cation depletion in the area. The investigations were carried out as part of the Gnangara Sustainability Strategy.

2. HYDROGEOLOGICAL SETTING

The Gnangara Mound (Fig. 1) is located on the Swan Coastal Plain, the surface expression of the onshore portion of the Perth Basin which is about 20 km wide near Perth, its eastern boundary being the Darling Fault (Figs 1 and 2). The Swan Coastal Plain is largely covered by sandy aeolian sediments of Quaternary age which may be up to 110 m thick. The plain lacks surface drainage due to the high permeability of the sediments, and the only fresh surface water in the region is in wetlands in interdunal depressions which are surface expressions of the water table.

The Swan Coastal Plain is underlain by a 12 km thick sequence of sediments of Permian to Cretaceous age belonging to the Perth Basin, but fresh groundwater is restricted to the uppermost 1500 m of the basin sediments. These sediments consist of interbedded sandstones and siltstones of Mesozoic age which form a number of regionally extensive aquifers that are important for water supply in Perth. The Mesozoic aquifers are generally confined by siltstones in the region, but are unconfined beneath the Gnangara Mound (Fig. 2) and consequently leakage from overlying sediments in this area is an important source of recharge for these aquifers. The Quaternary sediments that overlie the Mesozoic aquifers form a regionally extensive superficial aquifer (Fig. 2) which has a saturated thickness of about 10 to 70 metres (Davidson 1995).

The Gnangara Mound is a distinct groundwater flow system within the unconfined aquifer to the north of Perth (Figs 1 and 2). Groundwater flows from an area of elevated dunes which form the crest of the mound radially towards the coast, rivers and estuaries which are the boundaries of the flow system (Appleyard et al. 1999; Appleyard 2000). The dunal sediments near the crest of the Gnangara Mound consist of highly leached white to grey coloured siliceous sands of Pleistocene age (Bassendean Sands) which are likely to have a very limited capacity to resist acidification. They are known to contain some framboidal pyrite below the water table (Bawden 1991), although limited sampling indicates that the pyrite content is highly variable and typically comprises less than 0.1% of the sediment matrix. Concentrations of pyrite often exceed 1% and may exceed 10% in peaty sediments in existing interdunal wetlands (Appleyard et al., 2004, 2006) and pyrite is known to be present in peaty or clayey material within the unconfined aquifer (Davidson, 1995).

The composition of groundwater within the superficial aquifer on the Gnangara Mound is dominated by sodium and chloride ions (Cargeeg et al., 1987; Davidson, 1995), reflecting the high rate of marine salt deposition in rainfall and dry fallout in the region (Hingston and Gailitis, 1976). The alkalinity of groundwater at the water table is typically less than 50 mg/L as $CaCO_3$ near the water table but commonly exceeds 100 mg/L as $CaCO_3$ at the base of the unconfined aquifer (Davidson, 1995). The total dissolved solids content of groundwater in the unconfined aquifer varies from about 250 mg/L near the crest of the Gnangara Mound to about 1000 mg/L near the coast.

The Gnangara Mound groundwater flow system is recharged by rainfall which is nominally about 800 mm a^{-1} and falls mostly during the period May to October each year. However, annual rainfall has generally been 20 to 30% below the long-term average since the mid 1970s, a trend that is observed throughout the southwestern corner of Australia and which appears to be at least partially due to climate change (IOCI 2002).

Currently, about 320 GL a^{-1} of groundwater is licensed for use from the Gnangara Mound for public water supply (about half of the groundwater use) and irrigation (McCrea 2004). It is estimated that an additional 60 GL a^{-1} of unlicensed pumping takes place for garden irrigation from household domestic wells (McCrea 2004). By comparison, the total groundwater withdrawal rate on the Gnangara Mound was about 50 GL a^{-1} in 1980. The combined effects of low rainfall, groundwater withdrawal and reduced recharge in areas covered by pine plantations (Bekele and Salama ,2003; Fig. 1) has caused the water table on the Gnangara Mound to drop by up to 5 metres and aquifer storage to decline by about 500 GL over the last 20 years (Salama et al. 2002; Yesertner 2002; Vogwill 2004).

3. FACTORS INFLUENCING SOIL AND GROUNDWATER ACIDITY ON THE GNANGARA MOUND

3.1 Potential sources of acidity

Under natural conditions, acidity in soil is controlled by the rate of input and output of acid forming and consuming ions by:

- Rainfall and dust deposition on a catchment;
- Weathering of minerals in soil;
- Ion exchange by soil minerals;

- Biological activity in the soil and vegetation that decomposes and recycles organic carbon and nutrients;
- Leaching to groundwater; and
- Emission of gases to the atmosphere.

(Langmuir, 1997)

A dynamic equilibrium is established between these factors which maintains relatively stable chemical conditions in soil and the underlying groundwater (Figure 1).

If the water table is very shallow or at the surface, or if subsoils are peaty, microbiological activity just below the water table will progressively decompose the organic carbon using ferric minerals, and soluble nitrate and sulfate ions leached from the soil for respiration (Kirk, 2004). This process creates large amounts of dissolved organic carbon, hydrogen sulfide gas and iron sulfide minerals (pyrite and poorly crystalline iron monosulphides) which accumulate below the water table. As this process also consumes acidity that may be leached from soil, water that leaches to deeper groundwater under these conditions (Figure 3) generally has a near-neutral pH.

Although soil pH remains constant for long periods of time under natural conditions, there is usually a slow loss of calcium and magnesium ("base cations") caused by leaching that progressively leads to soils becoming more acidic (typically over time frames of tens of thousands to hundreds of thousands of years). In this way, soils gradually evolve, and continue to do so until rejuvenated by a geological event which provides a new source of base cations. For example, the highly leached and naturally acidic Bassendean Sand soils have evolved from calcareous sands similar to the Spearwood Sands over a time frame of about 100 000 years (McArthur and Bettenay, 1960).

Changes in air quality, land use and/or the water balance in a catchment can alter these geochemical processes and trigger regionally extensive acidification of soil and groundwater (Figure 4). This issue was discovered in Europe and North America in the 1970s when it was found that widespread air pollution by sulfur and nitrogen oxides from industrial activity and vehicle exhausts gave rise to rainwater and dust with a low pH which disrupted the acid-base reactions in soil (so-called "acid rain"). The acidification can be greatly exacerbated by excessive fertiliser use and harvesting or logging which removes calcium and magnesium from soils (Figure 4) unless replaced by lime application. For instance, Huntington *et al.* (2000) have predicted that logging practices in forests in the southeastern U.S.A. will deplete calcium and acidify soils to the point that commercial forestry will not be viable in about 80 years time.

The observed acidity in soil and shallow groundwater on the Gnangara Mound is likely to have been derived from a combination of natural and anthropogenic sources. Natural organic acids associated with podzols are likely to form a significant component of the acidity in sandy areas, whereas sulphide oxidation is probably the most significant source of acidity in drying wetland sediments. However, work by Hingston and Gailitis (1976) and Bawden (1991) has indicated that these natural acidity sources are being augmented in the area by sulphur compounds from urban air pollution. Intensive fertiliser use in horticultural areas and pine silviculture are also likely to be significant anthropogenic sources of acidity on the Gnangara Mound.

3.2 Evidence of acidity changes with time

Soil profiles on the Gnangara Mound are extensively podzolised and are naturally acidic. However, three lines of evidence indicate that the level of acidity in soils and shallow groundwater in the area is likely to have increased over recent decades on at least a local basis.

Firstly, research by Edith Cowan University has indicated that at least eight wetlands in the area have become either permanently or episodically acidic in recent years, particularly in areas where there has been a large decline in water table elevation and where fire has caused the destruction of pyritic peaty sediments in the base of the wetland. Lake Gnangara was the first wetland in the area to have acidified in recent times (in the late 1970s – see Fig. 5), but the nearby lakes Jandabup and Mariginiup are now showing similar trends of declining pH. Much of the acidity in these wetlands is due to the oxidation of pyrite in lake bed sediments with falling water tables, but some wetlands, including Lake Gnangara and Lake Mariginiup, are also receiving inputs of acidic groundwater. Diatom assemblages in lake sediments indicate that some wetlands on the Gnangara Mound have previously experienced acidification events in recent geological history (McHugh, 2004), but the rate at which these systems acidified and recovered from these events is not known.

A second line of evidence is increasing groundwater acidity that is being observed as a result of construction dewatering in some new urban developments on the Gnangara and Jandakot Mounds. Information being collected by the Department of Environment and Conservation (DEC) for the environmental assessment of new residential areas on Bassendean Sand is indicating that prolonged dewatering (several weeks to months in duration) for the installation of sewers can trigger rapid and large pH drops and increases in iron, aluminium and heavy metal concentrations in groundwater after a few weeks pumping (Fig. 6) when the alkalinity is low. Groundwater appears to be particularly vulnerable to acidification by construction dewatering when alkalinity prior to pumping is less than 30 mg/L as $CaCO_3$ (Swedish EPA, 2002).

Existing water quality information also suggests that water supply production bores in the Mirrabooka borefield on the Gnangara Mound are triggering acidification near the water table. Groundwater pumped from production bores is from the lower part of the superficial aquifer and is not directly affected by changes in acidity, but long-term increases of sulphate and iron concentrations and of the sulphate/chloride ratio (Fig. 7) in groundwater measured in production bores are indicative of the oxidation of sulphide minerals and organosulphur compounds in sediments exposed to oxygen within the cone of depression of the borefield. Long-term increases in concentrations of calcium and magnesium ions measured in groundwater from some production bores (Fig. 8) are indicative of base cation leaching from overlying soils.

However, it has not been possible to determine the severity of acidity in soil and shallow groundwater in the Mirrabooka borefield and beneath the adjacent pine plantations due to the almost complete lack of monitoring information at shallow depth in the aquifer. The following investigations were undertaken to provide additional soil and groundwater quality data to partially address this information gap.

4. METHODS AND MATERIALS

4.1 Sediment and groundwater pH profiles

Investigation boreholes were drilled at eighteen sites during the period December 2007 to February 2008 using a sonic drilling rig (Table 1; Fig. 9). Wherever possible, sediment samples were collected at 25 cm intervals for on-site testing of the pH values of both a 1:5 sediment to deionized-water paste (pH_f) and a 1:5 sediment to 30% strength hydrogen peroxide paste (pH_{fox}). However, it was not possible to collect sediment samples at a number of sites (Table 1) due to drilling problems in dry running sand. Vertical profiles of pH_f and pH_{fox} values for each site that these data were collected are shown in Appendix 1.

At each site, a monitoring bore was constructed with 50 mm diameter PVC casing that was slotted from the water table to the bottom of the borehole. Each bore was developed by airlifting with compressed air to remove fine particulates and then allowed to recover for about four weeks before pH testing was carried out. Profiles of groundwater pH below the water table were measured at 25 cm intervals at each site using a downhole pH probe in April 2008. Groundwater pH profiles for each site are also shown in Appendix 1.

4.2 Sediment and groundwater sampling

Sediment samples were collected at specific depths (Table 1) at sites 1, 5, 11, 13, 17 and 18 for chemical analysis using the Chromium-Reducible Sulphur (S_{Cr}) and the Suspension Peroxide Oxidation Combined Acidity and Sulphur (SPOCAS) methods (Ahern et al., 2004) to determine the magnitude of various forms of available and stored acidity in sediment profiles.

Table 1. Location and soil testing details for the investigation sites

Site	Total depth (m)	SWL (m)	Construction date	Field testing of sediment	Sediment sample depths (m)	Co-ordinates	
						Easting	Northing
1	7	2.62	13/12/2007	No	4.00 (+duplicate), 6.00, 6.25, 7.00	399129	6476137
2	6	4.32	13/12/2007	No		397629	6477901
3	14	5.45	13/12/2007	Yes		397362	6479722
4	14	5.44	13/12/2007	No		397195	6481759
5	10	7.01	12/02/2008	Yes	5.25, 6.25, 7.25, 7.75, 9.25	396560	6483684
6	14	5.52	14/12/2007	No		394920	6484477
7	14	5.33	14/12/2007	No		396870	6490051
8	14	4.46	14/12/2007	No		398624	6490466
9	14	-	14/12/2007	No		391370	6493842
10	14	-	14/12/2007	No		389422	6493441
11	8	4.01	13/02/2008	Yes	4.00, 4.75, 6.00	389685	6489744
12	14	7.87	13/02/2008	Yes		392038	6490867
13	12	6.36	31/03/2008	Yes	2.50, 3.50, 6.25, 7.00, 8.00, 9.50, 11.50	391964	6487654
14	17	14.12	31/03/2008	Yes		393729	6487752
15	14	8.90	3/04/2008	Yes		393837	6487042
16	11	8.08	12/02/2008	Yes	5.25, 8.00, 9.25, 10.00	395790	6485920
17	10	5.67	12/02/2008	Yes	4.00, 5.75, 6.50	393760	6483396
18	10	5.49	18/01/2008	Yes	4.50, 5.00, 5.75, 6.25, 7.00	400109	6479766

Table 2 Groundwater sampling field measurements

Investigation site	Sampling date	pH	Temperature (°C)	EC (mS/cm)	Redox (mV)	DO (mg/L)
1	23/05/2008	5.18	22.1	0.138	-99	0.35
2	30/05/2008	4.00	23.76	0.274	309	1.56
3	23/05/2008	4.45	18.44	0.211	202	5.65
4	27/05/2008	5.94	21.19	0.153	-51	5.97
5	27/05/2008	3.78	21.02	0.230	-5	4.75
6	27/05/2008	5.33	23.64	0.329	-124	0.51
7	29/05/2008	5.02	21.71	0.285	-79	1.1
8	29/05/2008	5.24	23.56	0.254	-96	0.35
9		Unable	to	sample		
10		Unable	to	sample		
11	29/05/2008	4.93	20.64	0.259	131	2.07
12	29/05/2008	4.89	20.7	0.309	-104	0.96
13	30/05/2008	6.32	23.56	0.276	-124	1.5
14	28/05/2008	4.35	21.52	0.3836	162	3.85
15	28/05/2008	4.79	23.21	0.2273	-48	1.05
16	28/05/2008	4.15	23.48	0.3275	-16	0.18
17	27/05/2008	5.53	22.32	0.4752	-129	0.38
18	26/05/2008	5.19	22.03	0.1872	-72	1.71

Monitoring bores at each site except sites 9 and 10 were sampled during the period 23 to 30 May 2008 to obtain groundwater samples for chemical analysis. Bores at sites 9 and 10 contained too much silt to be sampled during this period. Each bore was pumped with a low-flow bladder pump until at least three casing volumes of water had been displaced and field readings of pH, temperature, electrical conductivity, oxidation-reduction potential and dissolved oxygen (Table 2) had stabilised before samples were collected in laboratory-prepared bottles. Samples were placed on ice and delivered to a laboratory for preparation and storage on the same day. Chemical analyses were carried out on each sample for a suite of major ions and metals typically associated with leachate from acidifying soil profiles.

The results of chemical analyses of both groundwater and sediment samples are tabulated in Appendix 2.

Geochemical mixing and reactive transport models were developed with these data using PHREEQC (Parkhurst and Appelo, 1999) to enable predictions to be made about geochemical processes that are likely to be taking place in the subsurface on the Gnangara Mound.

5. RESULTS

5.1 Indicators of groundwater acidity at the water table

The distribution of pH values at the water table (Fig. 10) indicates that shallow groundwater is generally acidic throughout the study area. Values of pH less than 4.5 where aluminium mobilisation often becomes significant were recorded at five sites in a corridor between Lake Mariginiup and Whiteman Park, and this area also had levels of titrateable acidity that exceeded alkalinity by more than 40 mg L^{-1} as $CaCO_3$ (Fig. 10).

Of more concern is that concentrations of soluble aluminium often exceed 1 mg L^{-1} in the southern part of this acidity corridor (Fig. 10), values that have the potential to be toxic to phreatophytic vegetation depending on the degree to which the Al is bound up in organic complexes. Three sites in the same area also have aluminium to calcium molar ratios in excess of 1 which are generally an indicator that woodland ecosystems are under great stress and that there is a high risk of tree deaths occurring. Sites with elevated Al concentrations and Al/Ca ratios in groundwater are located in both mature pine plantations and in partially revegetated agricultural land in Whiteman Park in areas which are within the cone of depression of production bores in the Mirrabooka borefield. Previous work (Cook et al., 2006) indicated that porewater in 10 to 15 cm thick horizons in sediments in this area contains high concentrations of aluminium (up to 7 mg/L) coupled with low pH values (as low as 3.1), indicating that there is the potential for the concentration of Al at the water table to further increase.

Another factor that could play a role in controlling water table acidity levels is variations in soil properties within the dunal soils that comprise the Bassendean Sand. The major soil types are humus podzols in the older, more easterly parts of the dunes (Gavin series), and iron-humus podzols (Jandakot series) in younger material (McArthur and Bettenay, 1960). In general, the older more intensively leached Gavin series of soils are more acidic than the Jandakot series.

However, the link between high groundwater acidity and the magnitude of water table decline is supported by a strong linear relationship between acidity and values of the groundwater sulphate to chloride ratio (correlation coefficient, R = 0.80; Fig 11), an indicator of the oxidation status of aquifer materials in areas where there is little or no fertiliser use. An inverse log-linear relationship between field measurements of oxidation-reduction potential and pH (R = 0.70; Fig 12) also suggests that shallow groundwater acidity is affected by the magnitude of water table drawdown.

5.2 Vertical distribution of acidity in the unsaturated zone

Profiles of pH at 25 cm depth increments for sediments in the unsaturated zone of sites 3, 5, 11, 13, 17 and 18 are shown in Appendix 1 together with peroxide-oxidisable pH values. These profiles indicate that soil pH measurements in the upper 2 m of the unsaturated zone, the depth interval that incorporates the current soil profile and zone of active pedogenesis, show little or no relationship with pH values in sediments and groundwater at the water table. This is possibly because sediments at shallow depth contain enough organic matter and have sufficient biological activity to moderate pH values over this depth interval. Most sites show lower sediment pH values at depths greater than 2 metres, but both the magnitude of the pH changes and thickness of sediments affected by lower pH values vary greatly between sites.

The pH profiles at sites 3, 5 and 18 show the largest variability and display distinct zones of low sediment pH at depths in the interval of about 2 m and the water table. Profiles of pH values at these sites closely resemble profiles studied in similar sandy sediments in Klosterhede in Denmark (Hansen and Postma, 1995) where pH values were buffered by aluminium oxyhydroxide(sulphate) phases (gibbsite and possibly jurbanite). Variations in pH at the Klosterhede site were attributed to temporal variations in the load of marine-derived salts deposited in rainfall and dry fallout on the catchment. This factor, combined with the low base saturation of acidified sediments, is thought to cause pulses of acidity to be eluted from sediments by slugs of infiltrating water with a high sea-salt content. These acidity pulses then slowly migrate towards the water table and superimpose a pH signature on the existing pH profile.

There are a number of similarities between the Gnangara study area and the Klosterhede site that makes it likely that a similar process is responsible for the observed pH profiles in Gnangara.

Firstly, coastal areas in the southwestern part of Western Australia share the distinction with Denmark and other parts of Scandinavia of having some of the highest rates of sea-salt deposition in rainfall and dry fallout in the world (Hingston and Gailitis, 1976), and groundwater chemistry on the Gnangara Mound is dominated by rainfall-derived salts. Previous studies in the area (Cook et al., 2006) have also indicated that measured cation exchange capacities of sediments in Gnangara of (0.01 to 1.6 cmole/kg) are similar to values measured in Klosterhede. Additionally, the largest pH variations in soil profiles were measured in areas where water supply production bores were showing trends of increasing base cation concentrations (see Fig. 8) due to leaching from overlying soils – i.e. the base saturation in soils in these area is decreasing, making them more vulnerable to acidification. The groundwater quality data collected in this study also suggest that the aluminium oxyhydroxide-sulphate mineral jurbanite could play an important role in controlling the solubility of Al near the water table on the Gnangara Mound (Fig. 13).

The large difference between water-sediment paste and peroxide-sediment paste pH measurements in the unsaturated zone indicates that there is a large store of potential acidity that has yet to be released by oxidation. This is especially the case at sites 13 and 17 where sandy sediments are overlain by a cover of native vegetation and where the pH of groundwater at the water table is similar to values recorded at depth in the superficial aquifer suggesting that there is only limited leaching of acidity at these sites.

5.3 Simulated changes of soil acidity with time

There are no data to indicate what the pH values of Bassendean Sand soil materials on the Gnangara Mound might have been prior to European settlement in the Perth Region, but they can be estimated by modelling the equilibration of unpolluted rainwater with constituents of the soil using the geochemical model PHREEQC (Parkhurst and Appelo, 1999) and the following data:

Using salt deposition data provided by Hingston and Gailitis (1976), the pre-European ionic composition of rainwater falling on the Gnangara Mound is estimated to be: Ca^{2+} – 0.8 mg L^{-1}; Mg^{2+} – 1.2 mg L^{-1}; Na^{+} – 9.4 mg L^{-1}; SO_4^{2-} - 7.6 mg L^{-1}; Cl^{-} - 17 mg L^{-1}. As a first approximation, the partial pressure of carbon dioxide in soils beneath undisturbed woodland and heathland vegetation on the Gnangara Mound can be determined by the following relationship with annual evapotranspiration (Brook et al., 1983):

$$\log P_{CO2} = -3.47+2.09.(1 - \exp(-0.00172.ET))$$

Given that ET on the Gnangara Mound is about 1800 mm a^{-1}, soil P_{CO2} beneath undisturbed vegetation prior to European settlement is estimated to have been about 0.03 Bar. Finally, data provided by Salama et al. (2001) suggest that the organic carbon content in soils beneath undisturbed *Banksia* woodland on the Gnangara Mound would have been of the order of 0.5 to 2.0% prior to European settlement.

These data were used in a PHREEQC simulation assuming that quartz, kaolinite, jurbanite and gibbsite were the only minerals controlling ion solubility at an average soil temperature of 20°C. The results of the simulation indicate that if the organic carbon content in soil was about 0.5% prior to European settlement, the pH of soil porewater would have been about 6.5 on the Gnangara Mound, which is currently the average pH of groundwater in the lower part of the superficial aquifer in the area.

The model was found to be extremely sensitive to organic carbon content, and if this was reduced to a level of 0.1% in soil, soil porewater pH dropped to 5.8. The model predicted that if soil organic carbon was totally removed by oxidation in the Gnangara Mound soils, porewater pH in the unsaturated zone would decline to about 4.1. It was not possible to get pH values lower than this in the unsaturated zone without supplying a strong acid such as sulphur dioxide in rainfall or dry fallout. Peroxide-oxidised pH values measured in sediments in this study were often less than 4.1 suggesting that natural organic matter is not the only source of acidity in these materials.

5.4 Acidity and distribution of metals in groundwater near the water table

Vertical profiles of groundwater pH below the water table shown in Appendix 1 indicate the presence of an acidification front (Kjøller et al., 2005; Appelo and Postma, 2005), a regional interface between shallow acidic groundwater and underlying non-acidic groundwater. This is particularly the case at sites 1, 11, and 14 to18 where groundwater pH increases by between about 0.5 and 2 pH units over a depth interval of 1 to 3 metres below the water table. At most other sites, large water table fluctuations near water supply bores appear to have distorted the acidification front by creating a very broad mixing zone between shallow and deeper groundwater with a greatly reduced pH gradient. However, shallow groundwater in these areas was still found to be acidic.

Above the acidification front, groundwater contains elevated concentrations of aluminium and other metals under pH conditions buffered by the solubility of aluminium minerals, but ion-exchange with Ca and Mg in aquifer sediments causes a sharp reduction in metals concentrations and moderates pH at the interface. Under conditions where there is prolonged leakage of acidity from soil profiles, an acidification front will progressively move downwards into an aquifer at a rate that depends on the hydraulic and geochemical properties of aquifer sediments. The acidification front creates a geochemical trap where metals leached from acidified sediments accumulate, and elevated concentrations of metals may occur in groundwater near the interface (Kjøller et al., 2005; Appelo and Postma, 2005).

This mechanism may explain the high concentrations of metals detected in groundwater at sites where there are currently no obvious sources of contamination. For example, at site 11, where there is a particularly sharp interface between acidic and non-acidic groundwater, elevated concentrations of copper (65 $\mu g\ L^{-1}$), lead (12 $\mu g\ L^{-1}$), nickel (26$\mu g\ L^{-1}$) and zinc (82 $\mu g\ L^{-1}$) in groundwater beneath an area of native vegetation in a semi-rural area. High concentrations of lead (up to 36 $\mu g\ L^{-1}$) were detected in groundwater at many sites, and elevated arsenic (24 $\mu g\ L^{-1}$) and cadmium (4 $\mu g\ L^{-1}$) concentrations were detected at sites 2 and 4 respectively.

A comparison of pH profile depths (Fig. 14) suggests that the average depth of penetration of the acidification front in the study area is between about 4 and 10 m, although this is likely to be highly variable depending on the extent to which groundwater and land use activities have altered solute transport rates in the unsaturated zone. Preliminary reactive transport modelling using PHREEQC and the methodology of

Appelo and Postma (2005) indicates that it would take about 100 years for an acidification front to reach these depths (Fig. 15) assuming ion exchange properties for sediments determined by Cook et al. (2006) and a vertical porewater velocity of about 1 m a^{-1}. The estimated rate of movement of about 5 cm a^{-1} for the acidification front is comparable with estimates made in sandy aquifers elsewhere (Kjøller et al., 2005; Appelo and Postma, 2005).

This factor, together with the need for strong acids in the unsaturated zone to account for the observed levels of acidity, indicates that soil and groundwater acidification on the Gnangara Mound is likely to be an anthropogenic feature rather than of natural origin. As the area has remained largely undeveloped over the last 100 years, it is likely that acidification was initiated by increasing levels of sulphur and nitrogen oxides in rainfall and dry deposition at the beginning of the 20th century due to the rapid increase in the use of fossil fuels (particularly sulphur-rich coal) on the Swan Coastal Plain at that time. The combined effects of low rainfall, increasing groundwater abstraction, horticulture and pine silviculture over the last 30 years are likely to have both increased and mobilised stored acidity, leading to increasing environmental problems in the area.

The association of groundwater acidity on the Gnangara Mound with increased air pollution following European settlement in WA makes it likely that similar problems are widespread on the Swan Coastal Plain in areas underlain by poorly buffered Bassendean Sand soil-materials.

6. CONCEPTUAL MODEL OF ACIDIFICATION ON THE GNANGARA MOUND AND IMPLICATIONS FOR MANAGEMENT

A conceptual model for acidification on the Gnangara Mound is summarised in a cartoon in Figure 16 and is outlined below:

It is likely that soil acidification commenced early in the 20th century with increasing fossil fuel use on the Swan Coastal Plain at that time, and an acidification front began to slowly migrate through the soil profile to its current average position of about 4 to 10 metres below the land surface. Although levels of sulphur dioxide in air have declined greatly in the region over the last 40 years, European and North American experience indicates that acid deposition on soils from rain and dry fallout can be sustained by nitrogen oxides associated with increasing traffic density. This could be the case on the Gnangara Mound as new urban development and arterial roads have progressively expanded into this area over the last 20 years.

The trend of declining water tables caused by low rainfall and increasing groundwater use since the mid 1970s has probably exacerbated soil and groundwater acidity problems on the Gnangara Mound by causing the oxidation of organic matter and sulphide minerals through the drainage of previously saturated and anoxic sediments, and increasing the leaching of base cations from soil profiles into groundwater.

Data from this study indicate that the rate of base cation loss from soils is particularly high within the cones of depression of water supply bores in the Mirrabooka borefield, but there is also a risk that base cations are being removed from soils in biomass harvested from land used for pine silviculture and horticulture in the area.

The rate of loss of base cations from soils in the Mirrabooka borefield can be estimated using the trend of increasing calcium and magnesium concentrations observed in production bore M140 (Fig. 8). By using these data and assuming an annual recharge rate of about 150 mm a^{-1}, the rate of base cation loss in this area is estimated to be about 0.7 keq ha^{-1} a^{-1}, and this figure also sets a lower limit to the amount of acidity that is being leached from soils in the area into groundwater. By contrast, data provided by Hingston and Gailitis (1976) suggest that the rate of base cation deposition on the Gnangara Mound in rainfall and dry fallout is about 0.4 keq ha^{-1} a^{-1}, so there is a significant risk that existing soil storages of calcium and magnesium are being depleted as the contribution of these ions from weathering reactions is likely to be negligible in this area.

These factors imply that current groundwater usage and land management practices on at least part of the Gnangara Mound are not sustainable under the current conditions of low rainfall and could progressively lead to the decline in health of *Banksia* woodlands in the area in addition to further wetland acidification. Additionally, the creation of a soil storage of acidity caused by the falling water table means that proposed measures to increase recharge in the area by clearing of vegetation for urban development, thinning vegetation by increasing fire frequency, or by the reinjection of treated wastewater would need to be managed carefully to minimise the risk of increasing the leaching of metals from soils into groundwater as the water table rebounds.

Although soil liming is a potential management measure to reverse the acidification trend, significant improvements in subsoil and shallow groundwater quality would only take place with the complete reversal of the ion-exchange processes that are causing the depletion of base cations and the creation of a pool of soluble aluminium in the unsaturated zone (Appelo and Postma, 2005). That is, the time frame for remediating the acidity problem could be comparable with the time it took for the problem to develop.

100 YEARS

7. RECOMMENDATIONS

This study has indicated that groundwater acidification is taking place in the superficial aquifer in at least part of the Gnangara Mound groundwater flow system, but the extent of the problem and its effects on the ecology of *Banksia* woodlands in the area are not known. It is therefore recommended that further investigations are undertaken and specific monitoring programs are established to provide information for managing acidification in the area. These include:

- Undertaking detailed soil investigations to quantify the inputs and outputs of acidity from the unsaturated zone, and to determine the extent to which base cations have been depleted and soluble aluminium species have accumulated in soil profiles in the area.

- Establishing a regional network of sites to monitor the composition and rate of deposition of solutes in both rainfall and dry fallout, and the rate at which they infitrate into soils on the Gnangara Mound.
- Establishing a regional network of bores to monitor changes in water quality at the water table and to enable the extent and depth of penetration of the acidification front to be determined.
- Undertaking investigations to determine the current health of woodland ecosystems, and to determine the relationship between ecological health and soil and groundwater quality in the area.
- Establishing a network of sites to enable changes in vegetation quality to be determined in relation to changes in soil and groundwater quality.
- Continue and possibly expand the current wetland monitoring program to enable changes in the biodiversity of aquatic fauna and wetland water quality to be determined.

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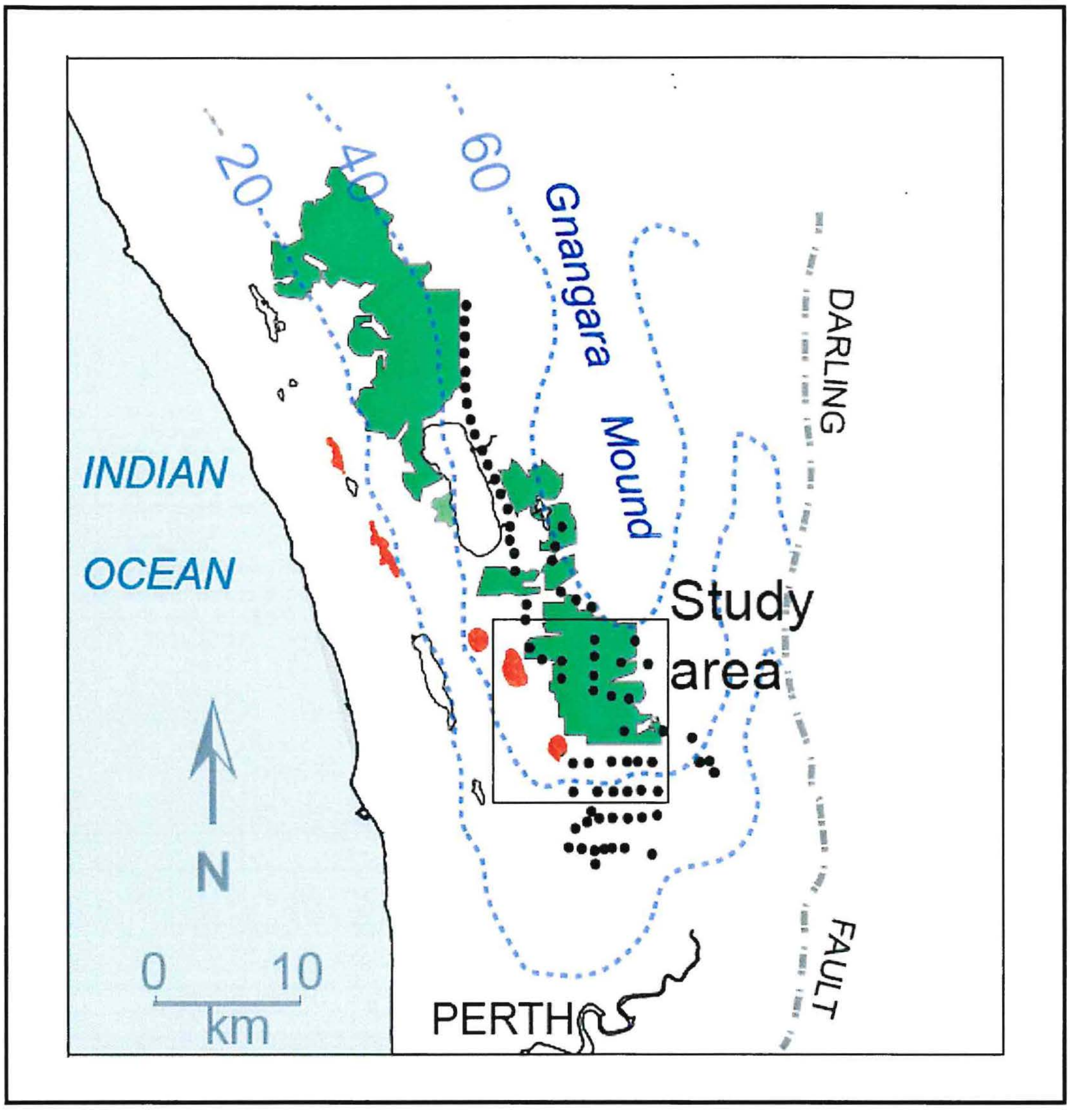


Figure 1. Location of the Gnangara Mound and the investigation area for this study in relation to the distribution of water supply production bores in the unconfined aquifer (black dots) and pine plantations (areas shaded in green). Water table contours (elevations in m AHD) are shown as dashed lines. Major wetlands on the Gnangara Mound that are known to have become either permanently or episodically acidic are shaded in red.

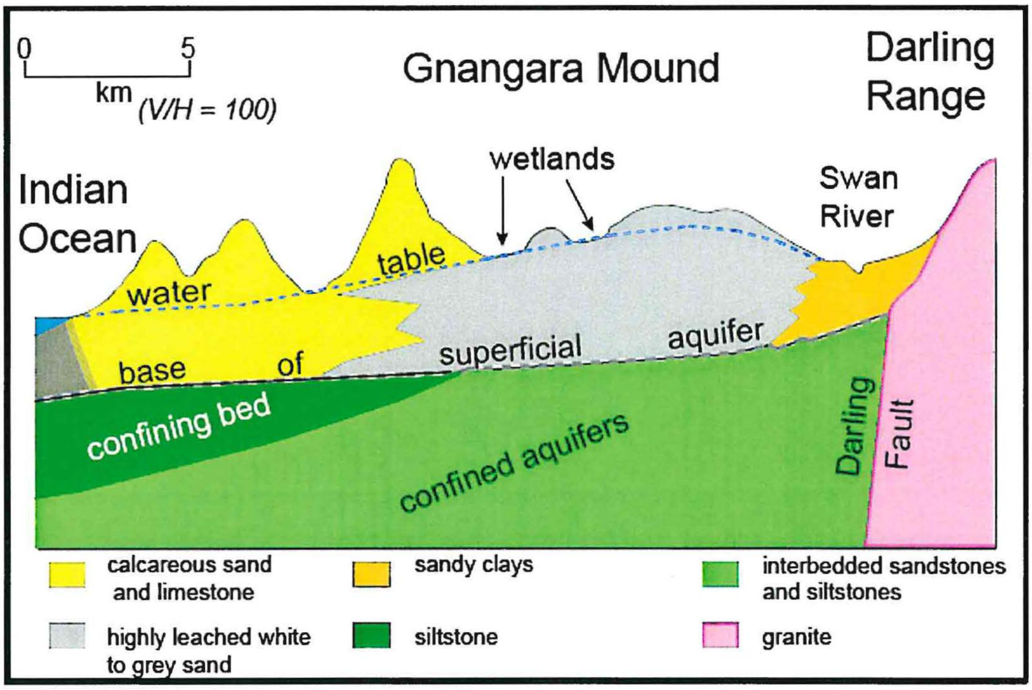


Figure 2. Schematic west-east cross-section of the Gnangara Mound showing variations in the lithology of sediments in the superficial aquifer across the Swan Coastal Plain. Groundwater in the highly leached siliceous sands in the centre of the Swan Coastal Plain (Bassendean Sand) is particularly vulnerable to acidification, and consequently this area was the target of investigations carried out in this study.

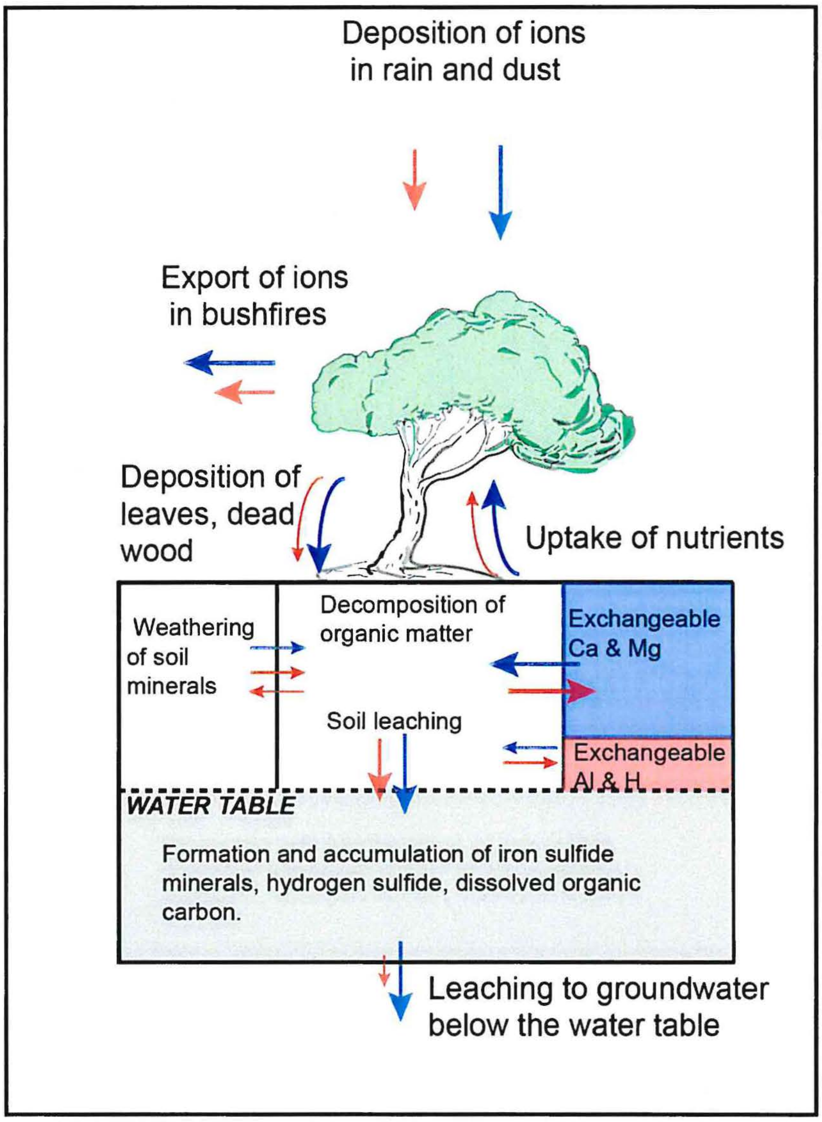


Figure 3. Acid and base inputs and outputs from soil due to geochemical interactions between the atmosphere, vegetation, groundwater and the soil. Acid inputs and outputs are shown as red arrows, and base inputs and outputs are shown as blue arrows. The size of each arrow is approximately proportional to the magnitude of each flux.

Under natural conditions, soils typically have a large "pool" of exchangeable calcium and magnesium (blue compartment) which help buffer the soil against large changes in acidity. Conversely, there is usually only a limited amount of exchangeable acids (hydrogen and aluminium ions) available to acidify soil (red compartment).

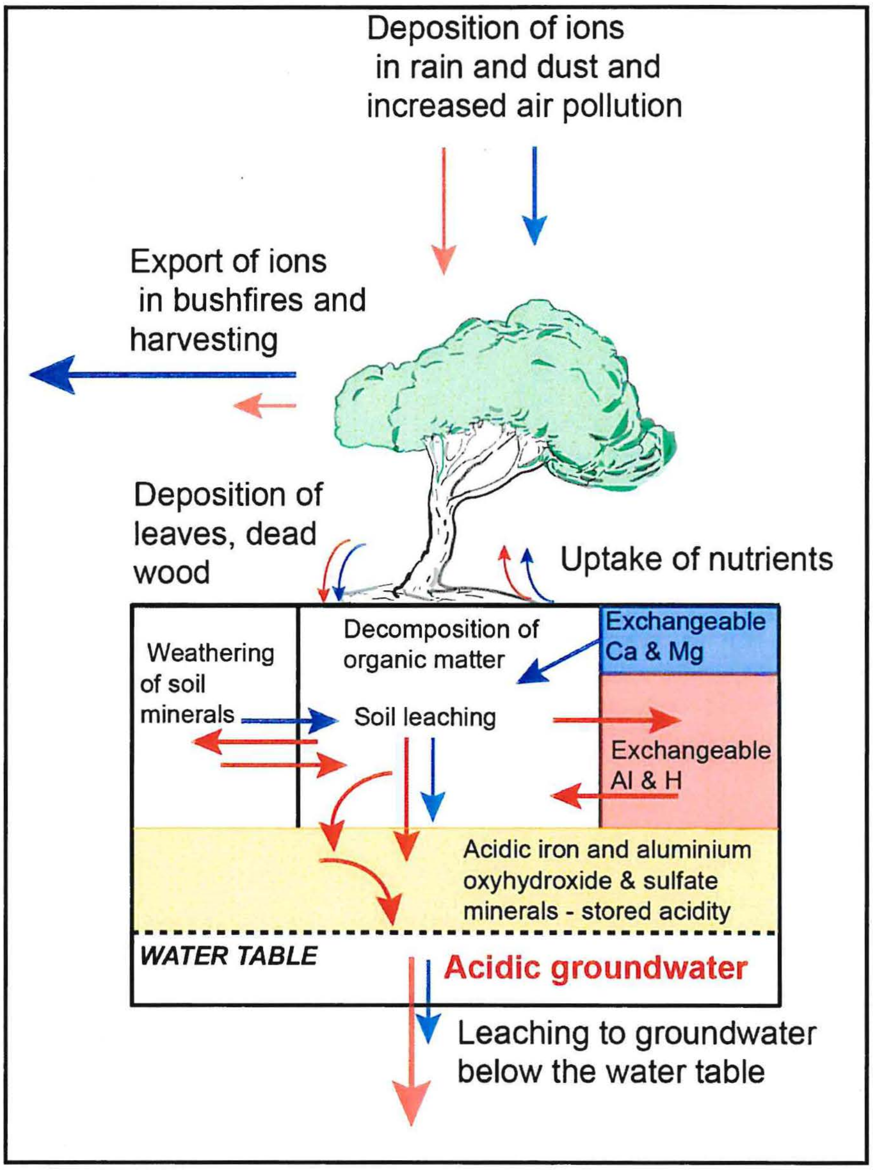


Figure 4. The lowering of the water table by pumping and low rainfall leads to progressive drying of the soil which accelerates the oxidation and loss of organic matter and increases soil acidity. This is usually exacerbated by the increased frequency and intensity of bushfires (and timber harvesting) which increases the rate of loss of calcium and magnesium from the soil. The rate of leaching of calcium and magnesium in soil also increases, and these ions are replaced by exchangeable aluminium and hydrogen ions. As the water table falls, iron sulfide minerals are oxidised, creating a large amount of stored acidity that progressively leaches to groundwater together with large amounts of nitrogen and phosphorus, and metals.

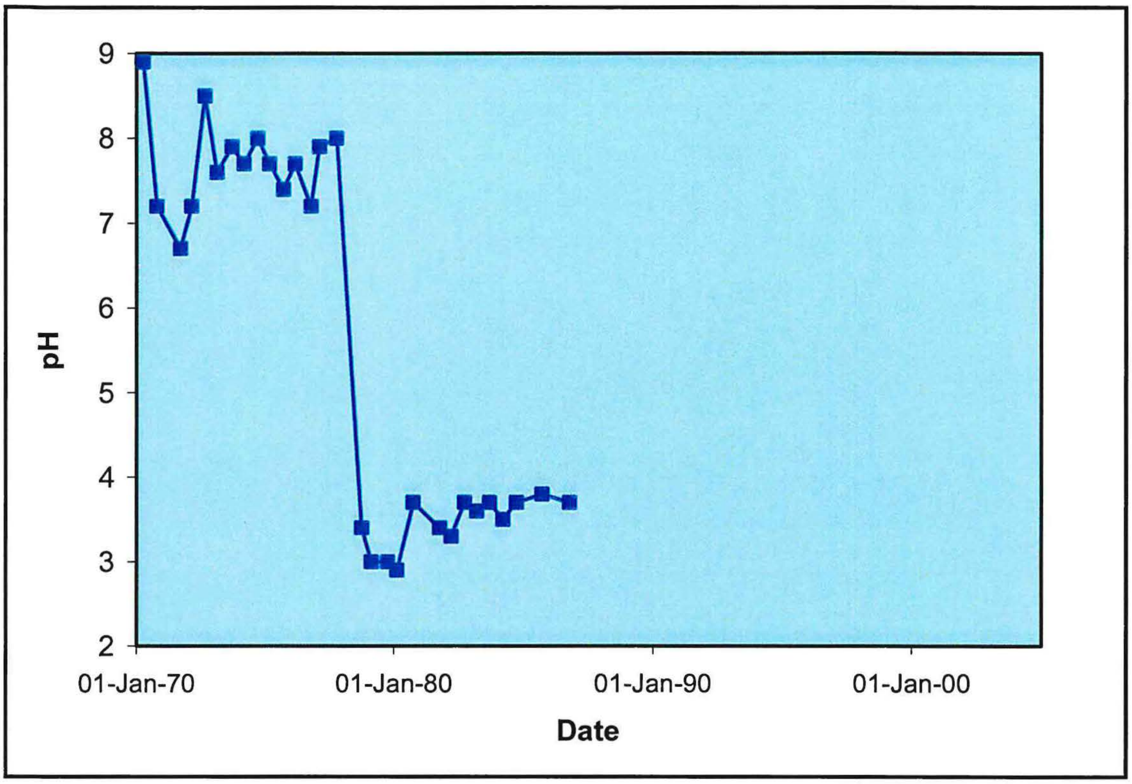
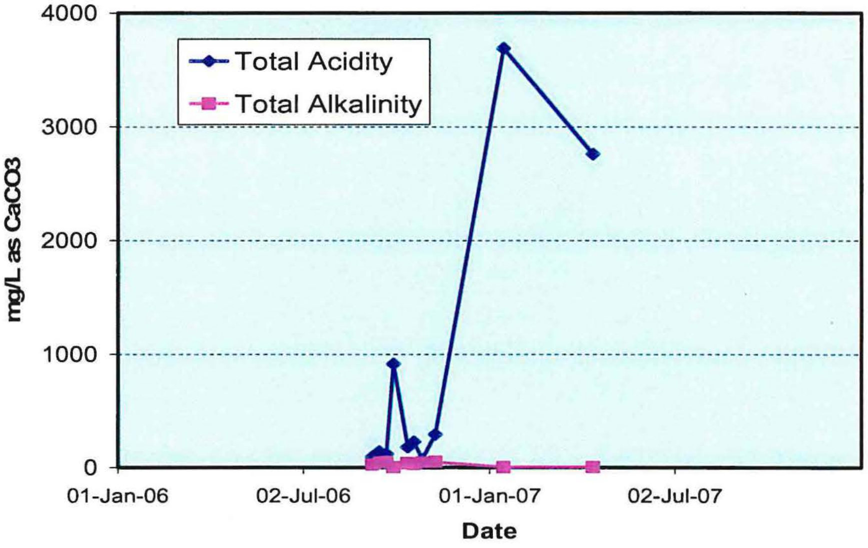


Figure 5. Historical changes in pH in Lake Gnangara.



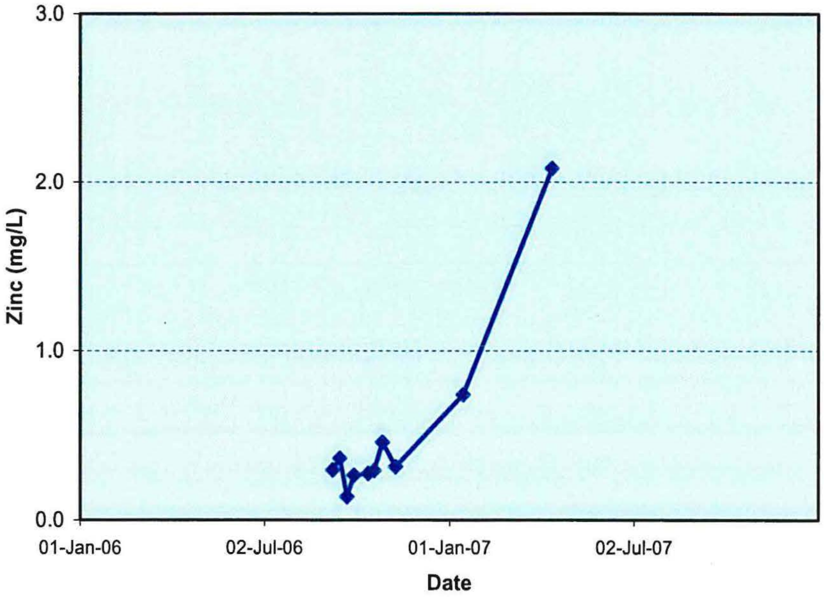


Figure 6. Acidification of groundwater caused by dewatering for sewer construction in Ellenbrook on the Gnangara Mound

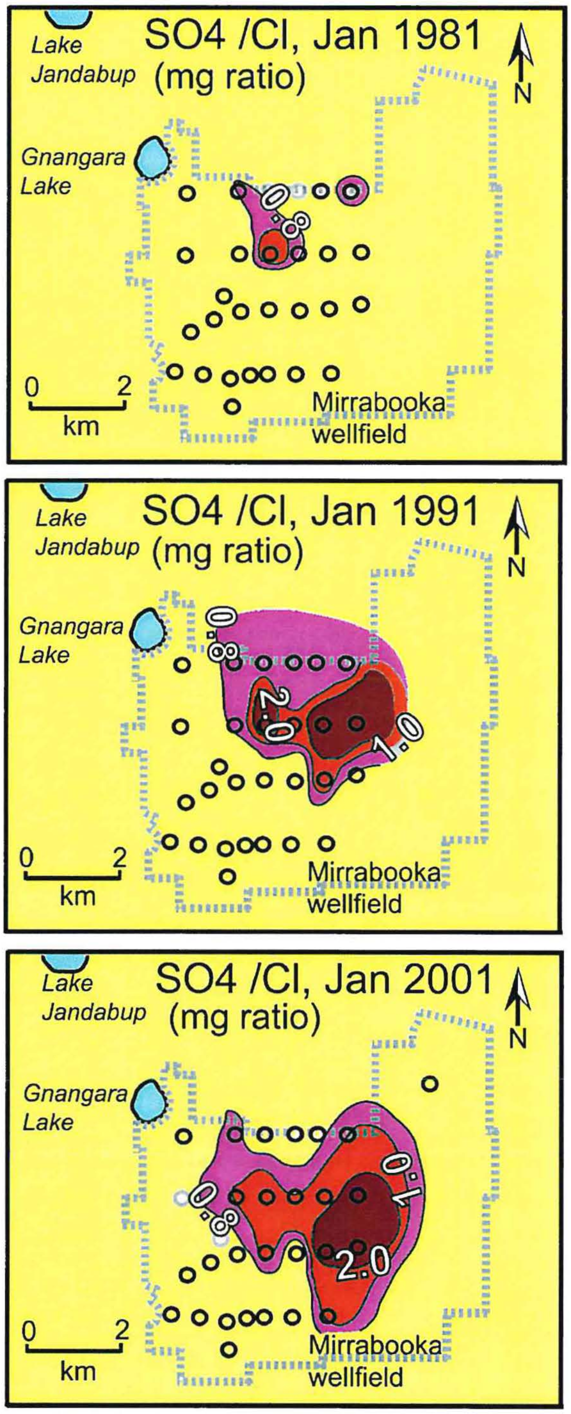


Figure 7. Changes in the sulphate/chloride ratio with time measured in production bores in the Mirrabooka borefield.

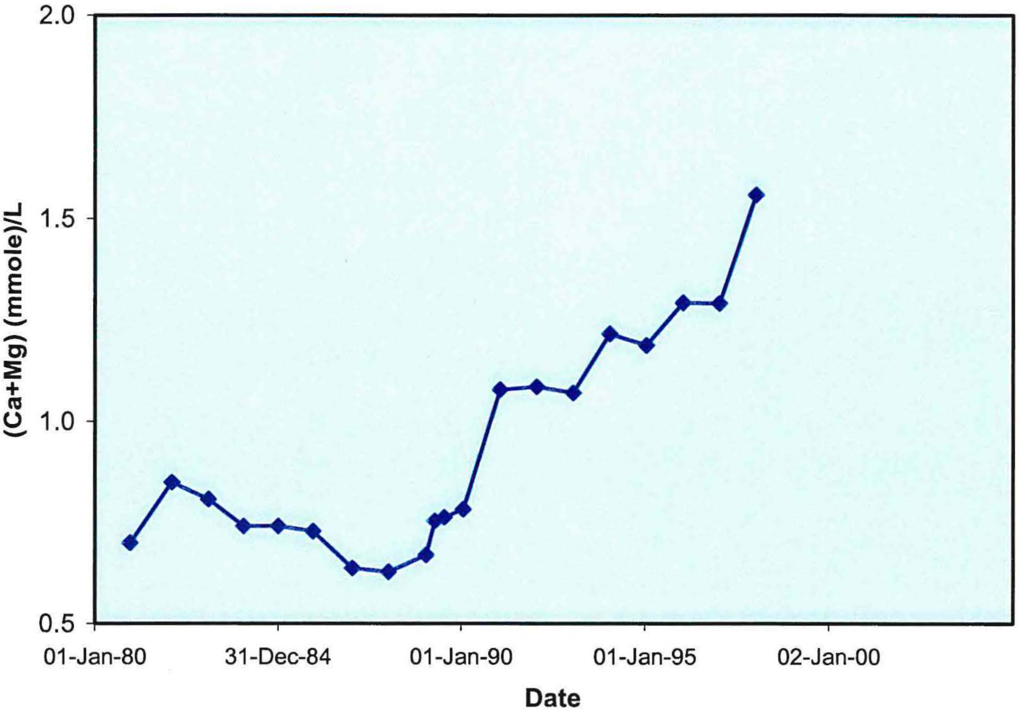


Figure 8. Progressive increases in concentrations of calcium and magnesium ions with time in groundwater sampled from Mirrabooka production bore M140, indicative of base cation leaching from soils in the area. This trend has a high level of statistical significance – the linear correlation coefficient for all the data is 0.82, and for the data commencing in 1988 is 0.96.

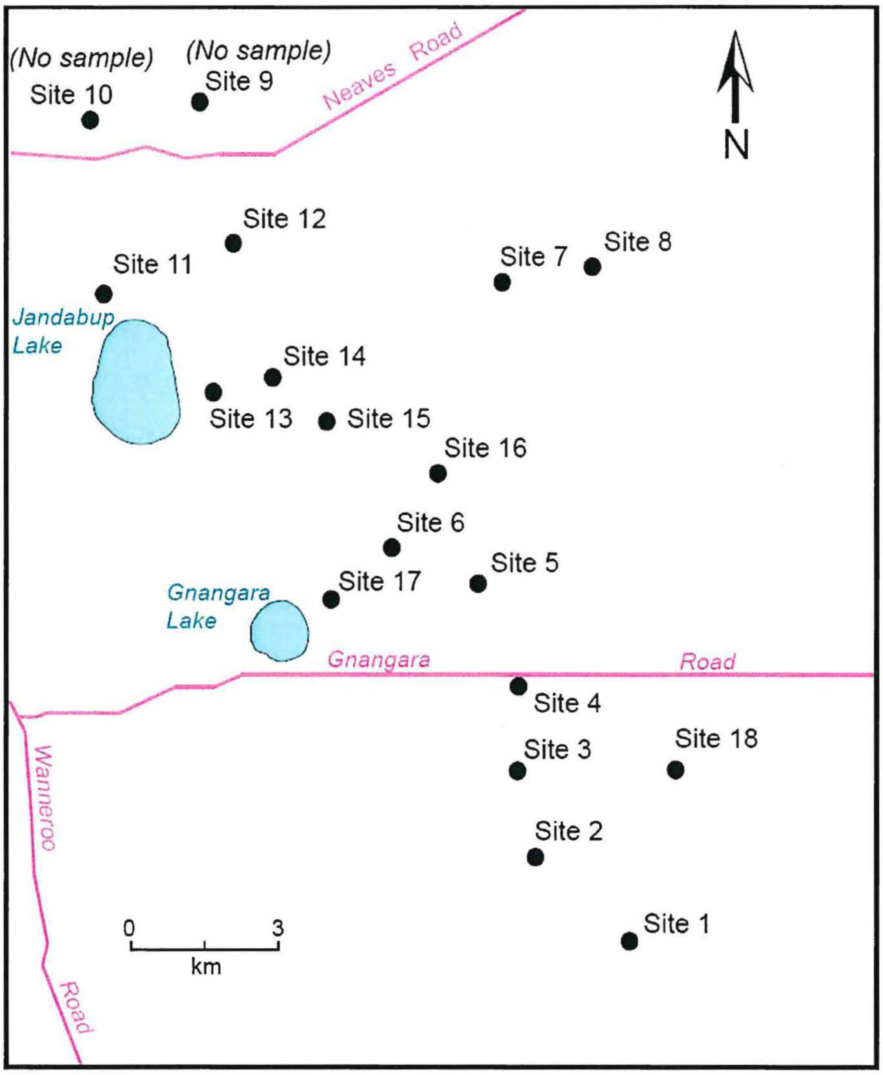


Figure 9. Locations of soil and groundwater investigation sites.

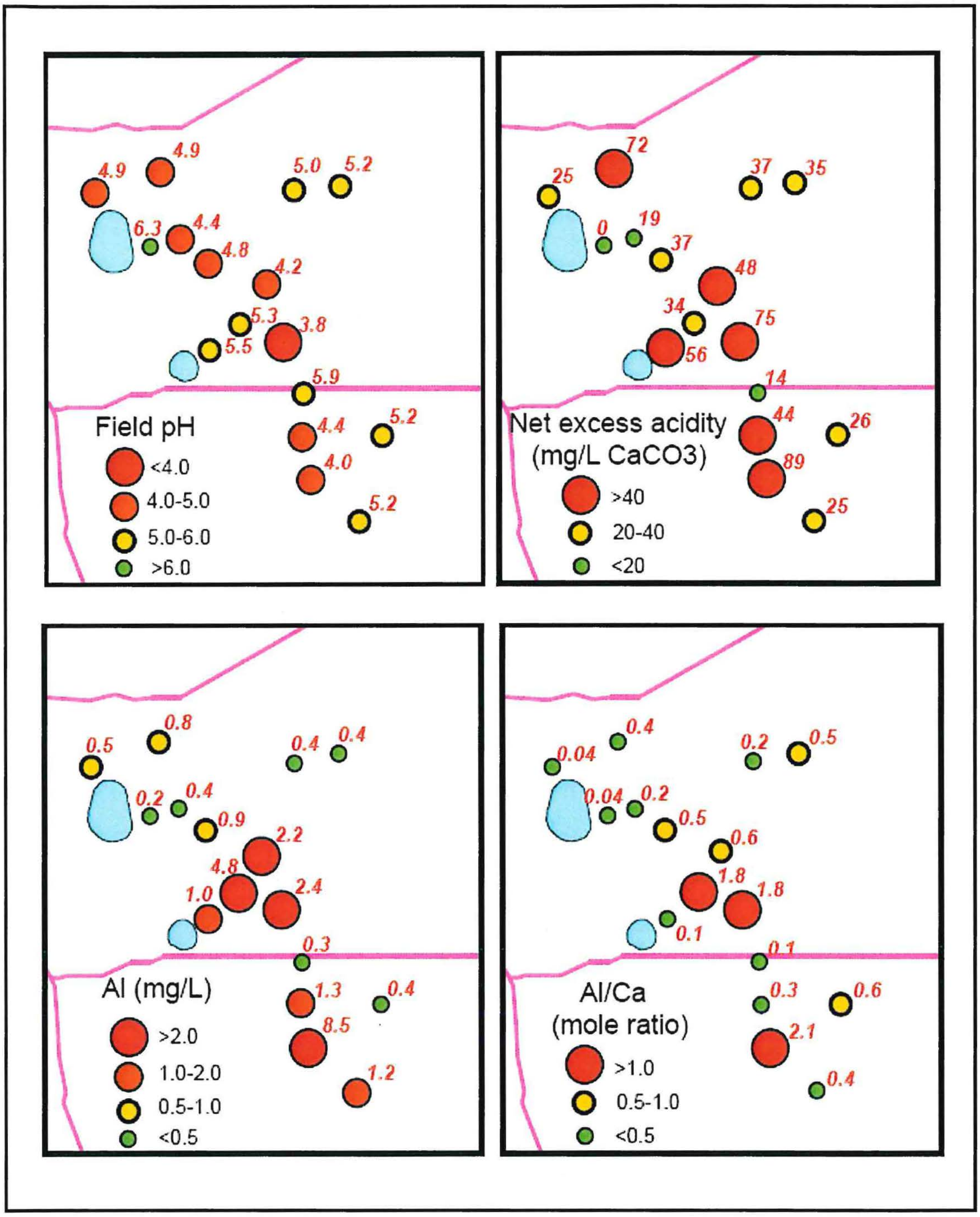


Figure 10 Indicators of groundwater acidity at the water table.

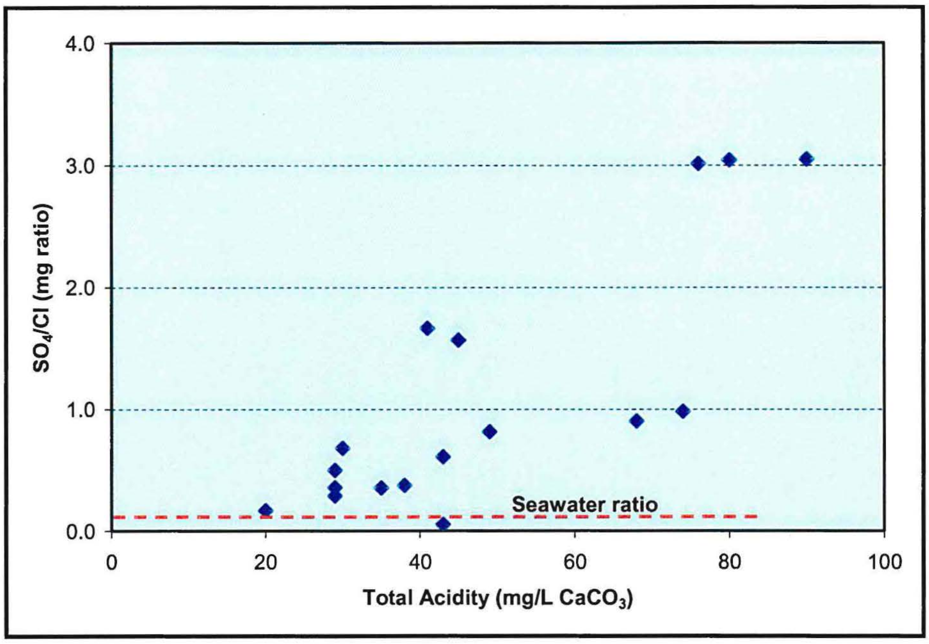


Figure 11. Relationship between SO_4/Cl and the acidity of groundwater indicating that acidic groundwater is receiving sulphur inputs in addition to seawater-derived salts in rainfall. Given the limited nature of fertiliser use in the area, this is most likely to be from the oxidation of reduced sulphur compounds with water table decline.

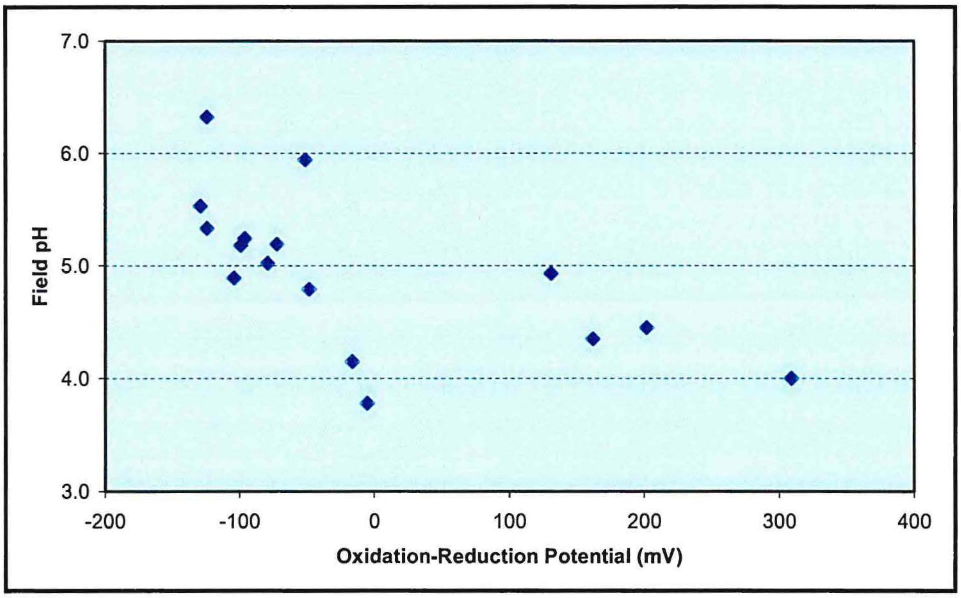


Figure 12. Relationship between field measurements of pH and oxidation-reduction potential in groundwater near the water table.

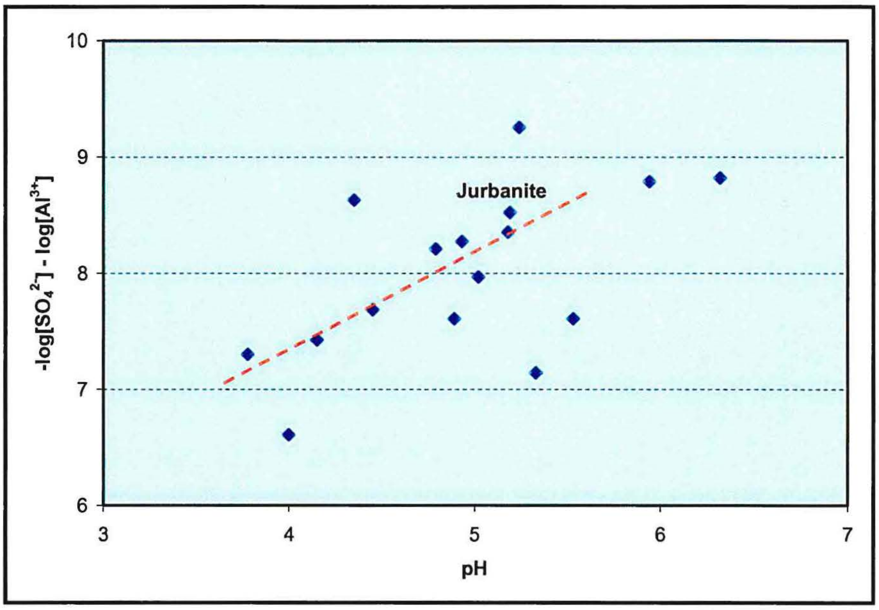


Figure 13. Thermodynamic data for 25°C from Ball and Nordstrom (1991) indicate that jurbanite could be one of the phases controlling aluminium concentrations in shallow groundwater in the Gnangara study area.

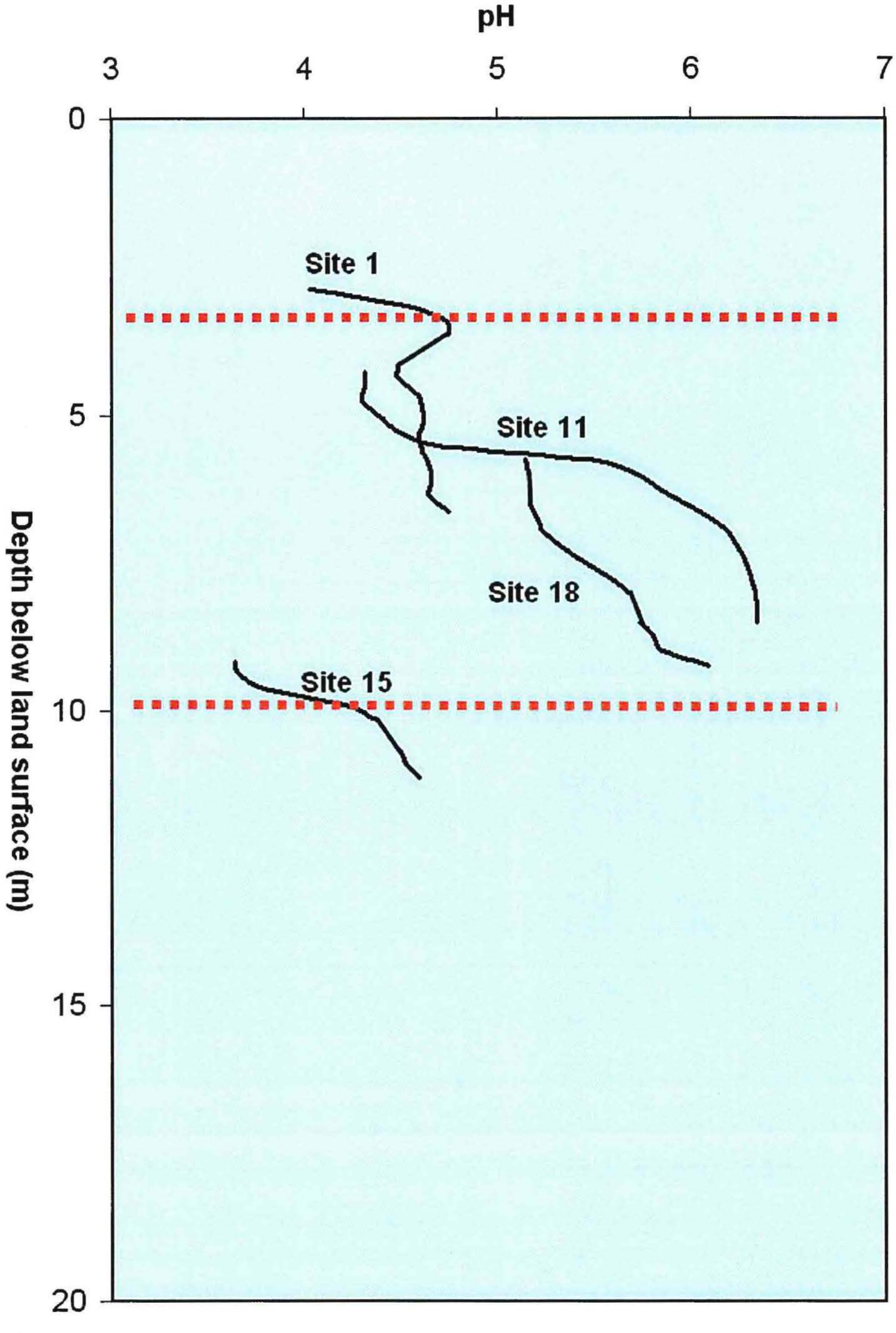


Figure 14 A compilation of pH profiles from investigation sites that suggest that the acidification front has on average penetrated to a depth of 4 to 10 metres. The acidification front may be much deeper at sites where changes in water balance caused by vegetation clearing or groundwater abstraction have increased the rate of movement of solutes in porewater.

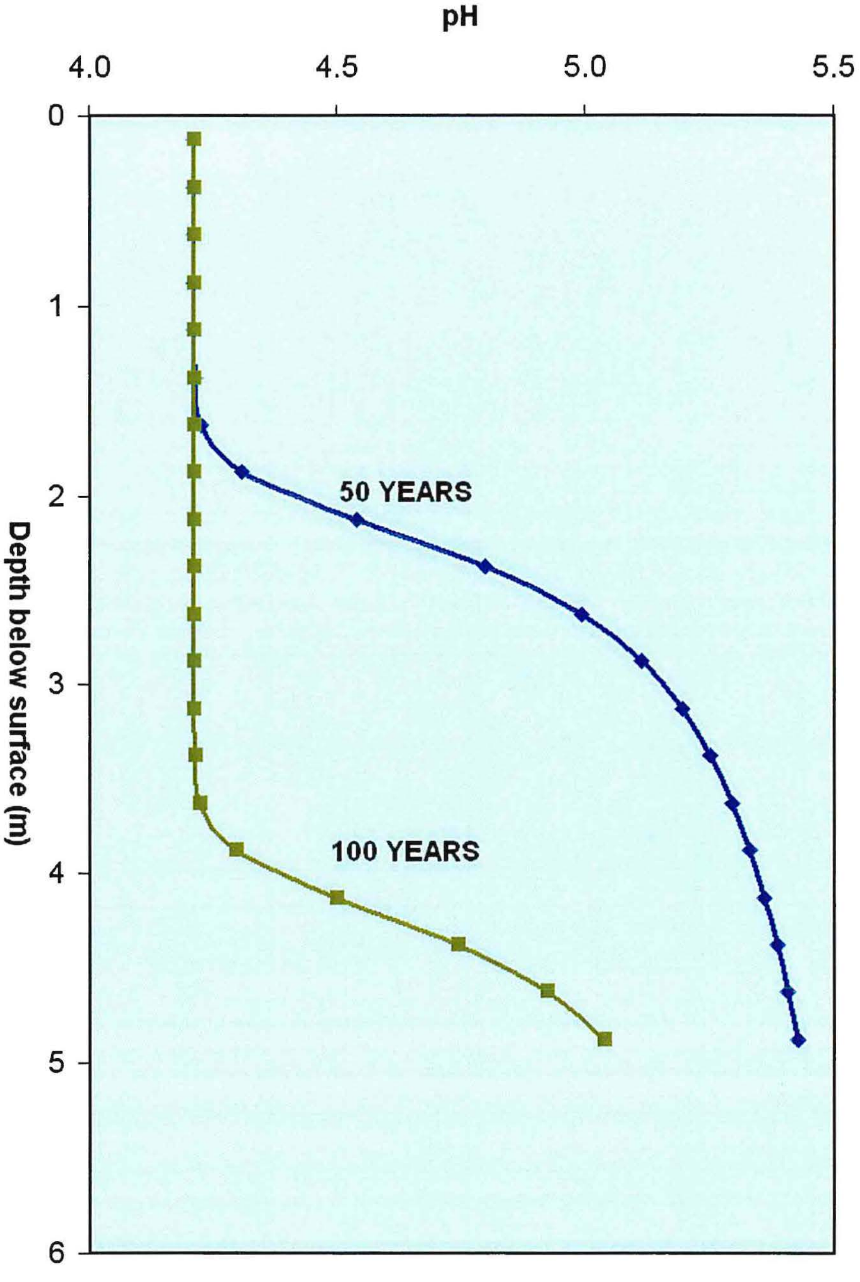


Figure 15. PHREEQC simulation of the development of an acidification front on the Gnangara Mound using the methodology of Appelo and Postma (2005)

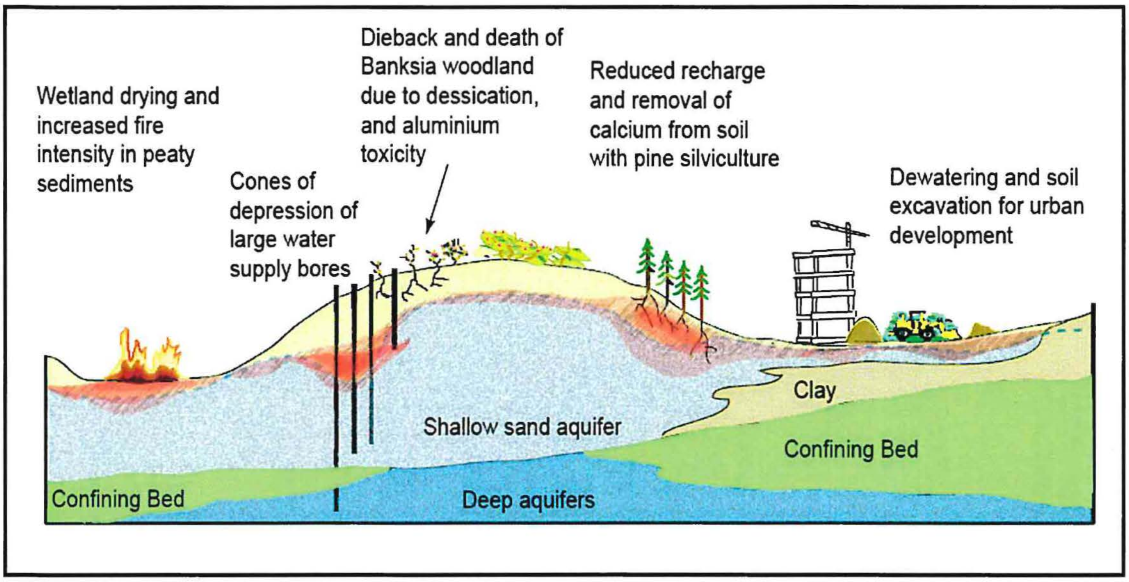
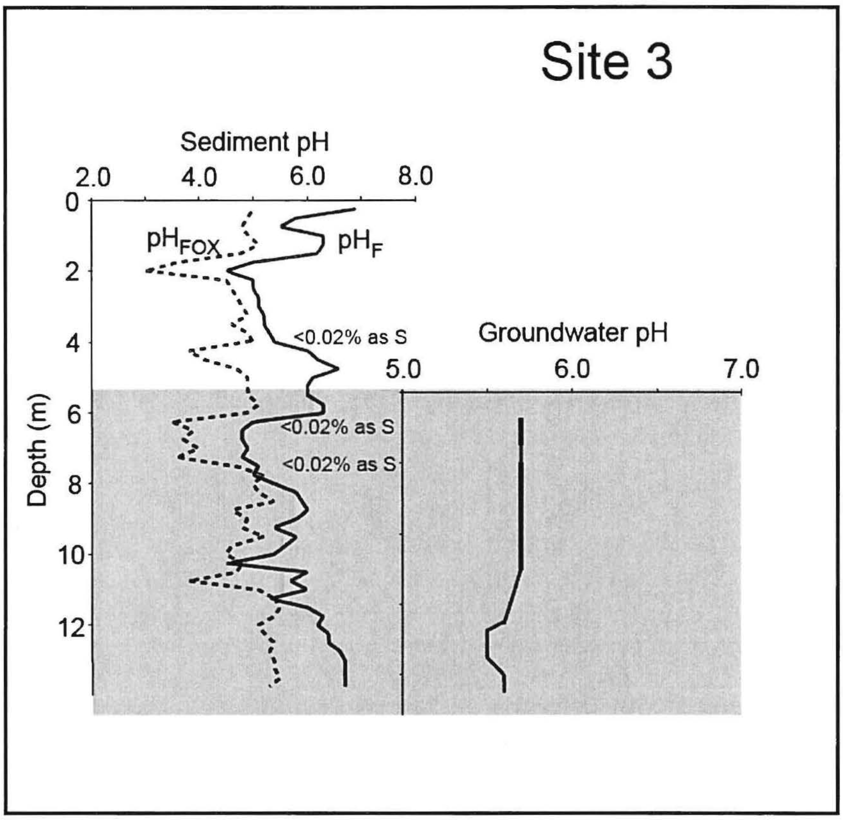
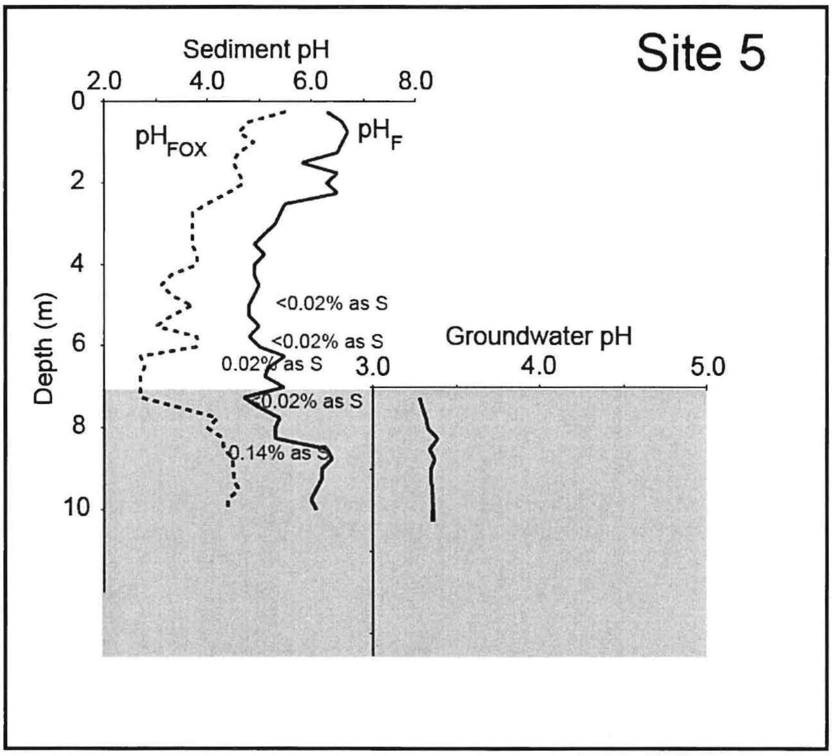


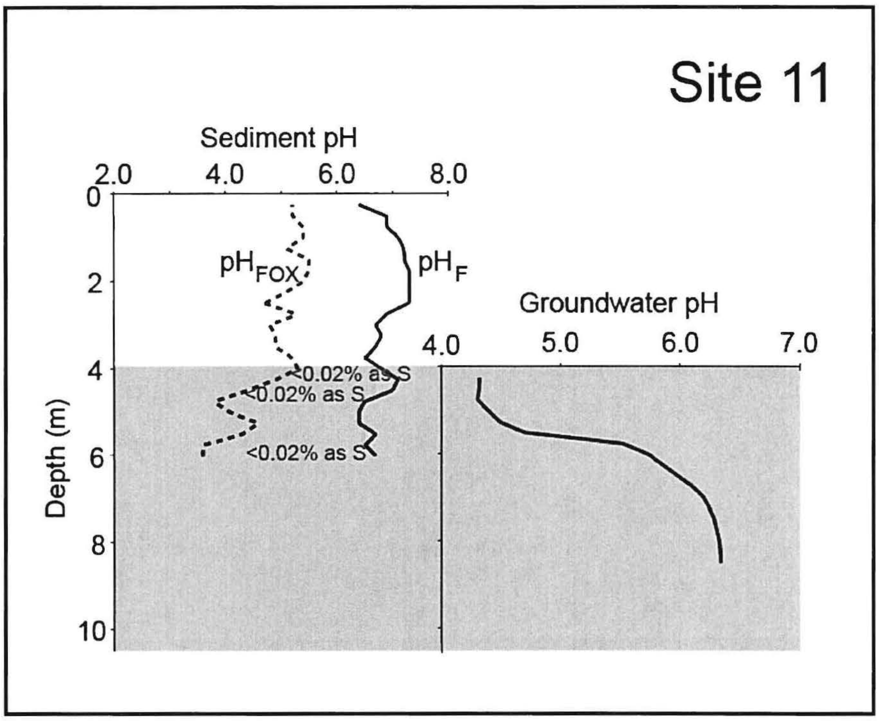
Figure 16. Conceptual model of acidification on the Gnangara Mound. A regional acidification front initiated by increasing air pollution levels at the start of the 20th century has penetrated on average 4 to 10 m below the land surface, and is below the water table in many areas. Low rainfall and increasing groundwater use over the last 30 years have caused the water table to fall and allowed calcium and magnesium to be leached from soil profiles, increasing the vulnerability of soils to aluminium toxicity. Pine silviculture and horticultural practices are also increasing soil acidity through the removal of calcium and magnesium in harvested biomass and through the introduction of acidic nitrogen compounds in fertilisers. The increased drying of wetland sediments and fire intensity has caused the oxidation of pyrite in peaty sediments, allowing sulphuric acid to be leached into groundwater. Most recently, dewatering associated with new urban developments on the eastern flank of the Gnangara Mound has increased groundwater acidity.

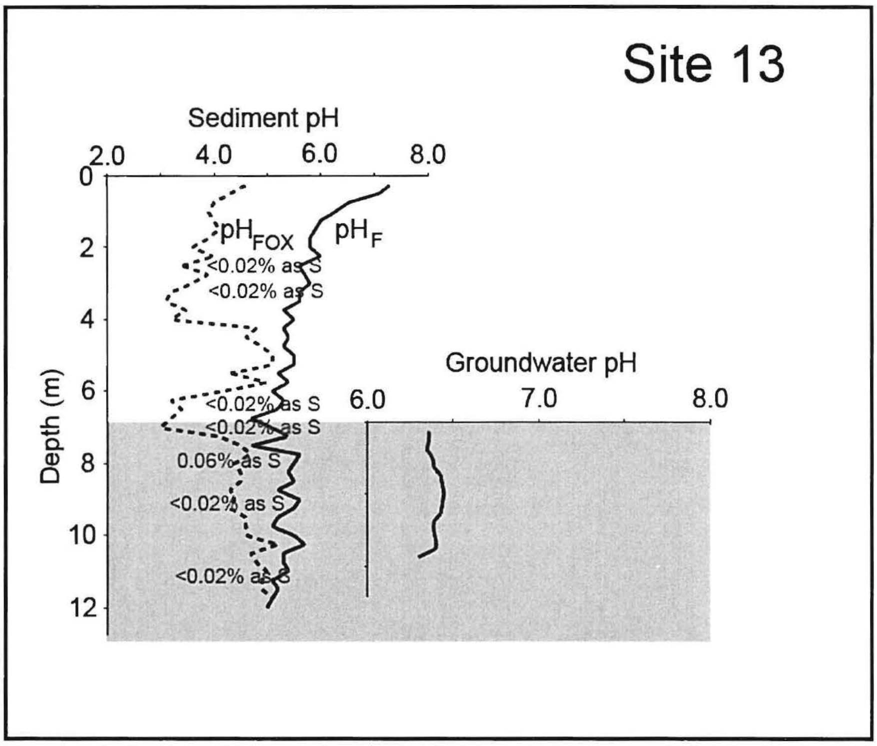
APPENDIX 1

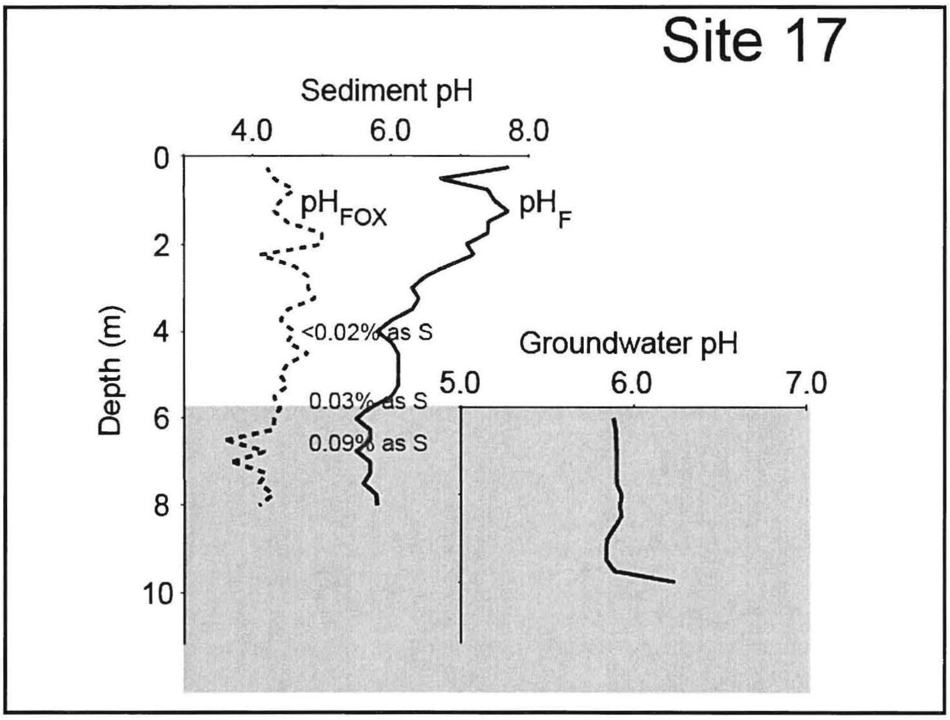
Sediment and groundwater pH profiles

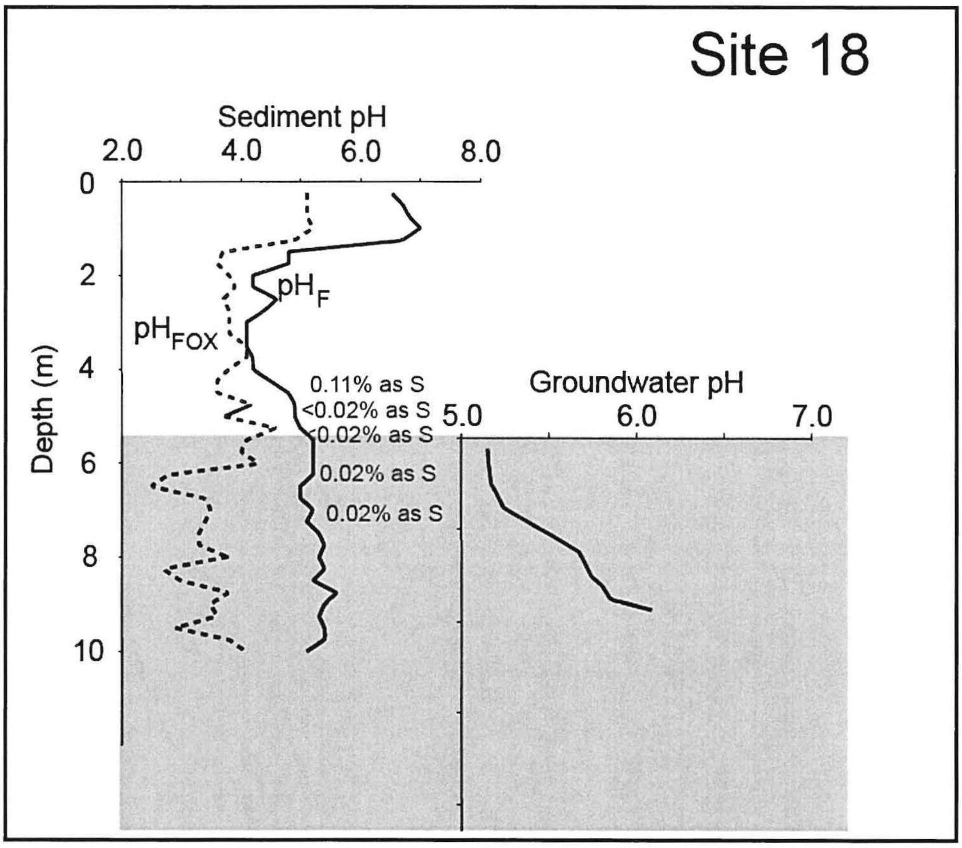

Site 3
Sediment pH
2.0
4.0
6.0
8.0
0
2
4
6
8
10
12
Depth (m)
pH$_{FOX}$
pH$_F$
<0.02% as S
<0.02% as S
<0.02% as S
Groundwater pH
5.0
6.0
7.0

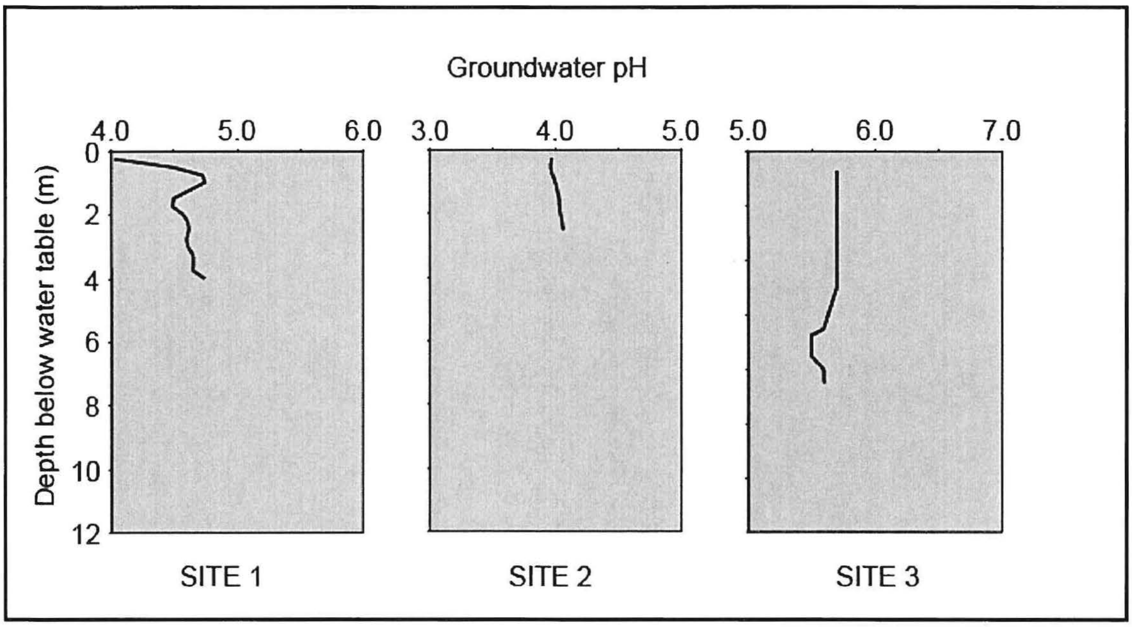

Site 5
Sediment pH
2.0
4.0
6.0
8.0
0
2
4
6
8
10
Depth (m)
pH$_{FOX}$
pH$_F$
<0.02% as S
<0.02% as S
0.02% as S
<0.02% as S
0.14% as S
Groundwater pH
3.0
4.0
5.0

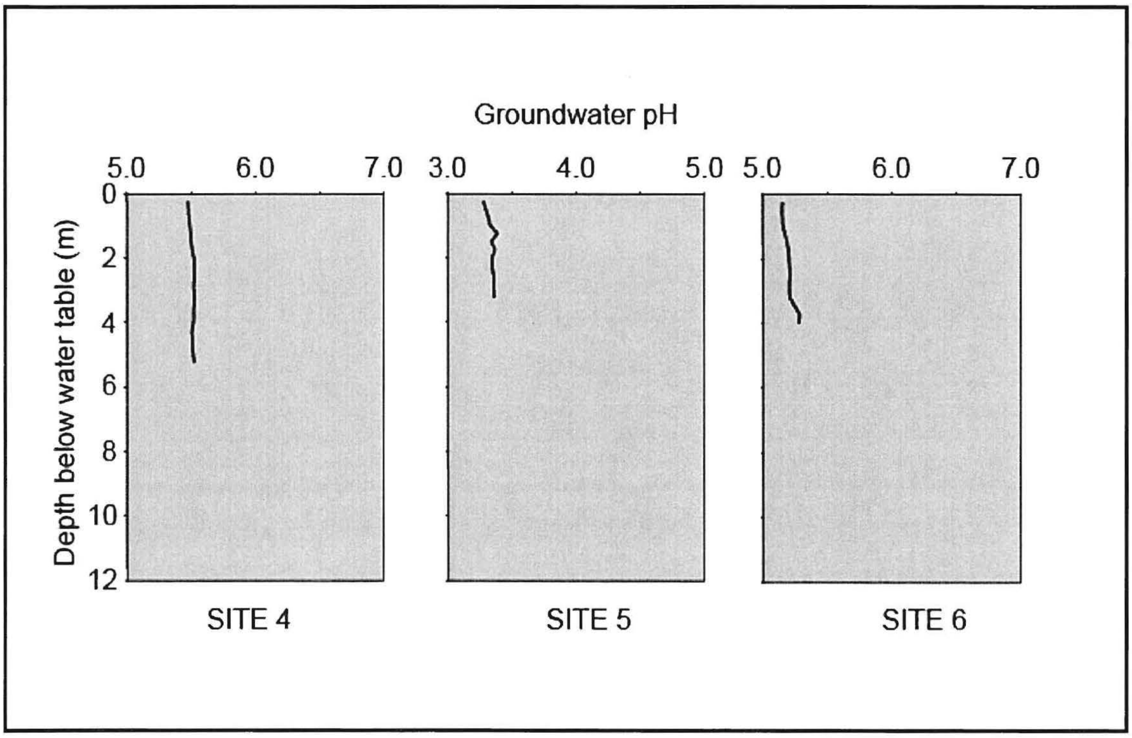

Site 11
Sediment pH
2.0
4.0
6.0
8.0
0
2
4
6
8
10
Depth (m)
pH$_{FOX}$
pH$_F$
<0.02% as S
<0.02% as S
<0.02% as S
Groundwater pH
4.0
5.0
6.0
7.0

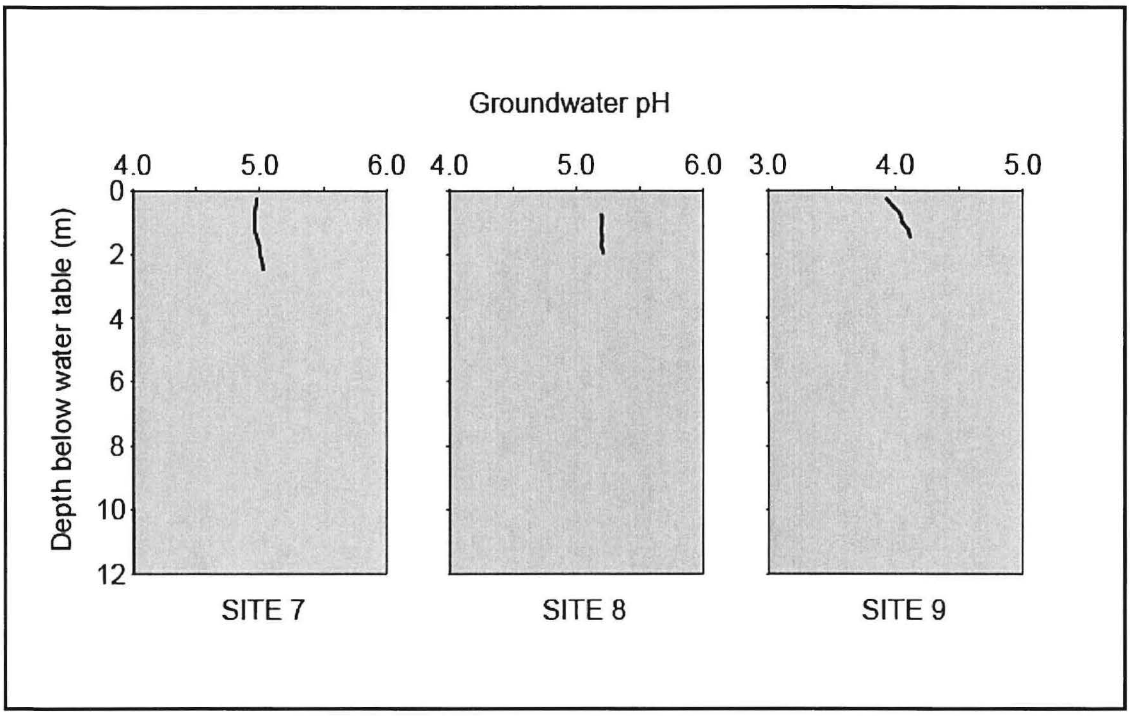

Site 13
Sediment pH
2.0
4.0
6.0
8.0
0
2
4
6
8
10
12
Depth (m)
pH$_{FOX}$
pH$_F$
<0.02% as S
<0.02% as S
<0.02% as S
<0.02% as S
0.06% as S
<0.02% as S
<0.02% as S
Groundwater pH
6.0
7.0
8.0

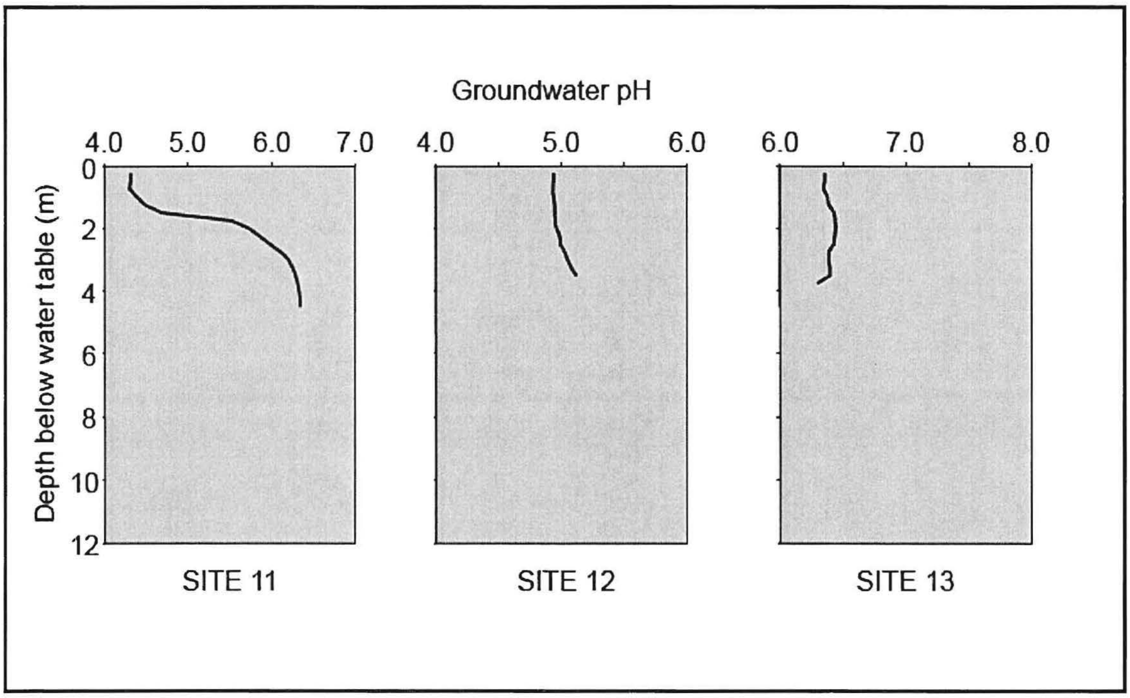

Site 17
Sediment pH
4.0
6.0
8.0
0
2
4
6
8
10
Depth (m)
pH$_{FOX}$
pH$_F$
<0.02% as S
0.03% as S
0.09% as S
Groundwater pH
5.0
6.0
7.0

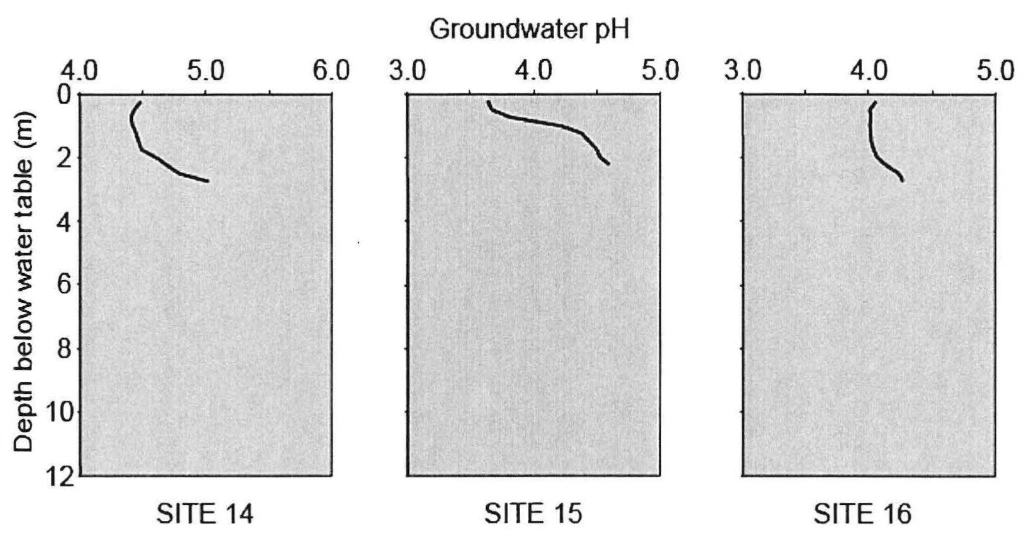

Site 18
Sediment pH
2.0
4.0
6.0
8.0
0
2
4
6
8
10
Depth (m)
pH$_F$
pH$_{FOX}$
0.11% as S
<0.02% as S
<0.02% as S
0.02% as S
0.02% as S
Groundwater pH
5.0
6.0
7.0

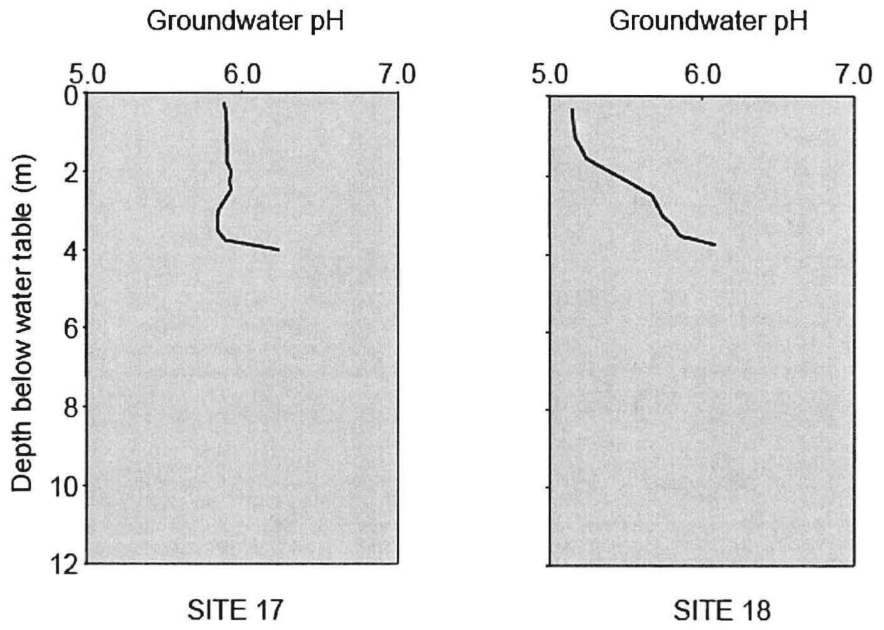

Groundwater pH
4.0
5.0
6.0
3.0
4.0
5.0
5.0
6.0
7.0
Depth below water table (m)
0
2
4
6
8
10
12
SITE 1
SITE 2
SITE 3


Groundwater pH
5.0
6.0
7.0
3.0
4.0
5.0
5.0
6.0
7.0
Depth below water table (m)
0
2
4
6
8
10
12
SITE 4
SITE 5
SITE 6


Groundwater pH
4.0
5.0
6.0
4.0
5.0
6.0
3.0
4.0
5.0
Depth below water table (m)
0
2
4
6
8
10
12
SITE 7
SITE 8
SITE 9


Groundwater pH
4.0
5.0
6.0
7.0
4.0
5.0
6.0
6.0
7.0
8.0
Depth below water table (m)
0
2
4
6
8
10
12
SITE 11
SITE 12
SITE 13


Groundwater pH
4.0
5.0
6.0
3.0
4.0
5.0
3.0
4.0
5.0
Depth below water table (m)
0
2
4
6
8
10
12
SITE 14
SITE 15
SITE 16


Groundwater pH
Groundwater pH
5.0
6.0
7.0
5.0
6.0
7.0
Depth below water table (m)
0
2
4
6
8
10
12
SITE 17
SITE 18

APPENDIX 2

Sediment and groundwater analyses

Table A2.1. Major ion analyses for groundwater samples

Site	Lab pH	TDS (mgL^{-1})	Alkalinity (mgL^{-1} $CaCO_3$)	Acidity (mgL^{-1} $CaCO_3$)	SO_4^{2-} (mgL^{-1})	Cl^- (mgL^{-1})	Ca^{2+} (mgL^{-1})	Mg^{2+} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})
1	5.8	167	10	35	10	28	4	3	23	<1
2	4.34	270	1	90	75	24.6	6	5	17	<1
3	4.52	238	1	45	42	26.8	7	6	23	<1
4	6.12	360	15	29	14	39	5	5	19	<1
5	3.75	366	1	74	54	55	2	7	41	<1
6	5.67	496	9	43	39	64	4	9	39	1
7	5.54	412	4	41	70	42	3	15	31	<1
8	5.78	564	8	43	4	72	1	4	40	2
11	5.73	300	7	30	30	44	18	4	20	3
12	5.44	506	8	80	76	25	3	15	27	1
13	6.49	272	32	29	17	58.5	8	6	33	1
14	4.6	286	1	20	16	94	3	7	46	2
15	5.19	158	1	38	17	45	3	4	27	1
16	4.27	202	1	49	44	54	5	6	33	1
17	5.85	510	12	68	65	72	4	17	44	1
18	5.59	192	3	29	19	38	1	4	23	<1

Table A2.2 Metal analyses for groundwater samples (in mg L^{-1})

Site	Fil. Al	Fil. Fe	T. Al	T. Fe	As	Cd	Cr	Cu	Pb	Mn	Ni	Zn
1	1.15	0.14	0.89	0.15	<0.001	<0.0001	0.001	<0.001	<0.001	0.001	0.001	<0.005
2	8.48	3.31	0.12	0.9	0.024	0.0005	<0.001	0.003	<0.001	0.195	0.005	0.006
3	1.27	2.7	20.8	5.04	0.002	<0.0001	0.024	0.004	0.04	0.004	0.006	0.013
4	0.3	0.3	2.4	0.3	<0.001	0.004	0.002	0.012	0.002	0.001	<0.010	<0.05
5	2.4	0.8	3.6	<0.05	<0.001	<0.0001	0.004	0.01	0.017	0.002	0.001	0.008
6	4.8	1.1	47	1.2	0.002	<0.0001	0.034	0.005	0.05	0.003	0.004	0.008
7	0.4	1.2	3.4	1.3	<0.001	<0.0001	<0.0001	<0.0001	0.017	0.002	0.001	0.006
8	0.36	0.18	12.9	<0.05	0.001	<0.0001	0.005	<0.0001	0.023	0.003	0.003	0.005
11	0.46	0.49	1.6	0.88	0.002	<0.0001	0.003	0.065	0.012	0.018	0.026	0.082
12	0.84	0.43	8.15	0.49	<0.001	<0.0001	0.003	0.001	0.026	0.003	0.002	0.009
13	0.23	3.38	0.04	0.24	0.004	<0.0001	<0.001	0.003	<0.001	1.18	0.004	0.006
14	0.38	0.07	5.9	0.24	0.001	<0.0001	0.004	0.002	0.018	0.001	0.002	
15	0.94	0.13	2.02	0.08	<0.001	<0.0001	0.001	<0.001	0.005	0.001	<0.001	
16	2.2	1.4	2.4	2.2	<0.001		0.001	<0.001	0.002	<0.001	0.011	
17	0.98	5.29	19.3	7.1	0.001	<0.0001	0.039	0.014	0.036	0.048	0.01	0.016
18	0.41	1.2	8.08	1.2	0.001	<0.0001	0.012	0.008	0.01	0.006	0.005	0.009

Notes: Fil. = filtered through a 0.45 μm filter; T = total unfiltered.

Table A2.3 Results of laboratory measurements of soil samples for acidity indicators. Refer to Ahern et al. (2004) for definitions and analytical methodologies for the parameters outlined in the Table.

Site	Sample depth (m)	$\mathrm{pH}_{\mathrm{KCl}}$	$\mathrm{pH}_{\mathrm{OX}}$	S_{Cr} (%S)	S_{POS} (%S)	TAA (%S)	TAA (mol H^+/tonne)	TPA (%S)	TSA (%S)	Net Acidity (%S)
3	4.00	5.4	4.6	< 0.02	< 0.02	< 0.02	2	< 0.02	< 0.02	< 0.02
	4.00	5.9	4.2	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	6.00	6.3	5.5	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	6.25	5.3	4.4	< 0.02	< 0.02	< 0.02	2	< 0.02	< 0.02	< 0.02
	7.00	5.4	4.3	< 0.02	< 0.02	< 0.02	2	< 0.02	< 0.02	< 0.02
5	5.25	6.0	3.8	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	6.25	5.9	4.1	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	7.25	5.5	3.5	< 0.02	< 0.02	< 0.02	4.0	0.02	< 0.02	< 0.02
	7.75	5.5	3.6	< 0.02	< 0.02	< 0.02	4.0	< 0.02	< 0.02	< 0.02
	9.25	5.3	3.6	< 0.02	< 0.02	0.03	17	0.14	0.11	0.03
11	4.00	6.0	3.9	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	4.75	6.1	3.8	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	6.00	6.1	4.3	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
13	2.50	6.4	5.0	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	3.50	6.2	5.0	< 0.02	0.02	< 0.02	< 2	< 0.02	< 0.02	0.02
	6.25	9.5	7.0	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	7.00	6.2	4.0	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	8.00	5.4	3.3	< 0.02	< 0.02	< 0.02	7	0.06	0.04	< 0.02
	9.50	5.7	4.2	< 0.02	< 0.02	< 0.02	2	< 0.02	< 0.02	< 0.02
	11.50	5.7	4.2	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
16	5.25	6.0	3.6	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	8.00	5.2	2.9	< 0.02	< 0.02	< 0.02	12	0.08	0.07	< 0.02
	9.25	5.0	2.8	< 0.02	< 0.02	0.02	15	0.10	0.07	0.02
	10.00	5.2	2.8	< 0.02	< 0.02	< 0.02	10	0.07	0.06	< 0.02
17	4.00	5.7	4.0	< 0.02	< 0.02	< 0.02	2	< 0.02	< 0.02	< 0.02
	5.75	5.5	3.8	< 0.02	< 0.02	< 0.02	6	0.03	< 0.02	< 0.02
	6.50	5.2	3.4	< 0.02	< 0.02	0.02	14	0.09	0.07	0.02
18	4.50	5.4	3.4	< 0.02	< 0.02	0.02	13	0.11	0.09	0.02
	5.00	5.6	4.0	< 0.02	< 0.02	< 0.02	2	< 0.02	< 0.02	< 0.02
	5.75	5.8	4.1	< 0.02	< 0.02	< 0.02	< 2	< 0.02	< 0.02	< 0.02
	6.25	5.0	4.2	< 0.02	< 0.02	< 0.02	10	0.02	< 0.02	< 0.02
	7.00	5.0	4.2	< 0.02	< 0.02	< 0.02	10	0.02	< 0.02	< 0.02