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Detecting the cause of acidification at a seasonal wetland on the Swan Coastal Plain, Western Australia, through laboratory and field mesocosm experiments

Kelli O'Neill
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**DETECTING THE CAUSE OF ACIDIFICATION AT A SEASONAL
WETLAND ON THE SWAN COASTAL PLAIN, WESTERN AUSTRALIA,
THROUGH LABORATORY AND FIELD MESOCOSM EXPERIMENTS**

By

Kelli O'Neill

A Thesis submitted in partial fulfillment of the requirements
for the award of Bachelor of Science (Environmental Management), Honours at the
School Natural Sciences, Edith Cowan University Joondalup.

Date of submission: 10 November 2000

USE OF THESIS

The Use of Thesis statement is not included in this version of the thesis.

ABSTRACT

Acidification ($\text{pH} < 4.5$) was detected at Lake Jandabup, a shallow, seasonal wetland on the Swan Coastal Plain, Western Australia. Concern has been raised because populations of invertebrate species have declined or disappeared since acidification, potentially compromising the status of the lake as a nature reserve.

The lake bed is underlain with pyrite (FeS_2), which oxidises when dry producing sulfates, hydrogen ions and ferrous iron. Being seasonal, Lake Jandabup would be expected to be naturally acidic, but the more recent trend has been a prolonged (> 1 year) and extreme acidification ($\text{pH} < 4.0$). This study endeavoured to explain why the lake may have undergone an acidic change, why it may have recovered and whether it will happen again.

It was hypothesised that the acidification may have been caused by prolonged drying of the lake causing excessive oxidation of pyrite which produced more acid than the wetland could neutralise through buffering. The hypothesis was tested through laboratory and field experiments. The laboratory experiment involved taking intact sediment cores from around the lake, drying them for various lengths of time, and measuring pH, sulfate, total iron, total alkalinity and total acidity upon rehydration. Dried sediment from diatomaceous earth under $\text{Fe}(\text{OH})_3$ precipitate gave the lowest pH of less than 4.0. High sulfates, low alkalinity and low pH were interrelated. While drying in its own right produced low pH, generally there was no significant difference between drying times for release of selected variables.

The field experiment involved the establishment of small *in situ* mesocosms to test for the effects of isolation of water on acid production and buffering capacity. Over an 18 week period between April and August 2000 weekly physico-chemical properties were taken inside and outside each *in situ* core and monthly, sulfate, total iron, total acidity and total alkalinity were tested. The field experiment showed an acidity producing area in the south western corner of the wetland in the diatomaceous sediment where iron hydroxide precipitate (an indication of acidification) occurs. Generally high sulfates and low total alkalinity were associated with low pH, providing evidence for pyrite oxidation.

Over the study period the pH appeared to recover from <4.5 pH to 6.0 pH units. It is though that this recovery is only temporary as the pH increase can be attributed to dilution by rain and groundwater inflow. Longer term recovery will depend on future water levels at the lake and ensuring that acid producing sediment remain anoxic.

The best management option therefore is to prevent oxidation of pyrite by keeping the acidity producing sediments wet, however there are other biological and chemical processes that rely on a seasonal water regime and if disrupted could affect the functioning of Lake Jandabup. A compromise needs to be made between controlling acidification and maintaining a seasonal water regime at the lake.

DECLARATION

I certify that this thesis does not, to the best of my knowledge and belief: incorporate without acknowledgment any material previously submitted for a degree or diploma in any institution of higher education; contain any material previously published or written by another person except where due reference is made in the text; or contain any defamatory material.

Signature..

Date.....29-1-2001.....

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I gratefully acknowledge the Water and Rivers Commission who provided financial assistance for water quality analysis. Without their help I would have spent many more hours in the laboratory.

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CHAPTER 1: INTRODUCTION

The acidification of wetlands is a worldwide problem leading to water quality degradation and loss of biodiversity in aquatic systems (Lamers, 1998; Psenner, 1994). Acidification occurs when various chemical and/or biological processes, through natural or anthropogenic means, cause the pH of water and/or sediments to decline temporarily or permanently.

Organic compounds, such as humic acids are produced when plant material decays and can naturally decrease the pH of the water (Allen, 1995; Wetzel, 1983). Lakes in volcanic regions or those with *Sphagnum* mats can have pH < 4 (Wetzel, 1983). However, the cause of most wetland acidification is from anthropogenic sources or actions. In the northern hemisphere acid rain is a primary cause of most acidification. Atmospheric deposition from the burning of fossil fuels can deliver nitrates and sulfates to aquatic ecosystems causing the pH to decline (Boulton and Brock, 1999; Kelly *et al.*, 1982; Psenner 1994; Schindler 1999; Wetzel, 1983).

In Australia, acid rain is yet to become an environmental problem, with most acidification associated with acid (coal) mine drainage (AMD) and Acid Sulfate Soils (ASS). Numerous studies have dealt with the problem of AMD where sulfide material (mainly iron pyrite FeS₂), exposed by coal mining can be oxidised and transported to aquatic systems via runoff, ground water and rain thus decreasing the pH of the receiving waters (Castro *et al.*, 1999; Cravotta 1998; Gyure *et al.*, 1987; Kim *et al.*, 1999; Kleeberg 1998; Lowson *et al.*, 1993).

Potential Acid Sulfate Soils (PASS) which are abundant in coastal environments are soils or sediment that contain reduced forms of sulfur (National Working Party on Acid Sulfate Soil, 2000; Wilson *et al.*, 1999). They form in anoxic conditions when sulfides from estuarine and marine waters react with available iron to form pyrite (FeS_2) (Wilson *et al.*, 1999). Under reducing conditions these soils are harmless but when exposed to air and water they can oxidise to sulfates which when rehydrated can form sulfuric acid. These are then termed acid sulfate soils (ASS) (Ferguson and Eyre, 1996; Wilson *et al.*, 1999).

Potential acid sulfate soils cover over 1 million hectares of land with major known occurrences in Australia, Asia, Africa and Latin America (Clark *et al.*, 1996; Crossland 1996). World wide, the impacts of these soils have been known for 100's of years (e.g. Astron and Bjorklund, 1995; Tin and Wilander, 1995) but in Australia the problem was only recognised around 50 years ago (National Working Party on Acid Sulfate Soils, 2000).

In Australia, PASS occur along 50% or 20 000km² of the Australian coastal zone. Increased land clearing due to urban development and floodplain drainage for agriculture can lead to disturbance and hence oxidation of these soils producing sulfuric acid when the soils rehydrate. Potential Acid Sulfate Soils are seen to be a large problem in Australia, for every tonne of pyrite that is oxidised 1.6 tonnes of sulfuric acid can be produced, this is ten thousand times that in existing mine dumps (National Working Party on Acid Sulfate Soils, 2000).

The impacts of drying and exposure of PASS have been well studied (e.g. Clark *et al.*, 1996; Ferguson and Eyre, 1996; Konsten *et al.*, 1994; Lin *et al.*, 1995; Rapport *et al.*, 2000; Sammut *et al.*, 1996a; Sammut *et al.*, 1996b; Sammut and Lines-Kelly, 1999; Walker, 1972; White *et al.*, 1996; Williams and Copeland, 1996; Wilson *et al.*, 1999). Most of these studies have focused on the drainage of waterways and waterlogged soils, in, for example, agricultural areas and the effects it has on rivers in the flood plain. No recent published literature reviewed examined the impacts that PASS could have in individual systems such as wetlands. Ecosystems such as these that contain PASS are especially at risk since unseasonal drying and/or altered hydrological regimes can cause the PASS to oxidise. These emerging areas are the focus of the study.

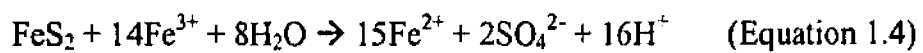
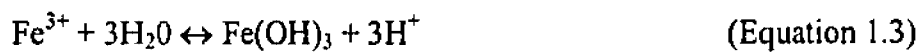
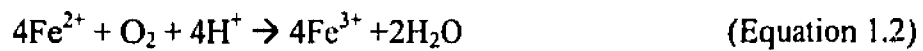
1.1 Chemical Cycles Associated with Acidification

The sulfur cycle, iron cycle and buffering processes are the major cycles/processes involved in the acidification of wetlands due to ASS. A discussion of these is vital in understanding the chemical processes behind pyrite formation and oxidation.

1.1.1 The Sulfur Cycle

Sulfur is a common element in freshwater systems. It can be found in organic and inorganic forms and is needed by all living organisms as a minor nutrient (Boulton and Brock, 2000; Cook and Kelly, 1992; Wetzel, 1983). Reduced sulfur in wetland sediments in the form of metal sulfides such as pyrite (found in PASS) can be oxidised producing sulfuric acid, lowering the pH of the system. The process of pyrite oxidation

is shown in equations 1.1 to 1.4 and it is this process that is the main focus of the study (Cravotta, 1996; Evangelou 1995; Gazea *et al.*, 1996; Howard, 1998; Lowson *et al.*, 1993; Manhan, 1993; Tin and Wilander, 1995; Wetzel, 1983; Wilson *et al.*, 1999; Zhang and Evangelou, 1998).



Step 1 involves the oxidation of pyrite with molecular oxygen to form hydrogen ions, sulfate and Fe^{2+} (Equation 1.1). The Fe^{2+} is then oxidised to Fe^{3+} and hydrolysed to solid ferric hydroxide (Equation 1.2 and 1.3). Under conditions of low pH (< 4) oxygen is not needed to oxidise pyrite, Fe^{3+} can then be the primary oxidant and therefore acid generation can continue (Equation 1.4) (Evangelou, 1995; Gazea, 1996).

The sulfur cycle in aquatic systems is dependent on: the redox potential and oxygen availability near the sediment surface, the presence of bacteria, and external inputs of sulfur (Figure 1.1) (Wetzel, 1983). External inputs of sulfur into a wetland are coastal sea spray, rain from production of sulfur dioxide through the burning of fossil fuels, volcanic inputs, runoff from fertilizers and/or influxes of sulfate rich groundwater (Boulton and Brock, 1999; Wetzel, 1983).

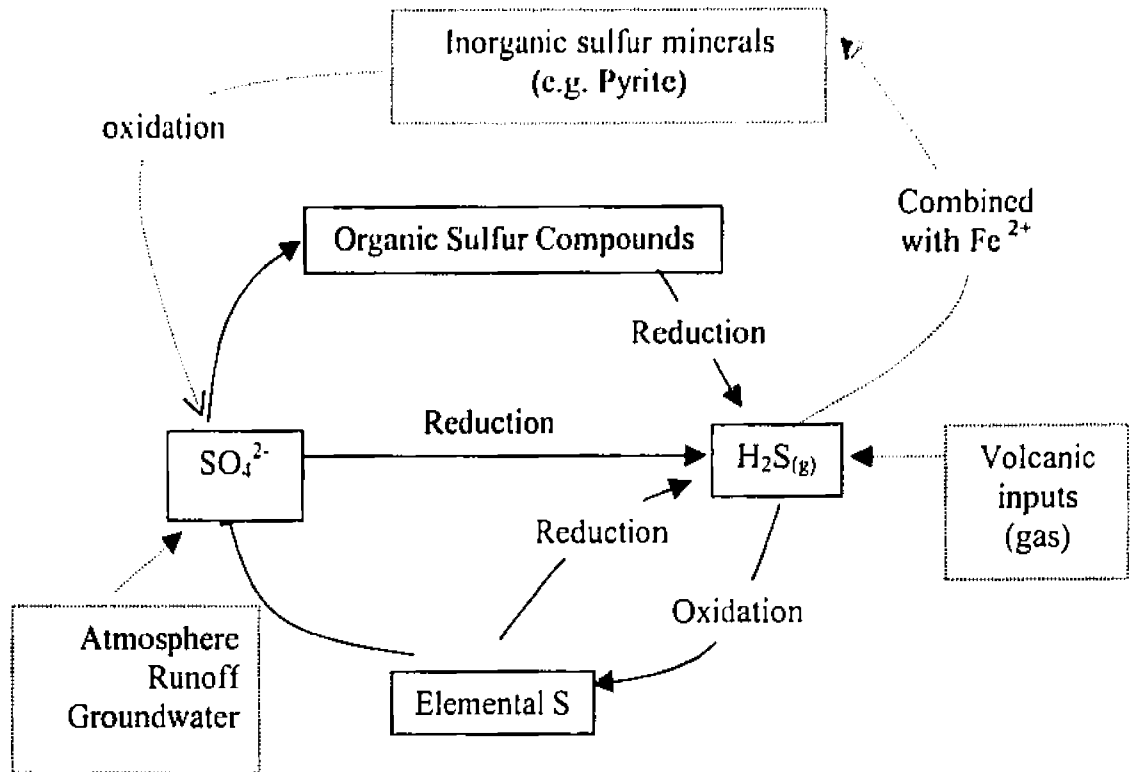
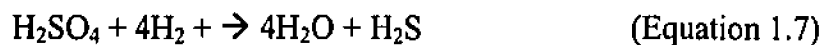
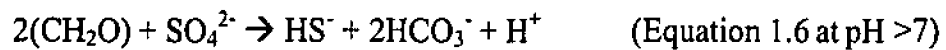
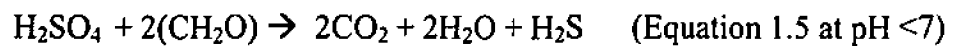


Figure 1.1: Simplified model of the sulfur cycle. Dashed boxes indicate external inputs and/or losses (Modified from Wetzel, 1983)

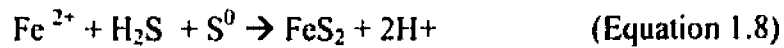
In fresh water, sulfate (SO_4^{2-}) is the most common form of sulfur (S) that is released from soils containing sulfides or free sulfur during geochemical weathering (Hreyson, 1990; Wetzel, 1983). It is the sulfate that contributes to the acidity (lowered pH) of the water. When redox potential declines, heterotrophic, anaerobic bacteria such as species of *Desulfovibrio*, *Desulfotomaculum*, *Desulfomonas*, *Desulfuromonas* can reduce sulfate, sulfite, thiosulfate, and elemental sulfur to hydrogen sulfide (H_2S) through the oxidation of organic matter (Equation 1.5 or 1.6) or molecular hydrogen (Equation 1.7)

(Boulton and Brock, 1999; Gazea *et al.*, 1996; Greyson, 1990; Hedin, 1989; Howarth *et al.*, 1992; Mitsch and Gosselink, 1993; Manhan, 1993; Prescott *et al.*, 1993; Sorokin, 1999; van Breemen, 1988; Wetzel, 1983; White *et al.*, 1989). In acidic wetlands sulfate reduction is desirable because a by-product is alkalinity generation which can neutralise acidity (Kelly *et al.*, 1982; Hedin *et al.*, 1989; Wendt-Potthoff and Neu, 1998; Wang and Morse, 1996). Herlihy and Mills (1983) suggest that when polluted water containing sulfate enters wetland ecosystems sulfate reduction in the anoxic zones may increase. Sulfate reduction occurs over a wide range of pH but highest rates occur at near neutral pH (Gazea *et al.*, 1996; Mitsch and Gosselink, 1993).

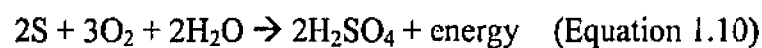
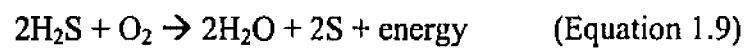


If free metals are available such as Iron II (Fe^{2+}) they will combine with hydrogen sulfide (H_2S) to form metal sulfides such as pyrite (FeS_2) which are insoluble at neutral or alkaline pH increasing the amount of reduced sulfur in the sediments (Equation 1.8) (Boulton and Brock, 1999; Gazea *et al.*, 1996; Lamers *et al.*, 1998; Wetzel, 1983). Accumulation of H_2S in the sediments will only occur if the water is acidic. In alkaline waters H_2S will only accumulate after all the Fe^{2+} has been precipitated as FeS_2 . Sulfate reduction can be enhanced and metal precipitation (i.e. formation of iron sulfides) decreased through vegetation cover. This is due to plant cellulose providing nutrients for sulfate reducing bacteria and the decaying plant material provides organic matter which is capable of removing free metals (Gazea *et al.*, 1996). However, vegetation

cover can also lead to increasing organic matter and deoxygenation of the water through higher biological oxygen demand (Boulton and Brock, 2000; Wetzel, 1983). These conditions are perfect for pyrite formation (Ferguson and Eyrce, 1996; Weber 2000).



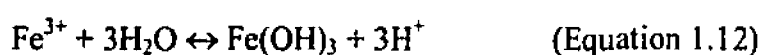
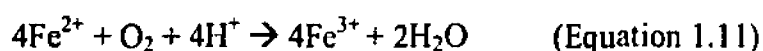
Finally, hydrogen sulfide can be oxidised rapidly with dissolved oxygen to sulfate by acidophilic, aerobic, chemosynthetic (colourless) bacteria such as species of *Thiobacillus* and *Beggiatoa* (Equation 1.9 and 1.10) (Gazea *et al.*, 1996; Prescott *et al.*, 1993; Schrenk *et al.*, 1998; Sorokin, 1999; Tortora *et al.*, 1997; Wetzel, 1983). Oxidation can proceed in anoxic conditions with the assistance of photosynthetic bacteria (Sorokin, 1999).



1.1.2 The iron cycle

Iron is an important macronutrient to flora and fauna of fresh waters because it is a mediator for oxygen and energy transport (Gerhardt, 1994; Wetzel, 1983). Similar to sulfur, the iron cycle is influenced by the redox condition and bacterial populations of wetlands. In fresh water, iron usually occurs as ferric hydroxide, in suspension as ferric (Fe^{3+}) or ferrous (Fe^{2+}) iron or adsorbed on seston particles (Hutchinson, 1975; Mitsch

and Gosselink, 1993; Wetzel, 1983). On exposure to air or in oxygenated waters ferrous iron (Fe^{2+}) will be oxidised to ferric iron (Fe^{3+}) and subsequently hydrolysed and precipitated as insoluble ferric hydroxide ($\text{Fe}(\text{OH})_3$) releasing protons and decreasing the pH of the water (Equation 1.11. and 1.12) (Howard, 1998; Manhan, 1993; Vile and Weider, 1993; Wetzel, 1983; Winfield, 1995). This reaction (Equation 1.12) occurs abiotically and is depended on total Fe^{3+} concentration and pH, as at $\text{pH} > 3$ there is little dissolved ferric iron (Gazea *et al.*, 1996). At $\text{pH} > 3$ most of the Fe^{3+} will have been hydrolysed into $\text{Fe}(\text{OH})_3$ and hydrogen ions thus producing more acidity. The net result of iron oxidation, hydrolysis and precipitation is addition of hydrogen ions to the wetland, an orange/brown scum on the sediment surface ($\text{Fe}(\text{OH})_3$) and decreased pH (Gazea *et al.*, 1996, Vile and Weider, 1993).



At $\text{pH} < 3.5$ iron oxidation is slow and bacteria such as the *Thiobacillus* – *Ferrobacillus* group become vital catalysts for the reaction (Equation 1.11) although this reaction will occur abiotically at neutral to alkaline pH (Boulton and Brock, 1999; Evangelou, 1998; Gazea *et al.*, 1996; Howard, 1998; Manhan, 1993; Mitsch and Gosselink, 1993; White *et al.*, 1989; Zhang and Evangelou, 1998). Therefore, iron in a soluble reduced state (Fe^{2+}) is only found in low oxygen, acid to neutral waters with low redox potential, and if oxygen levels rise, Fe^{2+} will oxidise and precipitate as $\text{Fe}(\text{OH})_3$ (Boulton and Brock, 1999). A simplified iron cycle is shown in figure 1.2.

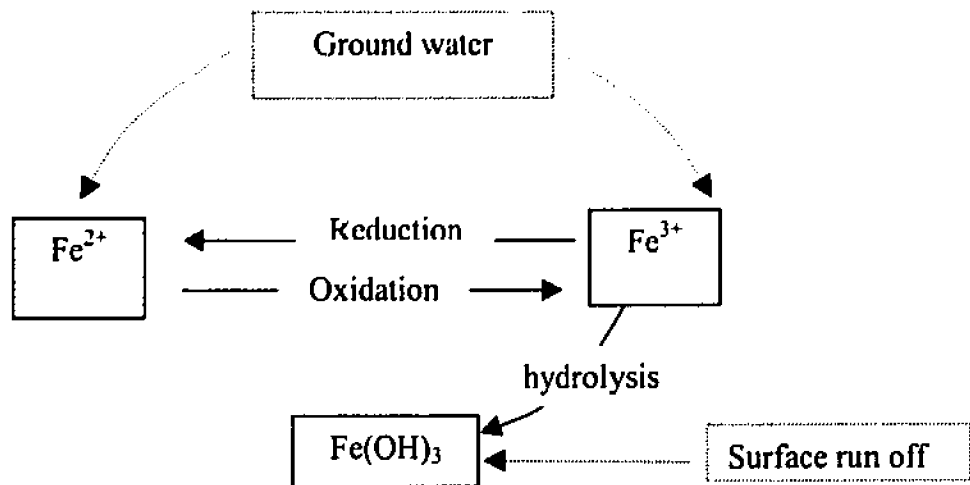


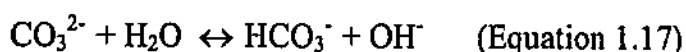
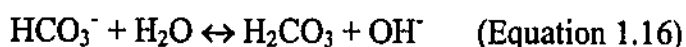
Figure 1.2: A simplified iron cycle. Dashed lines represent external sources and/or losses (Various sources as described in text).

1.1.3 Alkalinity, buffering capacity and acidity

Alkalinity and acidity (as mg L^{-1} of CaCO_3) are important parameters to measure when characterising acidic water and they have become one of the central issues in aquatic ecosystem management (Gazea, 1996). The alkalinity and acidity of water are determined by buffers. A buffer is a solution that can resist changes in pH when acids or

bases are added and is usually a combination of a weak acid or a weak base and one of its salts (Boulton and Brock, 1999).

Alkalinity is a measure of water's ability to neutralise incoming or internally produced acid and is measured by the sum of all titratable bases to pH 4.5 (Allen, 1995; Gazea *et al.* 1996; Keskitalo and Eloranta, 1999; Sherlock, 1995; Wetzel, 1983; Winfield, 1995). Alkalinity is primarily a function of the carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydroxide (OH^-) equilibrium (Wetzel, 1983). The amounts of each depend on pH. At pH less than 4.3 there is little bicarbonate or carbonate; at pH 4-5 to 10 there is mostly bicarbonate and at pH greater than 10 carbonate is the predominate form (Allan, 1995; Sherlock, 1995; Wetzel, 1983). The CO_3^{2-} , HCO_3^- and OH^- ions mainly originate from carbon dioxide dissolving in water and forms weak carbonic acid, which quickly dissociates into bicarbonate ions (Allen, 1995; Boulton and Brock, 1999; Sherlock, 1995; Wetzel, 1983) (Equation 1.13 – 1.15). The bicarbonate ions further dissociate to establish an equilibrium (Equation 1.16 – 1.18) (Allan, 1995; Boulton and Brock, 1999; Sherlock, 1995; Wetzel, 1983).



As long as the equilibrium presented above (Equation 1.16-1.18) is operational the pH of solution will remain relatively unchanged (Wetzel, 1983). If the supply of CO_3^{2-} and HCO_3^- ions in the system is depleted, alkalinity will be zero and the system will no longer be able to neutralise incoming acid.

Alkalinity can be generated by ways other than the carbonate/bicarbonate system. Oxidation of Fe^{2+} , denitrification, photosynthesis, methanogenesis, sulfate reduction and metal precipitation and dissolution can also generate alkalinity (Gazea *et al.*, 1996; Gyure *et al.*, 1987; Hedin *et al.*, 1989; Herlihy *et al.*, 1987; Kelly *et al.*, 1982; Kim *et al.*, 1999; Sherlock, 1995; Vile and Weider, 1993; Wendt-Potthoff and Neu, 1998; Evangelou, 1998). For example, reduction processes generate alkalinity because they use hydrogen ions therefore decreasing acidity (Gazea, *et al.* 1996). Methanogenesis can increase carbon dioxide concentrations therefore influencing carbonate and bicarbonate levels (Boulton and Brock, 1999). High photosynthetic productivity can result in rapid assimilation of nitrate thereby reducing acidity and can also remove carbon dioxide from the water which increases pH. Sulfate reduction can remove hydrogen ions, which can also increase pH. Silicates, which are soluble at low pH and warm temperatures can react with carbonic acid producing silica and carbonates thus increasing pH (Wetzel, 1983).

Total acidity measures the ability of water to react with a strong base to obtain a pH near that of sodium hydroxide. It gives indication of how quickly the pH will increase when a base (e.g. through alkalinity production) is added (Wetzel, 1983).

1.2 Impacts of Acidification

Acidification can have detrimental effects on the ecology and functioning of the system. The biological effects of acidification can start to occur at pH 6 – 6.5 and can cause extinctions or decreased abundance of sensitive species of fish, invertebrates and aquatic plants (Bastarache *et al.*, 1997; Psenner, 1994; Sammut and Lines-Kelly, 1999). One of the most detrimental effects of acidification is the increase in metal bioavailability and hence toxicity to aquatic organisms. The metals of particular concern are aluminium, cadmium, iron, manganese and mercury (Crowder, 1991; Herrmann *et al.*, 1993; Nelson and Campbell, 1991; Sammut *et al.*, 1996a).

Aluminium can become highly toxic to aquatic organisms and at pH 4.0 to 5.5 high levels of Al^{3+} can be released and affect the osmotic pressure of gills leading to suffocation (Abel 1989; Psenner, 1994; Weber 2000). A study by Gerhardt (1994) on the mayfly *Leptophlebia marginata* indicated that at low pH, increased levels of precipitated iron can coat its body preventing feeding and respiration. In Australia metal toxicity due to acidification has caused kills of fish, crustacean and other invertebrates. For example, in Northern New South Wales a flood event and resultant acidification caused death of all fish (National Working party on Acid Sulfate Soils, 2000). Another characteristic of acidified systems is high water clarity due to high levels of aluminium causing suspended particles to clump together and drop to the sediment surface (National Working Party on Acid Sulfate Soils, 2000).

Exposure to acidified water also damages fish skin which increases the susceptibility to infection by *Aphanomyces* (red spot disease) this can reduce the ability of fish to take in oxygen or to regulate their intake of salts and water. Outbreaks of *Aphanomyces* can affect up to 80% of the fish population (National Working party on Acid Sulfate Soils, 2000; Sammut and Lines-Kelly, 1999; Sammut *et al.*, 1993; Sammut *et al.*, 1996a).

The metal contaminants, particularly aluminium and manganese, can be toxic to plants decreasing their productivity and even eliminating some species, thus altering the structure and diversity of the habitat (Crowder, 1991; Moss, 1989; National Working Party on Acid Sulfate Soils 2000). Smothering effects of iron oxyhydroxides or the direct effects of acid can be detrimental to plant communities (Sammut *et al.*, 1996a). Under long term acidity the species richness of aquatic plants tends to decline leaving only a few dominant acid tolerant species. Such species include *Nymphaea* and *Eleochari* which can grow and reproduce at $\text{pH} < 3$. Once established these species can prevent other native species from reestablishing even if the pH returns to normal (National Working Party on Acid Sulfate Soils 2000; Sammut *et al.*, 1996a).

Changes in composition, distribution and abundance of biota at the lower end of the food chain have been linked with acidification (Abel, 1989; Moss, 1989). These decreases in lower order food chain organisms can indirectly effect invertebrates, fish, amphibians and water birds through by and/or decreasing their food source (DesGranges and Gagnon, 1994; Elmberg *et al.*, 1994). Communities of bacteria, phytoplankton and zooplankton can be adversely effected (Findlay *et al.*, 1999; Rao and

Dutka 1983). Amphibians are affected as their eggs can usually only survive in neutral waters (National Working Party on Acid Sulfate Soils, 2000; Sammut *et al.*, 1996a).

1.3 Acid sulfate soils: Seasonal Wetlands and the Swan Coastal Plain

If wetlands on the Swan Coastal Plain become acidified they may experience many of the problems described above. A potential source of acidity for Swan Coastal Plain wetlands are ASS. Large areas of the state, particularly the Swan Coastal Plain are underlain with ASS. Areas known to contain ASS and associated acidity include the Kimberley and Pilbara coastlines, locations around the Perth – Avon River and the areas of Bassendean, Guildford and Bayswater. More specifically, Beenyup mine (17 km north east of Augusta) and bridge construction around Garnett Road and Guildford (Perth) have been proven to be the cause of acidity in the area (Weber, 2000). Wilson *et al* (1999) states that coastal areas are especially vulnerable to the problems of ASS due to development and expanses in agriculture disturbing these soils.

The Swan Coastal Plain covers 4000 km² running approximately 80 km north and 70 km south of Perth, Western Australia; it is bounded by the Darling and Gingin scarps to the east and the Indian Ocean to the West (Davidson, 1995). The climate of the Swan Coastal Plain is Mediterranean with cool wet winters and hot dry summers (Davidson, 1995).

The Swan Coastal Plain has two major ground water mounds which supply large quantities of Perth's domestic water and support extensive wetland and vegetation

ecosystems (Davidson, 1995). Many of the 9600 wetlands that lie on the Swan Coastal Plain are seasonal and are maintained by ground water flow and precipitation; many are surface expressions of the unconfined ground water aquifer (Davidson, 1995).

The chemistry and biology of wetlands are maintained by the water regime and the biota are usually adapted to seasonal drying and reflooding (Boon *et al.*, 1996; McComb and Qiu, 1998). The climatic pattern of the Swan Coastal Plain has led to the formation of seasonal wetlands; decreased groundwater during summer, low rainfall, high temperatures and high evaporation usually combine to cause wetlands to dry seasonally. It is these wetlands that are most at risk from the effects of ASS (Wilson *et al.*, 1999).

The potential impact of ASS on seasonal wetlands of the Swan Coastal Plain is high as many have sediments that are underlain with pyrite, particularly those that occur in the Bassendean dune system (Davidson, 1995). When the lake bed dries oxidation of the iron sulfides would be expected and acid production could occur following refilling. In these seasonal wetlands natural acidification would be expected, but there are few acidic wetlands on the Swan Coastal Plain. It is possible that mechanisms present in these wetlands have prevented acidification from occurring. Such means can include seasonal flushing out of acidic water as the wetland fills during late winter and/or a high buffering capacity of the water and sediments causing the acid to be neutralised.

Non-seasonal wetlands that are maintained by groundwater flow are of particular concern; increased groundwater abstraction means that these wetlands are becoming susceptible to unnatural drying which can lead to oxidation of pyrite contained in the

sediments. These wetlands would probably have no mechanisms to control acidification and therefore would be unable to prevent a pH decline.

Other former wetlands may lie just metres under the surface, having been covered by moving sand dunes (Weber, 2000). If the sediments of these wetlands contain pyrite, exposure of sediments due to, for example, urban development could result in acidification. Discharge lakes, which form groundwater sinks with the surrounding environment are not seasonally flushed with rainfall or ground water inflow (Davidson, 1995). Weber (2000) states that these wetland types have the perfect conditions for pyrite formation (i.e high organic matter and anoxic sediments). Although the sediments of these lakes are not usually exposed to oxygen, disturbance due to development can lead to oxidation and therefore acidification.

Small decreases in groundwater levels can affect the seasonal wetlands of the Swan Coastal Plain causing prolonged or unseasonal drying (Davidson, 1995). Weber (2000) states that water table fluctuations in areas that contain ASS can initiate oxidation of iron sulfides as discussed above. This is one focus of the study, that excessive drying of lake bed sediments may be causing increased acid production in seasonal wetlands containing ASS. Wilson *et al.* (1999) states that the processes and chemistry behind ASS is complex and that it requires careful analysis of the hydrological regime and patterns of drying. Ferguson and Eyre (1996) agree and further argue that the single most important factor in determining if a PASS will oxidise is the water table level. This study will provide information on drying regimes and acid production due to ASS, information which appears to be lacking, especially for Swan Coastal Plain wetlands.

1.4 Aims of the project

Lake Jandabup is a shallow, seasonal wetland on the Swan Coastal Plain, Western Australia. In 1997, during regular monitoring of the lake, acidification ($\text{pH} < 4.5$) was detected together with a high spatial variability in pH (Sommer *et al.*, 2000). The bed of Lake Jandabup is underlain with pyrite associated with palaeolake deposits although the spatial variability of this is not known (see Davidson, 1995).

The objective of this project was to determine the cause of the recent acidification of Lake Jandabup. This was achieved by addressing the following aims.

- i. To determine, for surface water at Lake Jandabup, the short term spatial and temporal variation in:
 - a. pH (and other physical and chemical properties),
 - b. buffering capacity and
 - c. total iron and sulfate levels.
- ii. To determine the influence of drying times on water quality, following of sediment taken from Lake Jandabup.
- iii. To formulate recommendations for the management of Lake Jandabup particularly regarding water level requirements.

CHAPTER 2: STUDY SITE

2.1 Location and Description

Lake Jandabup ($31^{\circ}44'S$, $115^{\circ}49'E$) is a seasonal wetland located 22 km north of Perth on the Swan Coastal Plain Western Australia (Figure 2.1). It lies in an interdunal swale between the Bassendean and Spearwood dune systems (Hill *et al.*, 1996). Lake Jandabup is a shallow ($<1.5\text{m}$), relatively large wetland of 330 ha, including 134 ha of sedge land dominated by *Baumea* spp., *Leptocarpus* spp. and other mixed Restionaceae and Cyperaceae (Froend *et al.*, 1993; Sommer, 1997). Over 50 percent of the lake bed (along the western side) contains organic sediments mainly diatomite while the remainder is covered in fine quartz sands containing ilmenite (FeTiO_3) and goethite (Fe(OH)_3) (Allen, 1979). Pyrite (iron sulfide) associated with palaeolake deposits is found in the lake bed (Davidson, 1995). Lake Jandabup is an 'A Class' reserve managed for nature conservation (Western Australian Planning Commission and Water and Rivers Commission, 1999).

2.2 Hydrology of Lake Jandabup

Lake Jandabup is an oval basin approximately 2.8 km long x 1.7 km wide bounded by an extensive reed bed with a 1.2 km^2 area of open water in the centre (Allen, 1979). It is a surface expression of the unconfined aquifer of the Gnangara Groundwater Mound (Allen, 1979; Davidson, 1995; Froend *et al.*, 1993). It has a hydraulic connection with this ground water that is a delicate balance between geology, climate and vegetation. It

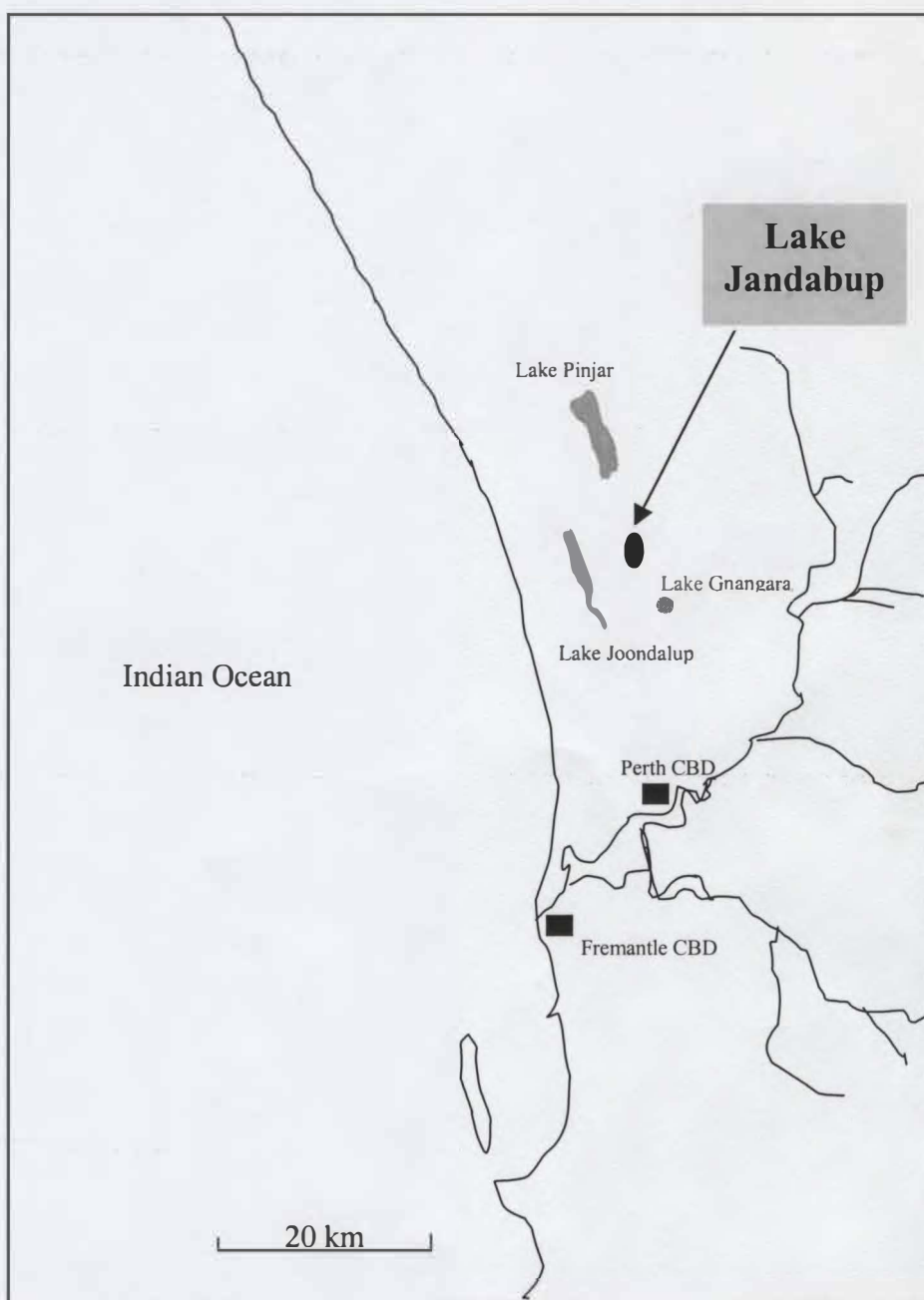


Figure 2.1: Location of Lake Jandabup on the Swan Coastal Plain. Wetlands in close proximity to Lake Jandabup are shown for location purposes. (Modified from Davis et al., 1993)

is classified as a groundwater through-flow lake/swamp meaning that the water level is maintained by groundwater inflow and precipitation on the lake's surface (Davidson, 1995). In these lakes the elevation at the down hydrological gradient side is lower than the lake water level resulting in outflow from lake to groundwater (Allen, 1979; Davidson, 1995).

At Lake Jandabup, groundwater inflow occurs on the eastern margins because the ground water is at a higher elevation than the lake bed (Figure 2.2) (Allen 1979). Discharge occurs through lake deposits along the relatively flat south-western margin (Allen, 1979).

The hydrology and seasonality of Lake Jandabup is directly related to the climate of the Swan Coastal Plain which is Mediterranean with cool wet winters and hot dry summers. The average annual rainfall is 840 mm with about 90% falling in the winter months between April and October. During the latter months of this period the lake will usually be full (Allen, 1979; Davidson, 1995). In summer, high evaporation rates (the annual average evaporation rate is twice that of rainfall), and decreased groundwater levels and low rainfall can cause the lake to dry completely (Allen, 1979; Davidson, 1995).

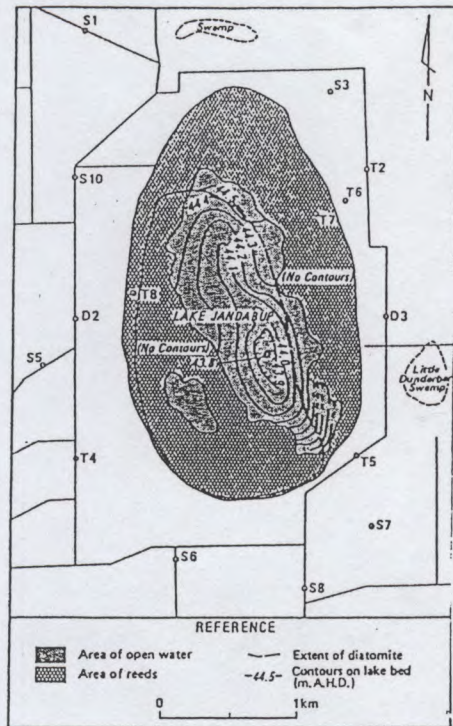


Figure 2.2: Contours of the bed at Lake Jandabup (Source: Allen, 1979)

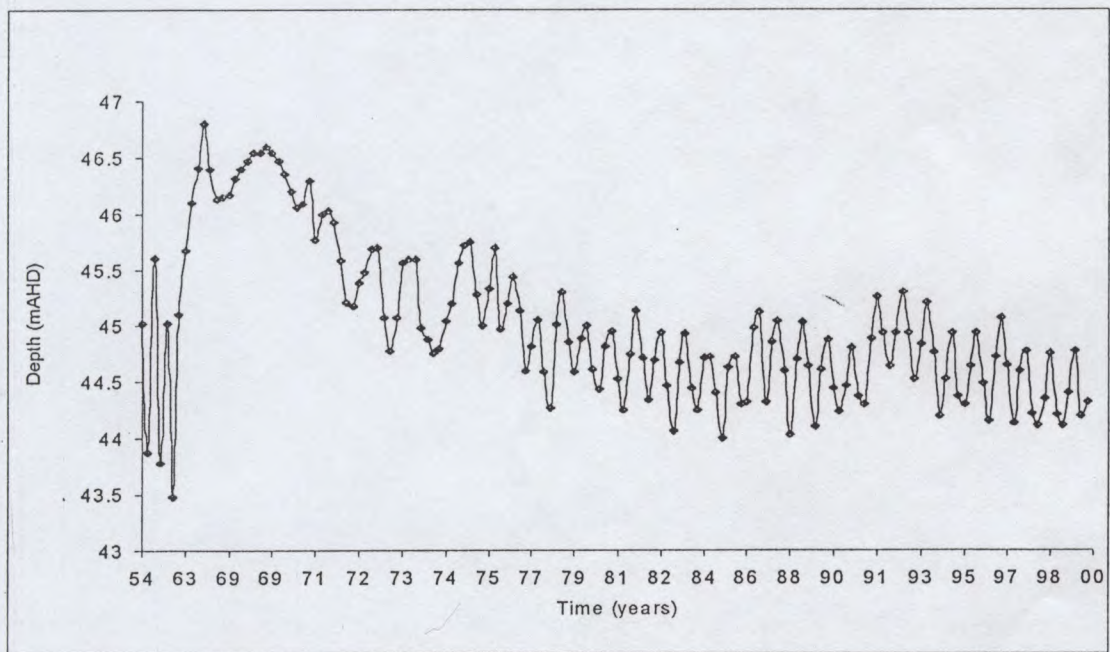


Figure 2.3: Surface water depth at Lake Jandabup (meters Australian Height Datum) between 1954 and 2000 showing the general decrease in surface water levels over time. (Source: Water and Rivers Commission, 2000).

Lake Jandabup's water level is maintained by ground water flow therefore any changes in groundwater levels can affect its hydrology. The hydrology of Lake Jandabup has been significantly modified since European settlement (Figure 2.3) mainly due to clearing of native vegetation, changes in surrounding land uses, groundwater abstraction and artificial maintenance (Water Authority of Western Australia, 1995). Table 2.1 summarises the water regime over the last 20 years.

Table 2.1: Minimum and Maximum water levels for Lake Jandabup over the past 20 years. Depth taken from staff gauges at the Lake (Source: R. Loomes, pers. comm. September 2000)

	Minimum Water Level (m)	Maximum Water Level (m)	Mean number of dry months
Past 20 years	0.08	0.9	0.71
Past 10 years	0.1	0.89	0.9
Past 5 years	0.01	0.8	1.8

Artificial maintenance is the act of adding water into wetlands to maintain a water level (Water Authority of Western Australia, 1995). For wetlands its primary purpose is to maintain ecological processes and life support systems so that the wetlands' values are maintained and/or enhanced (Water Authority of Western Australia, 1995). Lake Jandabup is one of a suite of wetlands on the Swan Coastal Plain that has minimum and maximum water levels set to meet particular management objectives. For Lake Jandabup these objectives include: maintenance of water bird habitat, removal of mosquito fish from the lake and maintenance of high species richness of aquatic macroinvertebrates, macrophytes and sedge vegetation (Water Authority 1995).

Artificial maintenance has been used to maintain minimum required water levels at Lake Jandabup. In the mid 1990's the lowest water level allowed was 44.3 mAHD (J. Miotti, pers. comm., May 2000). In 1995 the lowest winter water level requirement was raised to 44.7 m AHD and a maximum water level of 46.1m AHD was set (Water Authority of Western Australia, 1995). Ground water from a nearby bore was used to pump water into Lake Jandabup in 1989, 1991, 1994, 1995, 1996, and 2000 (Table 2.2). Artificial maintenance was not needed in 1992 and 1993 due to sufficient recharge by rainfall. Between 1997 and 1999 the lake bed was allowed to dry completely in an attempt to eradicate the mosquito fish *Gambusia holbrooki* (Sommer *et al.*, 2000). The added bore water has relatively low iron and sulfate levels and neutral pH (Table 2.3) (J. Miotti, pers comm., May 2000).

Table 2.2: Summary of artificial maintenance at Lake Jandabup (Source: J. Miotti, pers. comm., May 2000).

Year	Dates Pumped	Amount Pumped ML
1989	unknown	unknown
1991	unknown	unknown
1994	18/3 - 20/5	203.20
1995	1/2 - 11/5	401.70
1996	18/1 - 11/5	407.20
2000	15/2 - 15/3	500.00

Table 2.3: Water quality of bore W255: the closest bore to Lake Jundabup that represents approximate water quality used in artificial maintenance. (Source: Water Corporation, 2000).

Parameter	1996/1997	1997/1998
Conductivity <i>in situ</i> ($\mu\text{S cm}^{-1}$)	450	460
pH <i>in situ</i>	7.20	6.51
Redox	-195	-187
Temperature	22.9	23.2
Turbidity	0.4	0.6
D.O. (%)	1.6	0.6
D.O. (mg/L)	0.15	<0.05
Colour	13	29
Alkalinity (CaCO_3)*	75	75
Bicarbonate (HCO_3)*	90	95
Carbon Dioxide*	9	47
Hardness (CaCO_3)*	120	<0.6
Carbonate	<0.6	
Total Filterable solids*	300	290
Iron Filtered*	<0.05	5.0
Manganese Filtered*	<0.04	0.05
Aluminum Filtered*	<0.008	0.015
Sodium*	44	44
Potassium*	4.0	55
Calcium*	36	26
Magnesium*	6.0	6.0
Chloride*	50	82
Sulfate*	45	5
Silica (SiO_2)*	20	17
Filterable Organic Carbon*	1.5	2.1
Fluoride*	0.15	<0.10

* results expressed in mg L^{-1} (milligrams per litre)

2.3 Lake Jandabup and Acidification

Lake Jandabup is part of a Gngangara Mound macroinvertebrate monitoring programme and has been regularly monitored since the summer of 1996 (Sommer *et al.*, 2000). Since spring 1997, a drop in pH from 6-8 to 4-5 was detected, with the largest decrease of ~2.0 units occurring between spring 1997 and spring 1998 when a low of 3.97 pH units was recorded. Table 2.4 shows the pH range across the lake during the monitoring (Sommer *et al.*, 2000).

Table 2.4: pH at Lake Jandabup between 1996 and 2000. Values show pH range measured across the whole lake (Source: Sommer *et al.*, 2000).

Time	pH range
Summer 1996	7.20-7.90
Spring 1996	6.32-7.06
Summer 1997	7.25-8.30
Spring 1997	4.58-6.71
Summer 1998	DRY*
Spring 1998	3.97-4.42
Summer 1999	4.32-4.34
Spring 1999	4.29-4.65
Summer 2000	3.4-6.23

* The lake bed was completely dry in 1998

Sommer and Horwitz (2000) have collated data and found from previous surveys that the highest pH readings have stayed in the range between 7.2 and 8.5, but the lowest pH recorded have been steadily declining (Table 2.5).

Table 2.5: Historical pH records taken during surveys or visits to Lake Jandabup. (Source: various, collated by Sommer *et al.*, 2000).

Year	Lowest pH recorded
Pre 1984	6.4
1987	3.7*
1987	6.1
1988	5.9
1992	5.8
1993	5.5
1996	4.9

* There was an anomaly in 1987 where a low of 3.7 pH units was recorded 3 days after an unseasonal rainfall event.

Since 1997 the lake bed has been drying for increasingly longer periods; less than 4 weeks in 1996, 4 weeks in 1997, 16 weeks in 1998 and 20 weeks in 1999 (Sommer and Horwitz, 2000). Artificial maintenance (addition of groundwater) prevented the lake from drying in 2000. Other chemical parameters also changed between 1996 and 2000 (Sommer *et al.*, 2000):

- i. gilvin decreased from 7.3 to <1 g440,
- ii. turbidity decreased from 11 to 4 FTU units,
- iii. ammonium concentration increased from ~10 to 4300 µg/L, but nitrate remained low between 1 µ/ L and 30µ/L,
- iv. total phosphorus levels increased from 14 µg/L to 28µ/L and
- v. chlorophyll 'a' decreased from 16 – 3.4 µg/L.

As a result of this acidification, iron and sulfate measurements have been included in subsequent monitoring of the lake. Lower pH (summer 1999) was associated with high

sulfate and total iron concentrations of 886 mg L⁻¹ and 5.09 mg L⁻¹ respectively (Sommer *et al.*, 2000). There was a significant positive correlation between sulfate and total iron indicating oxidation and reduction of iron sulfide (Sommer and Horwitz, 2000). Between Summer 1999 and Summer 2000 iron and sulfate levels generally decreased possibly indicating (a) the precipitation of iron (i.e. no soluble iron in the water to be detected) and/or (b) less sulfate oxidation.

Lake Jandabup has a macroinvertebrate species diversity of 53 families which is relatively high compared to other areas of the Swan Coastal Plain (Sommer *et al.*, 2000). It was found that species richness was higher during spring when water levels and hence available habitat were higher (Sommer and Horwitz, 2000). The prolonged dry period in 1998/1999 did not appear to effect macroinvertebrate fauna possibly due to faunal adaptation to a seasonal water regime (Balla and Davis, 1993; Sommer *et al.*, 2000).

Although family species richness has remained relatively unchanged since acidification and prolonged drying, community structure has altered. Isopods and oligochaete worms have become less abundant, and molluscs, amphipods and ostracods have disappeared. Abundances of Ceratopogonids (Diptera) and Macrothricid cladocerans increased (Sommer and Horwitz, 2000). Other studies of the effects of acidification on invertebrates have also found that species richness can decrease and community structure can change (Eleberg *et al.*, 1994; Hermann *et al.*, 1993).

CHAPTER 3: RESEARCH PLAN AND METHODS

3.1 Research plan

The objective of this study was to determine the cause of acidification at Lake Jandabup. The research is based on the assumption that the pH decline is caused by the oxidation of pyrite upon drying and refilling of the lake. A conceptual model for this process at Lake Jandabup is presented in Figure 3.1. As shown in the middle of the diagram the lake bed seasonally dries, moving left, when the lake bed refills there is natural production of sulfates, iron (II) and hydrogen. However as indicated the buffering capacity is sufficient enough that the acid is neutralised and the pH stays at its current level. The right hand side of the model indicates what might happen under conditions of prolonged drying. It was hypothesised that longer drying would, (a) increase pyrite oxidation (i.e. increase the production of sulfate, iron (II) and hydrogen ions produced) and/or (b) decrease the buffering capacity of the water and sediments (i.e. it can no longer neutralise the acid being produced). This hypothesis is based on the knowledge that Lake Jandabup dries, therefore acidification would be expected seasonally. However, it has only been in the past 3-4 years that acidification has been detected, the major thing that has changed since acidification is that the lake bed has been drying for longer over summer.

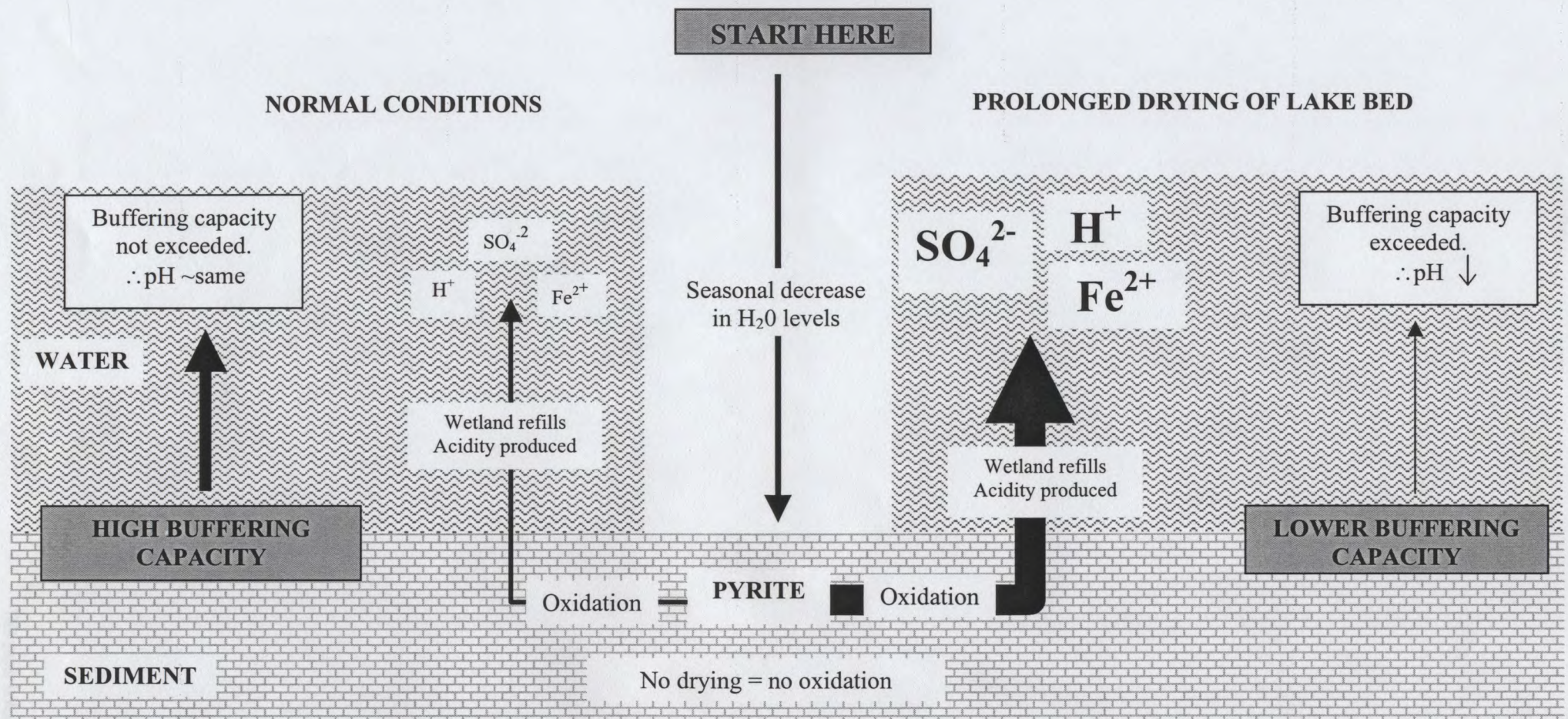


Figure 3.1: Conceptual model of possible causes of acidification at Lake Jandabup. The left hand side shows what is hypothesised would happen under normal condition; that is oxidation of pyrite will occur, but it will be minimal and the natural buffering capacity of the water and sediments can neutralise any acid being produced. The right hand side indicates what might happen under conditions of prolonged drying of the lake; that is oxidation will be enhanced and the pH will decline because the buffering capacity is not sufficient to neutralise the acid being produced.

The current research tested the conceptual model through field and laboratory experiments. The field experiment sought to identify the spatial variability of acidity at Lake Jandabup. It involved mapping the wetland for pH, sediment type and vegetation coverage. From these maps (Figure 3.2 – 3.4) study sites were chosen for the field and laboratory work based on the following criteria. There should be:

- i. at least 1 acidic site (pH <4.5) and 1 neutral site (pH >6.0).
- ii. at least 1 site in each of the three dominant sediment types which are; sand only, sand and/or organic under iron hydroxide precipitate, and diatomaceous earth (it was understood that the choice of sand and/or organic under iron hydroxide precipitate gave a site which has undergone acidification).
- iii. at least 1 site taken in the vegetation and 1 site in open water.
- iv. at least 1 site in northern, southern, eastern and western parts of the wetland.
- v. at least 1 dry site (if available) from each sediment type and/or location in the wetland (i.e. north, south, east and west).

On the basis of this criteria 10 study sites were chosen because this was the number needed to fulfill all of the above variables. Plate 3.1 shows the location of the 10 study sites and table 3.1 and plates 3.2-3.3 give a description of the study sites.

The laboratory study was focused on testing the effects of drying and reflooding of intact sediment taken from Lake Jandabup. It involved drying of intact sediment cores from each of the 10 study sites for various lengths of time (0 days, 10 days and 30 days) and measuring water quality (pH, sulfates, total iron, total alkalinity and total acidity) upon rehydration.

The field experiment involved the establishment of small *in situ* mesocosms (referred to as cores) at each of the 10 sites used in the laboratory experiment. It was designed to complement the laboratory study by assessing acid and alkalinity (i.e. buffering capacity) production in the field when the external influence of lake water mixing was removed. A core therefore constricted a piece of sediment and the water above it, isolating both from surrounding sediment and lake water. Cores were monitored inside and outside on a weekly basis for pH (and other physical and chemical properties) and monthly for sulfates, iron, total alkalinity and total acidity. In addition, once off cation and anion survey was completed to assess if there was a relationship between these variables and pH.

Table 3.1: Description of sites for field and laboratory study

Site	Location (DGPS readings)	~ initial pH from mapping experiment	Sediment Description	Vegetation	Algae (green/brown filamentous)	Initial water depth (cm)
1	90 921 E 86 980 N	DRY	Sand	Dense mixed Restionaceae	0%	Dry until wk 15
2	90 671E 87 723 N	5.5	Sand	Open Water	0%	40 cm
3	90 313 E 88 330 N	7.7	Sand	Open water	60%	15 cm
4	90 665 E 87 716 N	6.0	Sand	Sparse mixed Restionaceae	100%	
5	90 310 E 87 026 N	DRY	Organic with decaying plant material visible on surface	Sparse <i>Baumea articulata</i>	0%	Dry until wk 9
6	90 261 E 87 499 N	3.3	Diatomaceous with small ($<10\text{cm}$) particles of $\text{Fe}(\text{OH})_3$ precipitate on surface	Sparse <i>Baumea articulata</i>	100%	20 cm
7	90 181 E 88 237 N	6.5	Diatomaceous with small ($<10\text{cm}$) particles of $\text{Fe}(\text{OH})_3$ precipitate on surface	Sparse <i>Baumea articulata</i>	0%	20 cm
8	90 411 E 87 631 N	4.4	$\text{Fe}(\text{OH})_3$ precipitate over organic matter over sand. o/m layer $\sim 15\text{cm}$. The sediment showed cracks on the surface.	Open Water	0%	40 cm
9	90 593 E 87 140 N	4.5	$\text{Fe}(\text{OH})_3$ precipitate over organic matter over sand. o/m layer $\sim 5\text{cm}$. The sediment showed cracks on the surface.	Open Water	0%	25 cm
10	90 442 E 87 296 N	DRY	Sand	Sparse mixed Restionaceae	100%	Dry until wk 9

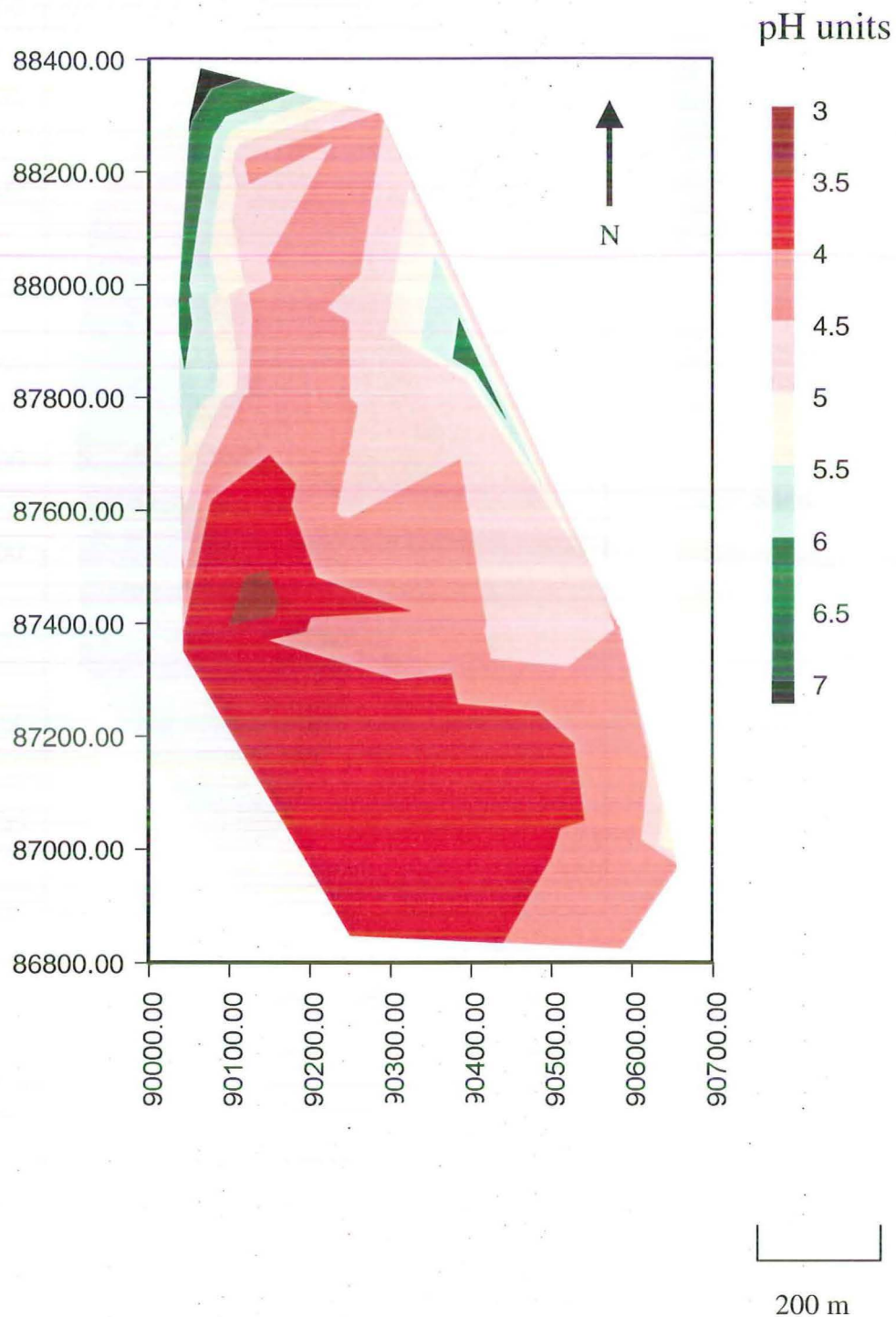


Figure 3.2: Spatial Map of pH at Lake Jandabup between 1st and 3rd of March 2000. NOTE: This map is not the entire wetland. It only includes the area bounded by the study sites chosen on Plate 3.1. This is because the peripheral part of the lake is bounded by a thick reed bed which was unable to be sampled. Axes are Australian map grid numbers.

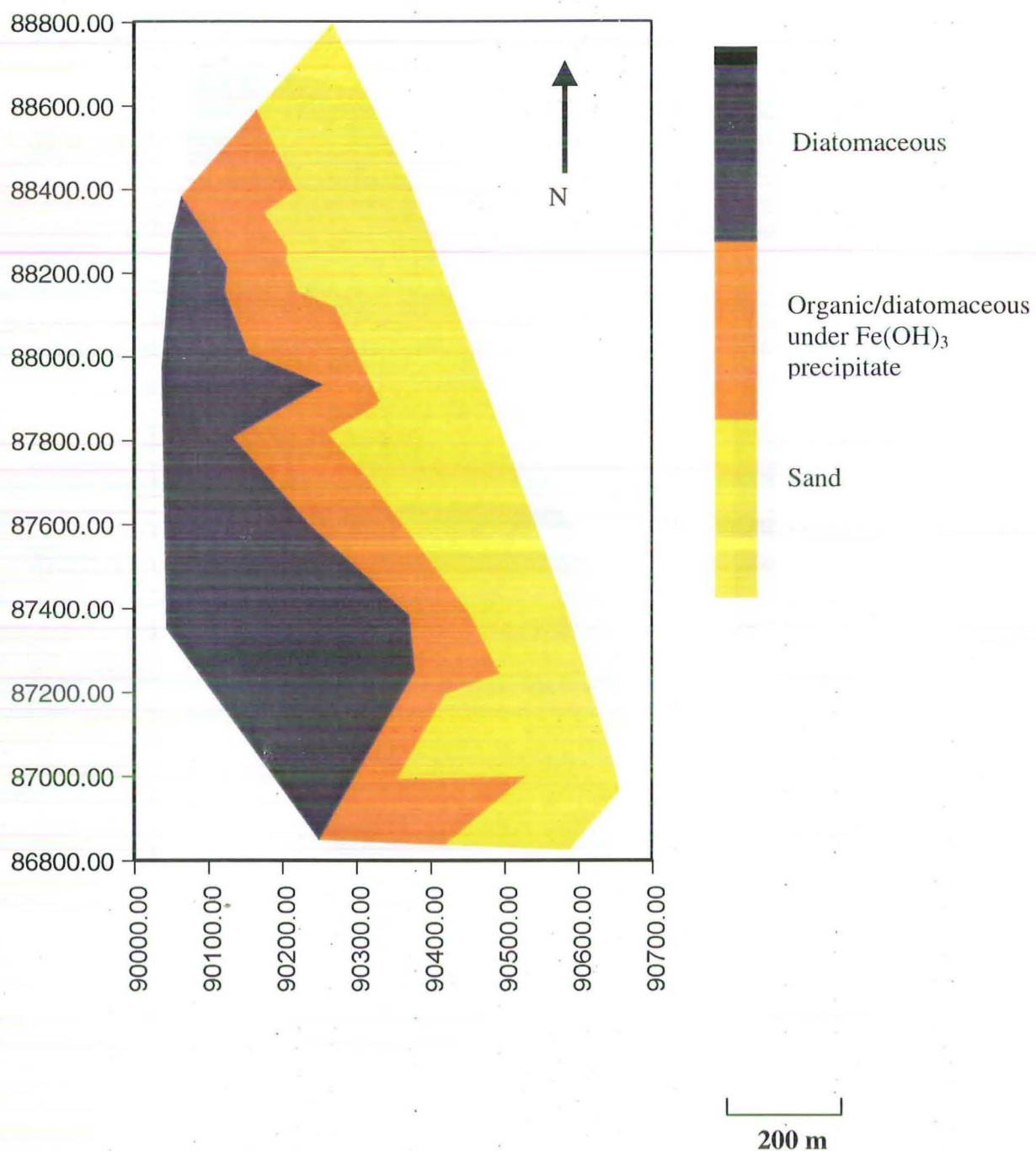


Figure 3.3: Spatial Map of sediment types at Lake Jandabup between 1st and 3rd of March 2000. Although strictly speaking $\text{Fe}(\text{OH})_3$ is not a sediment type (it is a product of acidification) it is included because it is significant for this project. NOTE: This map is not the entire wetland. It only includes the area bounded by the study sites chosen on Plate 3.1. This is because the peripheral part of the lake is bounded by a thick reed bed which was unable to be sampled. Axes are Australian map grid numbers.

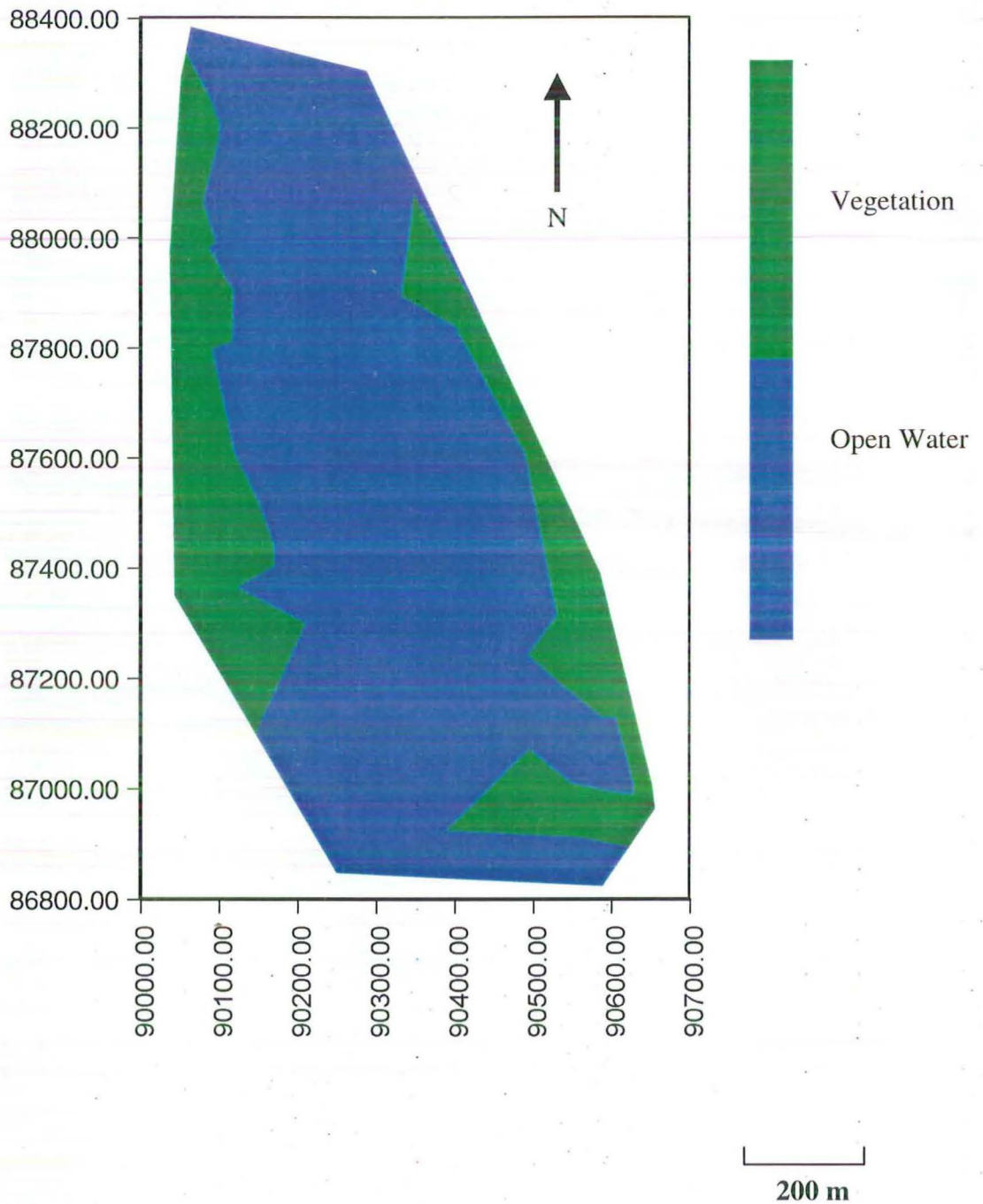


Figure 3.3: Spatial Map of vegetated areas at Lake Jandabup between 1st and 3rd of March 2000. NOTE: This map is not the entire wetland. It only includes the area bounded by the study sites chosen on Plate 3.1. This is because the peripheral part of the lake is bounded by a thick reed bed which was unable to be sampled. Axes are Australian map grid numbers.



Plate 3.1: Location of the 10 study sites at Lake Jandabup. Notice the distinct light coloured section running down the centre of the photograph which is the boundary between the sand and organic/diatomaceous sediment Also notice the red tinge to the west (left) of this line, this is likely to be iron hydroxide precipitate. The photo was taken in January 1999. Scale: 1:12 500 (Source: Department of Land Administration, 2000).



Plate 3.2: Example of study sites at Lake Jandabup. The top photo represents a vegetated site on the western side with diatomaceous sediment, the middle photo represents an open water site with organic sediment under $\text{Fe}(\text{OH})_3$ precipitate and the bottom photo represents a vegetated site on the eastern side with sandy sediment.

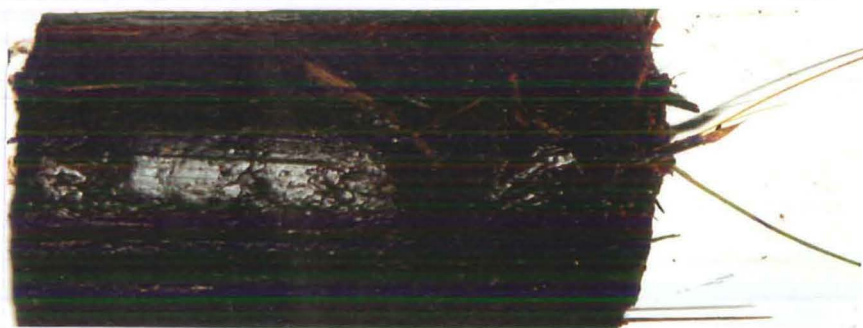
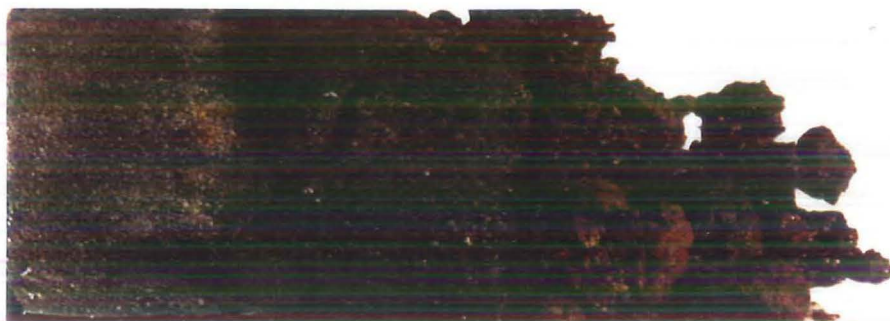


Plate 3.3: Example of sediment types at Lake Jandabup. The top photo represents sandy sediment (notice the orange iron colouring at the top of the core, the middle photo represents sand and organic under iron hydroxide precipitate (the iron hydroxide is the orange clumps seen at the top of the core and the bottom photo represents diatomaceous sediment. Each core of sediment is approximately 20 cm long and the top of the core is at the right hand side of the photo.

3.2 Rationale for Chemical Analyses

Total Iron and Sulfate were chosen because it was suspected that the process of pyrite oxidation contributed to the acidification problem. Sulfate was measured to give an indication of the amount of sulfuric acid in the water. High sulfates would be expected if oxidation of pyrite was the cause of acidity. Total Iron was measured due to high iron levels being consistent with certain stages of pyrite oxidation. However, the iron can be precipitated as solid $\text{Fe}(\text{OH})_3$ therefore total iron levels could be low. Visual observations of $\text{Fe}(\text{OH})_3$ on the lake bed were done to account for this potentiality.

Total Alkalinity measures the buffering capacity of the water. It was measured because it will give an indication of the wetlands ability to neutralise incoming or internally produced acid (Wetzel, 1983). Total acidity measures the ability of water to react with a strong base to obtain a pH near that of sodium hydroxide. It was measured to give an indication of how quickly the pH will increase when a base (e.g. through alkalinity production) is added (Wetzel, 1983).

The anions and cations chosen (sodium, calcium, magnesium, potassium, chloride, carbonate, bicarbonate and sulfate) are the most dominant ions in fresh water and are those most commonly measured on the Swan Coastal Plain (Davis and Rolls, 1987; Davis *et al.*, 1993; Kinnear *et al.*, 1997; Wetzel, 1983). They were measured to assess if there was a relationship between them and acidification.

Carbonates and bicarbonates were measured to give an idea of the buffering capacity at each site and also because it gives a more precise measurement than total alkalinity for carbonate concentration. Silicate was measured because under certain conditions diatomaceous earth containing silicon can react with carbonic or other acids, producing carbonates and silica thereby increasing pH. (Wetzel, 1983). This is especially important for lake Jandabup as the western side of Lake Jandabup contains diatomaceous earth and this may facilitate the buffering capacity of sediments.

3.3 Laboratory Experiment

The laboratory study experimented with intact sediment cores and 3 different drying regimes: 0 days, 10 days and 30 days. The drying regime refers to the number of days of extra air drying (after being oven dried) before rehydration. The experiment had cores that were only air dried (i.e. not oven dried) and hence were controls for oven drying. Plate 3.4 shows an example of set up of the experimental set-up.

3.3.1 Collection of cores

At each site (consisting of a 30 m x 30 m quadrat) 20 intact sediment cores were randomly collected in a 500 mm long by 90 mm wide length of PVC stormwater pipe. Approximately twenty centimetres of sediment was collected in each core by hammering the core into the sediment. A PVC pipe end plug was placed on the top of each core creating a vacuum and cores were then removed from the sediment. The other end was then plugged and the top plug removed. The bottom plug allowed water to

slowly drain from the core. Drainage was enhanced by drilling a 4 mm drainage hole into each plug on return to the laboratory. Cores were left to drain for up to 2 weeks.

3.3.2 Treatment of cores

Fifteen cores from each site were oven dried at 50 °C for 12 days. This was the time required for the cores to lose less than 1% moisture per day. This temperature was chosen because it was assumed that this would be the near maximum temperature on the dry lake bed during summer. Five replicates from each of the ten sites were then used for each drying regime of 0 days, 10 days and 30 days. However, for the 30 days drying experiment only 5 sites were used. The five sites were selected according to criteria given in section 3.3.4. After being oven dried, cores were sealed at the end plug using PVC plumber's glue and Selleys 'Aqua Knead It TM' was used to plug the drainage hole.

The 0 days drying cores were rehydrated immediately after being removed from the oven. The 10 days and 30 days cores were left to air dry in a temperature controlled environment of between 16 °C and 20°C for 10 days and 30 days respectively before being rehydrated. Cores for the 10 and 30 days drying were weighed at the beginning and end of the drying period to ensure that they were losing and not gaining moisture. The five control cores were rehydrated as soon as possible after collection from the lake.

After being dried for the specified period of time cores were rehydrated with 1.5 L of rainwater by pouring the water into the top of the core, the water level in the core was marked. After approximately 1 hour cores were topped up with more rainwater to the

marked level to account for seepage of water into the sediment. Rainwater was used to simulate natural conditions in the field. It was collected from the School of Natural Sciences rainwater tank on the Joondalup Campus. Due to the close proximity (15 kilometres) of Lake Jandabup to the campus, it was expected that the rainwater properties at Lake Jandabup would be similar to that collected in the tank. Initial physico-chemical properties (pH, redox, dissolved oxygen and conductivity) of the rainwater were taken using WTW field meters. Two samples of rainwater were taken for later total iron and sulfate analyses. The total iron sample was acidified to 1% with 0.1M Hydrochloric Acid for preservation. Both samples were frozen until needed.

3.3.3 *Physical and chemical analyses*

All cores were aerated every day for 1 hour to keep the oxygen level above 7 mg L⁻¹, then left to settle for at least 1 hour after aeration, to account for any artificial pH differences resulting from aeration. After the settling period the water above each core was tested for: pH, redox, conductivity and temperature on days 1, 5, 10, 15 and 22 after rehydration.

On day 22 (after rehydration) two water samples of 200 ml each were taken, one for sulfate and one for total iron (the latter was acidified using 2 ml 0.1M HCl). Water samples were frozen for later analyses. Also at day 5 and day 22 each core was analysed for total acidity and total alkalinity using the method described in section 3.6.2. All water samples and acidity and alkalinity were completed only after the physico-chemical properties were recorded for that day.

Only 5 sites and 3 replicates were analysed for total iron and sulfate due to financial and time constraints. These were the same sites chosen for the 30 days drying experiment. Criteria for selecting these sites are given in section 3.3.4. Within each site replicates were chosen randomly, but, due to the high within site variation, selection was overridden in favor of including the full range of variation (i.e. at least 1 extreme replicate was chosen).

3.3.4 Criteria for selection of 5 sites

The data collected from the control, 0 days and 10 days drying experiment and the field monitoring was used as a basis for site selection for further analyses as previously described. The five sites chosen were 2,4,6,7, and 9 based on the following criteria. There should be:

- i. at least 1 acidic and 1 neutral site,
- ii. at least 1 site in each of the three dominant sediment types, which are sand only, sand and organic with iron hydroxide precipitate and diatomaceous earth,
- iii. at least 1 site taken from amongst emergent vegetation and 1 site in the open water,
- iv. at least 1 site showing a difference between inside and outside field placed cores and,
- v. at least one site showing similar results in the laboratory and the field.

3.3.5 *Basic stratigraphy of sediment*

After the cores had been used in the experiment the sediment of one core from each site (from the control set) was removed intact to describe the stratigraphy of the core. Cores were divided up based on visible sections and the sediment described. In addition to this each section from each core was analysed for organic matter which was determined by loss on ignition (LOI) at 500°C for 2 hours.

3.4 **Field Study**

At each site 5 *in situ* cores were placed randomly into the sediment to a depth of 20 cm. Each core consisted of a 1m length of PVC pipe 90 mm in diameter. Physico – chemical properties of the water were measured inside and outside each core at time of placement (prior to removal of sediment cores for laboratory experiments).

3.4.1 *Physico– chemical monitoring*

From the time of core placement in April until the end of August 2000, physico-chemical properties and water depth were measured inside and directly outside each *in situ* core, at all ten sites on the same day every week. However, it must be noted that three sites remained dry for approximately half the study period, therefore physico-chemical data were not available for those sites until they became filled from the winter rains and/or increased groundwater levels. If water depth rose above the top of a core inside measurements ceased (but outside measurements continued) because the water

was no longer isolated. Plate 3.4 gives an example of an *in situ* core and physico-chemical monitoring techniques.

Wherever possible, measurements at each core were made at approximately the same time each week between 8:00 am and 3:00 pm to account for diurnal differences. Due to Lake Jandabup's large size and shallow nature, movement around the lake was on foot for most of the study period. With the large number of sites and replicates, time constraints permitted only the middle of the water column to be tested (inside and outside each *in situ* core). Due to the high spatial variability of Lake Jandabup, both between and within sites, it was deemed important to focus on spatial variability. As many sites remained relatively shallow for much of the study period, stratification was unlikely to be a significant factor during the early months.

3.4.2 Total Iron, sulfate, acidity and alkalinity

Monthly water samples were collected from inside and directly outside each *in situ* core at the middle of the water column from all wet sites for analyses of total acidity, total alkalinity, sulfate and total iron. Total acidity and total alkalinity were analysed immediately upon return to the laboratory using water collected in 250 ml bottles that were fully filled to prevent any mixing with air in transportation. Methods are described in section 3.6.2. Two separate samples were collected for sulfate and total iron, with the total iron sample being acidified to 1% using 2 ml 0.1M HCl. Sulfate and total iron samples were frozen immediately on return to the laboratory for later analyses. Due to the large number of sites and replicates and the need to complete titrations the day of the sample being taken, the monthly field work was completed over 2 or 3 days.

Only 5 sites and 3 replicates were analysed for total iron and sulfate. For criteria on how the sites were chosen see section 3.3.4. Within-site replicates were chosen randomly, but due to the high variation with some sites, selection was over ridden in favor of including the full range of variation therefore least 1 extreme replicate (for pH) was chosen.

3.4.3 *Anions and cations*

A once off total anion and cation survey of Lake Jandabup was completed to assess if there were any relationships between the spatial distribution of pH and these ions (see section 3.2). It was anticipated that a bulked sample should be taken using water from inside and outside each *in situ* core to obtain 2 water samples per site. Due to some sites being dry, water samples were not taken until 19th July. However, on this sampling day the pH unexpectedly rose. Owing to the need to have cation and anion data for when the pH showed maximum differences across sites, it was decided to use spare water samples taken from the monthly sampling (as described in section 3.4.2, only 3 out of the 5 replicates were analysed, leaving 2 spare samples).

To decide which samples were to be analysed Table 3.2 was used. The June sampling was chosen because in this month the pH was low, there was the greatest difference between inside and outside the cores, and spatial variability was clearly noticeable. Sites 5 and 10 were dry in June so July water was used for those sites. For sites 2,4,6,7 and 9 (the sites selected from criteria in section (3.3.4) June and July water was used to show differences over time. For these sites (2,4,6,7 and 9) a bulked water sample was made

from the 2 spare samples that were not analysed. For sites 3,5,8, and 10, two replicates were randomly selected from the five to make two bulked samples for each site, one for inside the core and one for outside the core.

Table 3.2: Mean pH for each site on day of monthly water sampling. (Note: number on top is pH inside the in situ core and number on bottom is pH outside the in situ core). For sites 2,4,6,7 and 9 both June and July were sampled. For Sites 5 and 10 July water was used and for all other sites only June water was used.

SITE	May	June	July	Total Number of samples per site
1	DRY	DRY	DRY	0
2	6.3	4.5	4.4	4
	6.1	4.8	5.6	
3	6.9	7.2	6.5	2
	6.9	7.2	6.4	
4	6.7	7.0	6.5	4
	6.3	6.8	6.4	
5	DRY	DRY	6.2	2
			4.3	
6	4.6	4.7	5.8	4
	3.9	4.3	5.2	
7	7.1	7.2	6.5	4
	6.7	7.2	6.5	
8	4.6	4.4	5.2	2
	4.3	4.3	6	
9	4.1	3.9	4.3	4
	5.3	4.7	5.2	
10	DRY	DRY	6.7	2
			6.5	

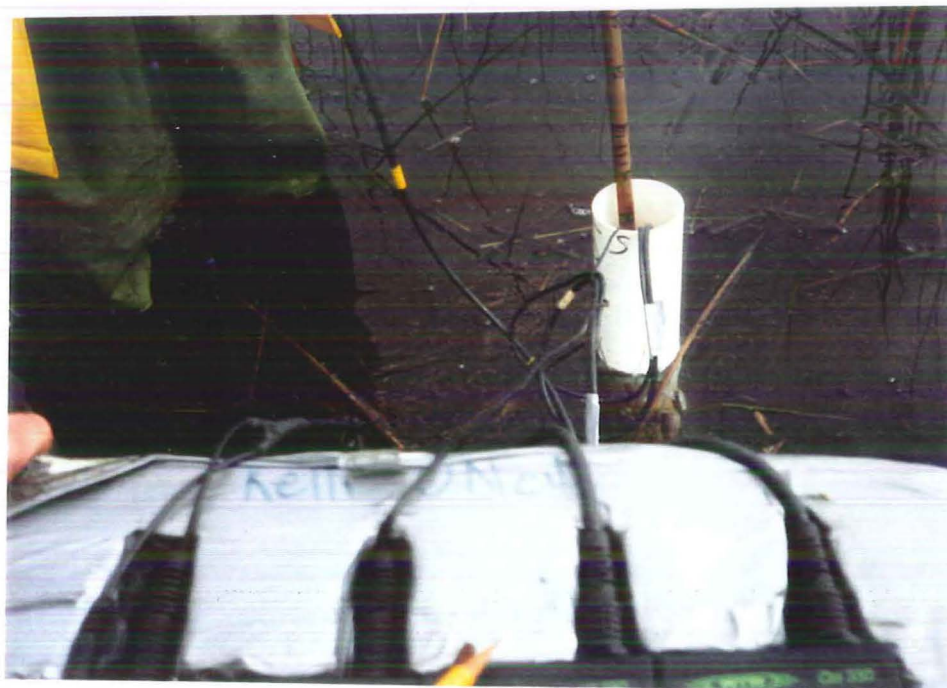
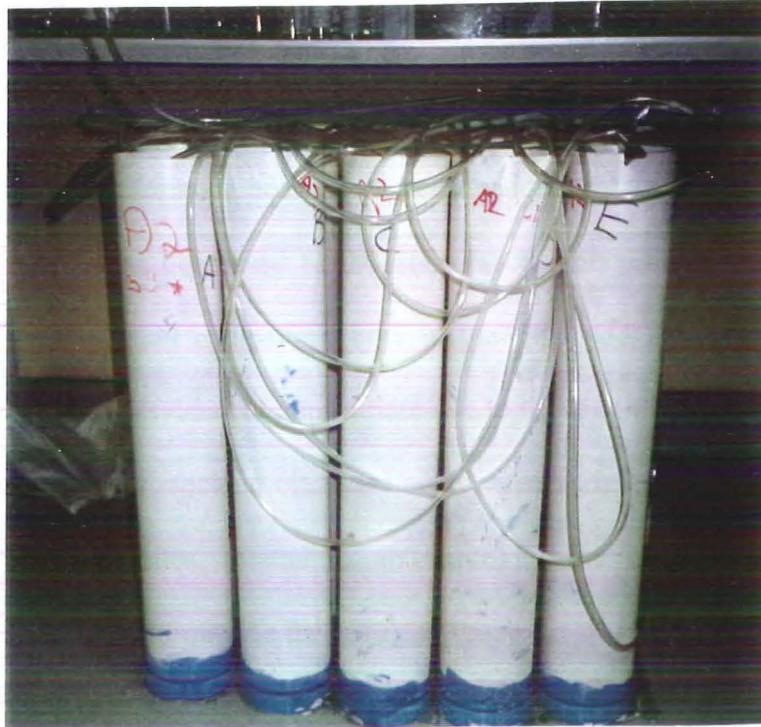


Plate 3.4: Example of laboratory and field experimental set up. The top photo is the laboratory core set up for 5 sites and 1 treatment (each core was 50 cm long and contained 20 cm of sediment) notice the plastic tubing delivering compressed air via an air stone (not shown). The bottom photo represents one in situ core and the method of measuring physico-chemical properties.

3.5 Statistical Analysis

All statistical analysis was undertaken using SPSS version 10.0 (SPSSTM SPSS Inc). Data were not transformed, but where homogeneity of variances was violated the significance level was decreased to 0.01 (E. Pascoe, pers. comm., September 2000). Due to the use of small enclosures, both in the field and laboratory study, repeated measures analysis was deemed appropriate due to the lack of independence of samples over time. Three-way repeated measures analysis of variance (ANOVA) evaluated the differences between sites, treatments and time for the laboratory study and sites, positions (i.e. inside and outside the core) and time for the field study. The Huyn-Feldt test of significance was used as this test is less likely to give a significant result when there is none (Vonesh and Chinchilli, 1997). This test was also used because in most cases Mauchly's test of sphericity was not able to be calculated (due to small sample sizes) and therefore it was not known if the assumption of sphericity had been violated. Bonferroni pairwise comparisons were used to examine main effects from the three way repeated measures ANOVA. For sulfate, total iron, total acidity and total alkalinity of the laboratory cores a two way ANOVA was used due to the absence of repeated measures effect.

Pearsons correlation coefficients were calculated between all variables to significant levels ($p < 0.01$ and $p < 0.05$) using SPSS version 10.0 (SPSS^M SPSS Inc).

Semi strong hybrid multidimensional scaling ordination (SSH) was performed on field data using the PATN ordination package (Belbin, 1989). The Gower metric association

measure was used because it automatically standardises by range which is suited to physico-chemical data (Williams *et al.*, 1987).

For all pH data a geometric mean was used because an arithmetic mean is unsuitable for logarithmic data (Boulton and Brock, 1999; Wetzel, 1983).

3.6 General Methods

3.6.1 Physico – chemical properties

All physico – chemical properties (pH, dissolved oxygen, electrical conductivity, redox potential and temperature) were measured on *Wissenschaftliche Technische Werkstätten* (WTW) field meters. A new pH probe was used to enable accurate pH measurements to be taken. The same probe and meters were used throughout the study to account for any slight differences between meters and probes. All meters and probes were calibrated regularly.

3.6.2 Chemical Analyses

All chemical analyses, except acidity and alkalinity were completed by AGAL (Australian Government Analytical Laboratories) using methods based on Clesceri *et al.* (1998) as described below.

Total alkalinity was analysed by potentiometric titration with 0.01M hydrochloric acid (HCl) to end point pH 4.5. Normally, a 0.1M solution is used but since sample water already had a low pH, a more dilute solution was used to enable accurate measurements. If the pH of the sample was below 4.5 it was deemed to have zero alkalinity. Total acidity was measured by potentiometric titration with 0.01M sodium hydroxide (NaOH) to end point pH 8.3. A 0.1 M solution of NaOH was made by dissolving 4g of NaOH in 1000ml of carbon dioxide free water (made by boiling deionised water for 15 minutes). This solution was diluted to 0.01M using carbon dioxide free water. Normality of the HCl and NaOH was measured for use in the calculation of total acidity and total alkalinity as shown below (Clesceri *et al.*, 1998).

$$\text{Alkalinity, mg CaCO}_3\text{/L} = \frac{A \times N \times 50\,000}{\text{ml sample}}$$

Where

A = ml standard acid used

N = Normality of standard acid

$$\text{Acidity, mg CaCO}_3\text{/L} = \frac{A \times B \times 50\,000}{\text{ml sample}}$$

Where

A = ml NaOH titrant used

B = Normality of NaOH

Total iron was analysed using the nitric acid digestion method followed by atomic absorption spectroscopy (AAS) (Clesceri *et al.*, 1998). Analysis of sulfate was based on single column ion chromatography with electron suppression of eluent conductivity and conductimetric detection method (Clesceri *et al.*, 1998). Silicate (SiO₂) was determined by a method based on standard method flow injection analyses for molybdate-reactive silica (Clesceri *et al.*, 1998).

Sodium (Na^+) and potassium (K^+) were determined using metals by AAS (direct air acetylene flame method). Magnesium (Mg^{2+}) was determined by metals by AAS (direct nitrous oxide-acetylene flame method). Calcium (Ca^{2+}) was determined using metals by AAS (direct nitrous oxide-acetylene flame method). Analyses of Chloride (Cl^-) was based on single column ion chromatography with electron suppression of eluent conductivity and conductimetric detection method. Carbonate and bicarbonate were measured using titrimetric methods (Clesceri *et al.*, 1998).

3.6.3 Licenses and Permits

One license and one permit were required from the Department of Conservation and Land Management (CALM) for the study. Licence number SF003129 was needed for incidental collection of fauna in sediment cores. Permit number NE002436 was used for research/educational excursion in a CALM estate.

CHAPTER 4: LABORATORY EXPERIMENT RESULTS

The results from the laboratory study showed that each site responded differently to drying and rehydration of sediment, but there were some distinct trends and sites could be grouped according to similar responses.

A high positive correlation ($r = .816$, $p < 0.01$) was found between pH and total alkalinity indicating that buffering capacity decreased with pH (Table. 4.1). Low pH was also correlated ($r = -.646$) with high sulfate levels supporting the hypothesis that pyrite oxidation is responsible for the acidification of the lake. A positive correlation ($r = .547$, $p < 0.01$) between sulfate and acidity reinforces this view. Total iron was not correlated with any other variable, except weakly to total acidity ($r = .346$, $p < 0.01$).

Table 4.1: Significant correlations for laboratory experiments (showing r values). For alkalinity and acidity ($n = 350$) and sulfate and total iron ($n = 120$).

	pH	sulfate	Total iron	alkalinity	acidity
PH					
Sulfate	-.646**				
Total iron	NS	NS			
Alkalinity	.816**	.560**	NS		
Acidity	-.441**	.547**	.346**	-.299*	

** = statistically significant at the 0.01 level
 * = statistically significant at the 0.05 level
 NS = Not statistically significant ($p > 0.05$)

At sites 1, 3, 4 and 10 the pH for all treatments and all times ranged between 6 and 7 pH units (Figure 4.1). There was little obvious difference between treatments and little within site variation. Generally for these sites the pH increased slightly over the 22 days. For sites 7, 8 and 9 the pH was between 5.0 and 6.5 pH units at time 1 (i.e. day 1). By time 5 (i.e. day 5) the pH had decreased by up to 1 pH unit where it remained constant for the remainder of the experiment (Figure 4.1). At these sites (7, 8 and 9) there was little difference between treatments, although the control generally had the highest pH. At site 2, time 1, the pH was between 4.5 and 6.0 pH units depending on the treatment (control had the highest and 0 days the lowest). Between time 1 and time 22 the pH for each treatment increased by up to 1.5 pH units. There was high within site variability of up to 1 pH unit. At site 5 the pH was between 5.5 and 6 pH units for time 1 to time 10, after which the 0 days drying cores decreased by 0.5 pH units, the control cores remained constant and the 10 days drying cores increased by 0.5 pH units. The pH of the initial rainwater was on average 7.0 pH units.

The temperature of the core water remained between 15 and 22 °C for the entire study period. Daily fluctuations were no more than 2°C. For conductivity the range was between 100 $\mu\text{S cm}^{-1}$ and 1700 $\mu\text{S cm}^{-1}$ over all treatments, all sites and all times. Sites 1, 2, 3, 4, 5, 8, 9 and 10 all had conductivities below or near 500 $\mu\text{S cm}^{-1}$ for all treatments and for all days tested. Sites 6 and 7 usually had a conductivity between 500 $\mu\text{S cm}^{-1}$ and 1000 $\mu\text{S cm}^{-1}$ and site 5 was always above 1000 $\mu\text{S cm}^{-1}$. Generally conductivities did not alter between the treatments, except that the control cores had slightly lower conductivities than the treatments. Redox remained constant between 100 and 300 mV for all sites, all treatments and all times.

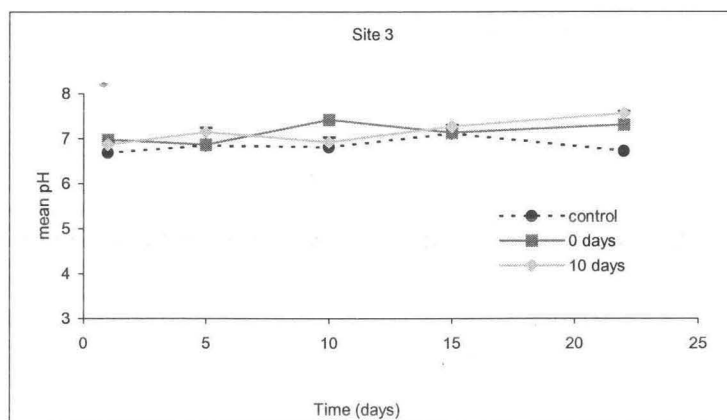
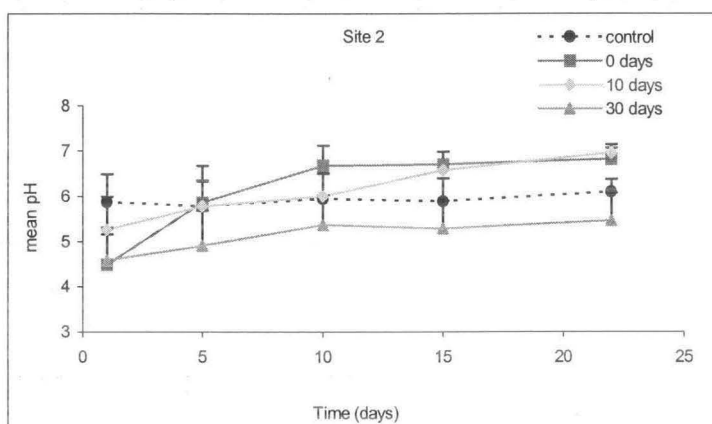
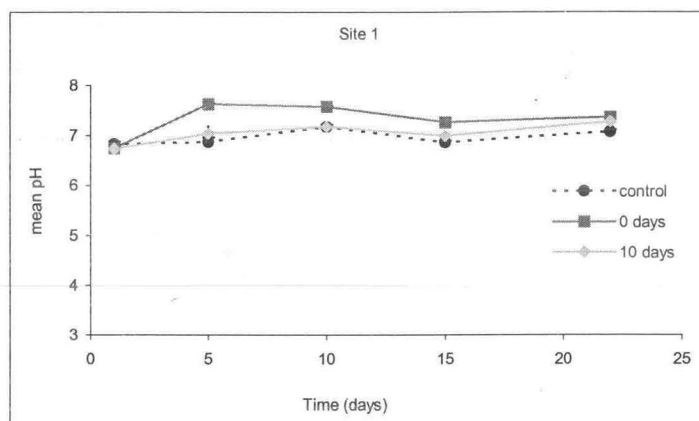


Figure 4.1: Mean and Standard Error for pH with time since rehydration for each site and each treatment ($n = 5$). CONTINUED NEXT PAGE

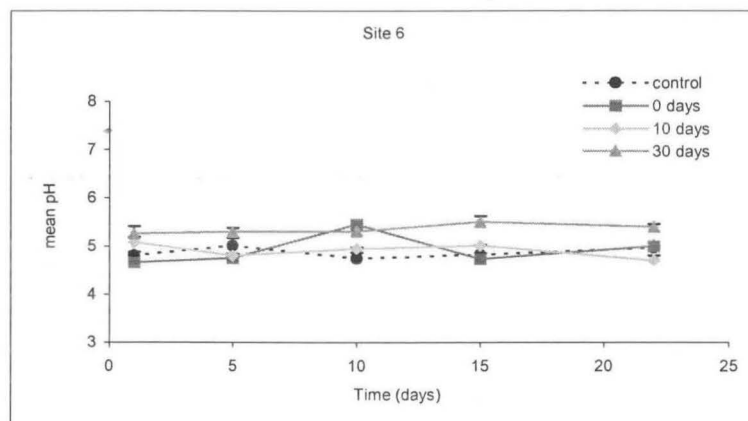
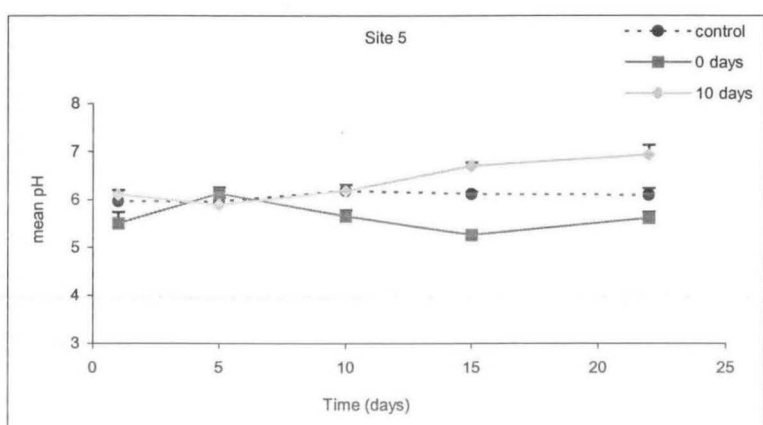
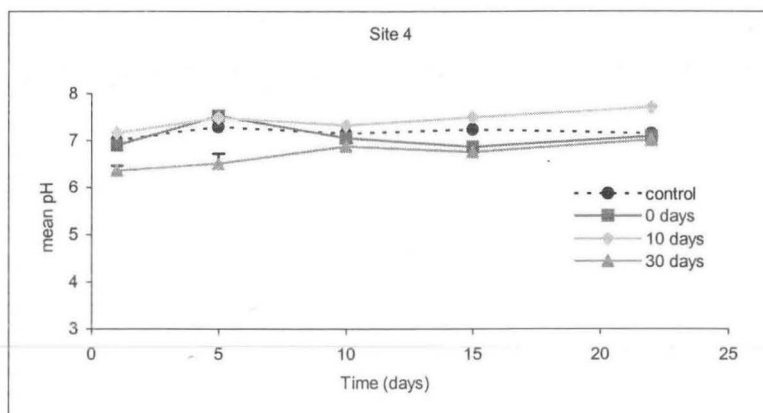


Figure 4.1 CONTINUED:: Mean and Standard Error for pH with time since rehydration for each site and each treatment (n = 5). CONTINUED NEXT PAGE

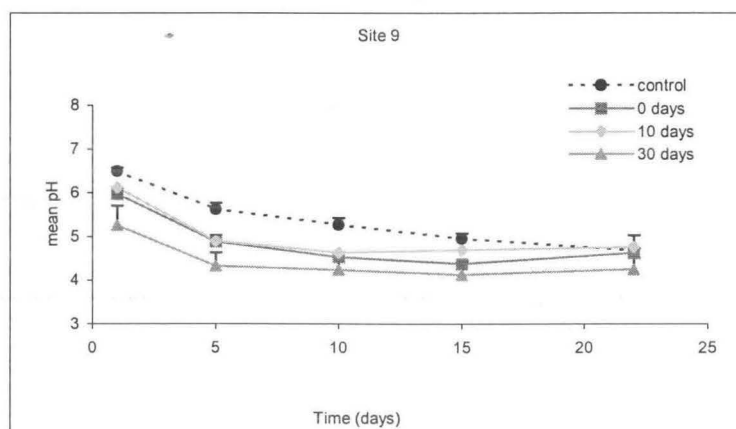
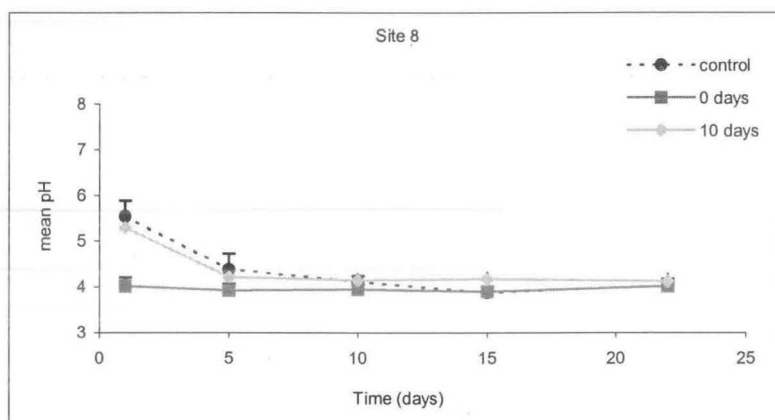
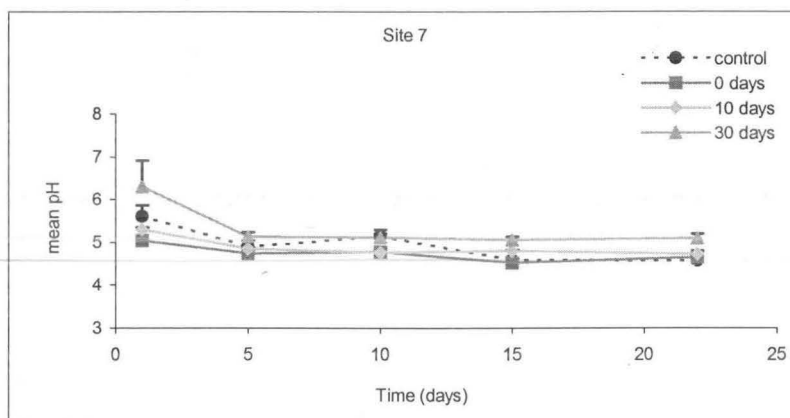


Figure 4.1 CONTINUED: Mean and Standard error for pH released over time since rehydration for each site and each treatment ($n = 5$). CONTINUED NEXT PAGE

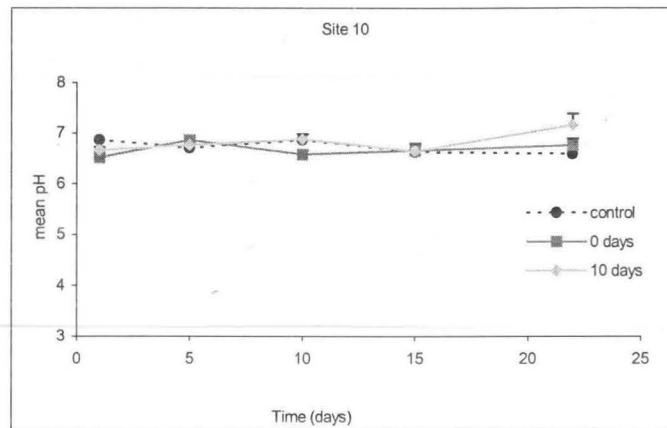


Figure 4.1 CONTINUED: Mean and Standard Error for pH with time since rehydration for each site and each treatment ($n = 5$).

These results show that there is usually high variability in pH between day 1 and day 5. If these data (from time 1) are used in the analyses they may affect the results because of the rapidly changing pH. Therefore day 1 was excluded from the statistical analyses unless otherwise stated. In addition to this, data from the control cores were excluded in the statistical analyses because the control was a control for oven drying and not for zero days drying (i.e. maybe it was the oven drying causing the pH decline, not the actual effects of drying or drying length). Before data was excluded a three way repeated measures ANOVA compared the control with the 0 days drying and the control with 30 days drying. This was done to ensure that oven drying was not affecting the results. The 0 days drying data was used as these cores were only oven dried and not air dried therefore the only difference between those and the control is being oven dried and the 30 days drying was chosen because it represents the greatest variation in drying times between the control and the treatment. No significant difference ($p < 0.05$) was found between oven drying and air drying (Table 4.2 and Table 4.3).

Table 4.2: Results of the three way repeated measures ANOVA showing significant levels for pH differences between oven drying (0 days treatment) and the control for all sites.

FACTOR	Three way repeated measures ANOVA				
	Variable = pH				
	df	Mean square	F - Value	P - Value	
Time	2.706	1.261	20.812	.000	*
Site	9	84.926	163.356	.000	*
Treatment	2	0.1229	.024	.977	NS
Treatment*Site	18	.813	1.599	.071	NS
Time * Site	24.351	.445	7.339	.000	*
Time*Treatment	5.411	.122	2.009	.071	NS
Time*Treatment*Site	48.702	.143	2.359	.000	*

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

Table 4.3: Results of the three way repeated measures ANOVA showing significant levels for pH differences between oven drying (30 days treatment) and the control for all sites

FACTOR	Three way repeated measures ANOVA				
	Variable = pH				
	df	Mean square	F - Value	P - Value	
Time	2.805	0.05360	1.057	.366	NS
Site	9	28.261	23.123	.000	*
Treatment	1	1.726	1.412	.239	NS
Treatment*Site	4	3.217	2.632	.043	*
Time * Site	25.247	.183	1.217	.343	NS
Time*Treatment	2.805	.416	8.203	.000	*
Time*Treatment*Site	165.510	.0507	1.127	.343	NS

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

Two data sets were analysed to assess if there was a significant difference in pH between treatments, sites and over time. Data set (a) used the 5 major sites (2, 4, 5, 6 and 9) over 3 treatments (0 days, 10 days and 30 days) and (b) used all sites and 2 treatments (0 days and 10 days drying). A 3 way repeated measures ANOVA of both data sets showed significant interactions between time, treatments and sites, indicating that all sites are responding differently upon drying and rehydration (Tables 4.4 and 4.5).

Due to the significant interactions all main effects are invalid (Underwood, 1999). However, the relationship between interactions can be examined using Bonferroni pairwise comparisons as per Underwood (1999). The results show that most sites are significantly different from one another, therefore it is probably site variability causing the interaction (Table 4.6). As the results from both data sets were similar only the larger data set (b) will be presented.

Table 4.4: Results of the three way repeated measures ANOVA testing significant difference in pH between sites and over time since rehydration. For consistency the Hyun-Feldt test of significance was used for all significance levels. It excluded time 1 data for reasons described earlier and used data set (a) i.e. 5 sites and 3 treatments.

FACTOR	Three way repeated measures ANOVA				
	Variable = pH				
	df	Mean square	F - Value	P - Value	
Time	2	.219	3.700	.028	*
Site	4	64.537	5.381	.000	*
Treatment	2	1.409	1.209	.306	NS
Treatment*Site	8	2.903	2.491	.021	*
Time * Site	8.018	.710	8.015	.000	*
Time*Treatment	4.009	.335	3.777	.006	*
Time*Treatment*Site	16.035	.206	2.330	.005	*

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

Table 4.5: Results of the Three way repeated measures ANOVA testing difference in pH between sites and over time since rehydration. For consistency the Hyun-Feldt test of significance was used for all significance levels. It excluded time 1 data and used data set (b) (i.e. 10 sites and 2 treatments)

FACTOR	Three way repeated measures ANOVA				
	Variable = pH				
	df	Mean square	F - Value	P - Value	
Time	3.437	.729	10.588	.000	*
Site	9	56.782	69.950	.000	*
Treatment	1	.788	.971	.327	NS
Treatment*Site	9	56.782	69.950	0.00	*
Time * Site	27	.499	9.102	.000	*
Time*Treatment	3.437	1.302	18.910	.000	*
Time*Treatment*Site	30.397	.350	5.092	.000	*

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

Table 4.6: Bonferroni post hoc tests showing significant ($p < 0.05$) differences between individual sites for pH released over time since rehydration. The table represents a matrix comparing each site with every other site. The data were averages across treatments and times. It excluded time 1 data for reasons described and used data set (b) i.e. 10 sites and 2 treatments i.e. 0 days and 10 days.

	site 1	site 2	site 3	site 4	site 5	site 6	site 7	site 8	site 9	site 10
site 1										
site 2	*									
site 3	NS	*								
site 4	*	NS	NS							
site 5	*	*	*	*						
site 6	*	*	*	*	*					
site 7	*	*	*	*	*	NS				
site 8	*	*	*	*	*	*	*			
site 9	*	*	*	*	*	NS	NS	*		
site 10	*	NS	NS	NS	*	NS	*	*	*	

* = statistically significant ($p < 0.05$)
 NS = Not statistically significant ($p > 0.05$)

In an attempt to reduce the effect of site differences a 2 way repeated measures ANOVA was undertaken on individual sites as this is the standard method for interpreting interactions (Underwood, 1999). Only data set (a) was used because it contained the maximum number of treatments, which is essentially what the experiment is testing (Table 4.7). There was a significant interaction for each of site 2 and 6 indicating that these sites are behaving differently over time and between treatments. For site 7 there was no difference between treatments, nor was there a difference over time. For sites 2 and 9 there was no significant difference between treatments but there was a significant ($p < 0.01$) difference over time.

Table 4.7: Individual two way repeated measures ANOVA for pH for sites 2,4,6,7 and 9 (data set (a)). It shows which sites have a significant difference ($p < 0.01$) between positions and over time.

FACTOR		Two way repeated measures ANOVA				
		Variable = pH				
		df	Mean Square	F - Value	P - Value	
Treatment						
	Site 2	3	3.504	.698	.569	NS
	Site 4	3	1.690	16.355	.000	*
	Site 6	3	1.105	9.422	.001	*
	Site 7	3	.819	2.712	.080	NS
	Site 9	3	1.842	3.289	.048	NS
Time						
	Site 2	2.199	2.083	7.662	.002	*
	Site 4	1.367	.237	9.403	.003	*
	Site 6	3	.138	6.192	.001	*
	Site 7	2.140	.157	4.689	.014	NS
	Site 9	1.908	1.137	9.568	.001	*
Time*Treatment						
	Site 2	6.596	.344	1.265	.300	NS
	Site 4	4.101	.425	16.838	.000	*
	Site 6	9	.212	9.475	.000	*
	Site 7	6.419	0.045	1.347	.251	NS
	Site 9	5.724	.219	1.841	.180	NS

* = statistically significant ($p < 0.01$)

NS = Not statistically significant ($p > 0.01$)

Note: probability levels had been altered to $p < 0.01$. As per Underwood (1999) when individual ANOVAS are completed based on interactions the probability level should be made more stringent by dividing the number of tests by the original probability level, in this case it is 0.05 divided by 5 which is the number of sites tested.

Sites 6 and 7 had the highest sulfate levels (up to 250 mg L^{-1}) and site 4 had the lowest ($\sim 50 \text{ mg L}^{-1}$) (Figure 4.2). The initial sulfate in the rainwater was 6 mg L^{-1} . Thirty days drying tended to produce higher sulfate levels and control cores tended to have the lowest levels. All sites had similar average total iron levels, ranging from $\sim 1 \text{ mg L}^{-1}$ (site 9) and 4.6 mg L^{-1} (site 7) (Figure 4.3). The initial rainwater had less than 1 mg L^{-1} of total iron. In general 30 days drying cores released the least total iron and control cores always had the lowest. Sites 5, 6, 7 and 9 had extremely low total alkalinity (or buffering capacity) levels, below $2 \text{ mg CaCO}_3 \text{ L}^{-1}$. Site 8 had zero alkalinity. Site 2 had a moderate alkalinity of $15 \text{ mg CaCO}_3 \text{ L}^{-1}$ on average over all treatments (Figure 4.4). Sites 1, 4, 3 and 10 had similar alkalinity levels of between $30 \text{ mg CaCO}_3 \text{ L}^{-1}$ and $90 \text{ mg CaCO}_3 \text{ L}^{-1}$. For most sites there was little difference between the treatments. These results indicate that there is a spatial variability for buffering capacity of sediments taken from certain areas around Lake Jandabup. For total acidity most sites had similar levels of less than $30 \text{ mg CaCO}_3 \text{ L}^{-1}$ averaged across all treatments (Figure 4.5). The exception was sites 6, 7, 8, 9 that had levels for some treatments up to $80 \text{ mg CaCO}_3 \text{ L}^{-1}$. For these sites there was a distinct difference between treatments. However there were no consistent trends regarding which treatments had the lowest or highest levels. For all other sites all treatments had similar values.

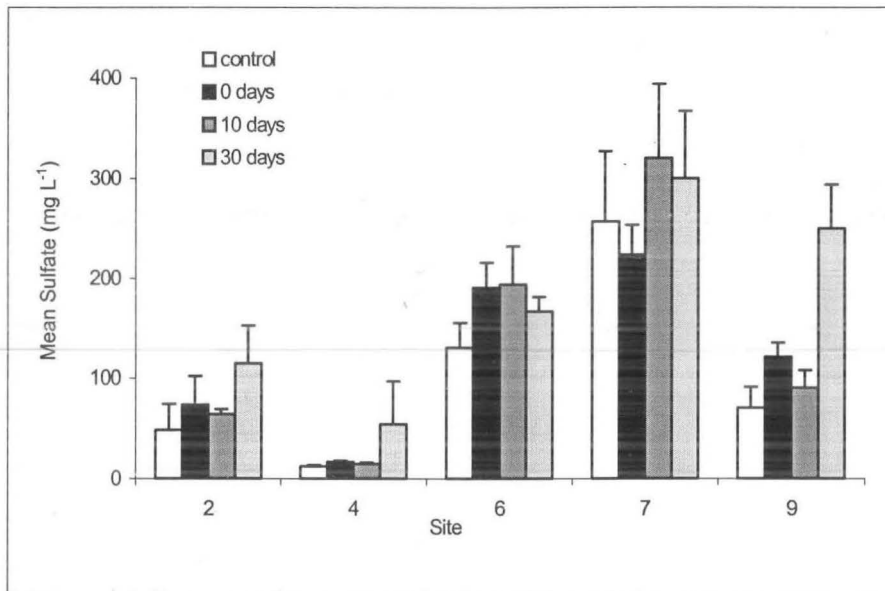


Figure 4.2: Mean and Standard Error ($n = 3$) for sulfate released after 22 days from rehydration for 3 treatments (0 days drying, 10 days drying and 30 days drying) and 1 control.

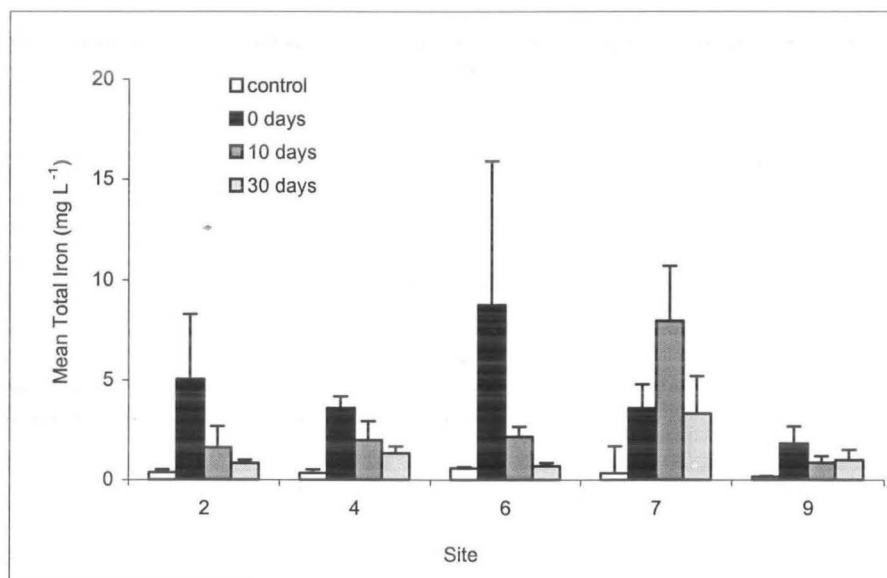


Figure 4.3: Mean and Standard Error ($n = 3$) for total iron released after 22 days from rehydration for 3 treatments (0 days drying, 10 days drying and 30 days drying) and 1 control.

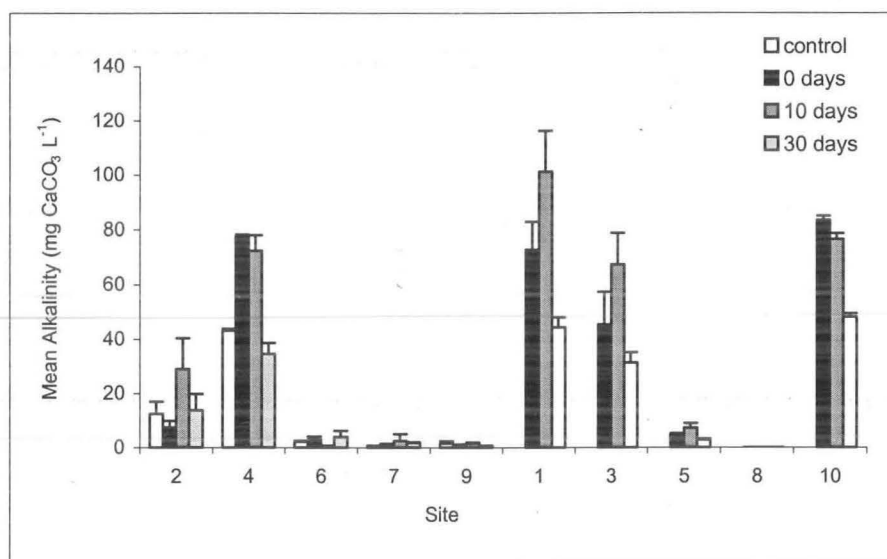


Figure 4.4: Mean and Standard Error ($n = 5$) for total alkalinity released after 22 days from Rehydration for 3 treatments (0 days drying, 10 days drying and 30 days drying) and 1 control. Note that sites 1,3,5,8 and 9 had no 30 days drying experiment.

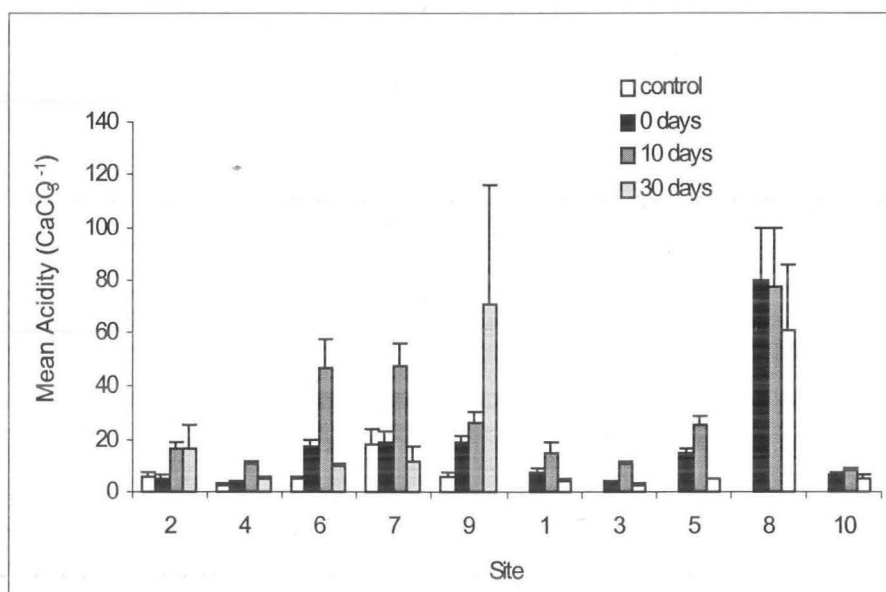


Figure 4.5: Mean and Standard Error ($n = 5$) for total acidity released after 22 days from Rehydration for 3 treatments (0 days drying, 10 days drying and 30 days drying) and 1 control. Note that sites 1,3,5,8 and 9 had no 30 days drying experiment.

Similar to pH for all statistical analyses of chemical data (i.e. sulfate, total iron, total alkalinity and total acidity) the data from the control cores were removed due to reasons previously explained. A two way ANOVA was performed to test differences from the control data. The results show that there were no significant ($p < 0.01$) differences between treatments indicating that oven drying is probably not affecting the results.

A two way ANOVA was performed on sulfate, total iron, total alkalinity and total acidity data for release after 22 days for 5 sites. Levene's test for homogeneity of variances was significant $p < 0.01$. Data transformation or removal of outliers was not done because there is natural (and wanted) variation in the data. To account for this, a more stringent Alpha significance level was set at $p < 0.01$. In addition to this there were only data available for 5 sites for sulfate and total iron. The tests show that for sulfate, iron and total acidity there were no significant interactions, therefore the results of the main effects are valid (Table 4.8). For sulfate there was a significant ($p < 0.01$) difference between sites but no significant difference between treatments. For total iron there were no significant differences between sites or treatments. Total acidity showed significant differences between sites and between treatments and nonsignificant interaction meaning that the differences across sites and treatments are independent of each other. Total alkalinity had a significant interaction indicating that sites were behaving differently over time and between treatments.

As per Underwood (1999), Bonferroni post hoc tests revealed which sites were significantly different from one another ($p < 0.01$). For sulfate most sites were significantly different from every other site, the exception was that sites 2, 4 and 9

showed similar responses (Table 4.9). For total acidity site 9 was not significantly different from any other sites except 7 and in general sites 2, 6, 4 and 7 showed similar responses (Table 4.10). Although there was a significant interaction for total alkalinity and the main effects tests are invalid the post hoc tests highlight the large differences between most sites; only site 6 with 7 and 9, and, site 7 and 9 were significantly ($p < 0.01$) different from one another (Table 4.11). Bonferroni post hoc tests also showed that for total acidity 10 days drying produced significantly less ($p < 0.01$) acidity compared with 0 days and 30 days drying (Table 4.12).

Table 4.8: Two way ANOVA for sulfate, total iron, total alkalinity and total acidity after 22 days from rehydration. Sulfate and total iron (n= 3) total alkalinity and total acidity (n=5)

FACTOR	Two way ANOVA				
Variable = Sulfate (S), Total Iron (Fe),Total Alkalinity (Ak) and Total Acidity (Ac)					
	df	Mean square	F - Value	P - Value	
Site (S)	4	83849.589	21.477	.000	*
Site (Fe)	4	19.464	1.290	.296	NS
Site(Ak)	4	5835.994	126.883	.000	*
Site (Ac)	4	712.819	7.445	.000	*
Treatment (S)	2	36.849	2.380	.100	NS
Treatment (Fe)	2	55.268	3.663	.038	NS
Treatment (Ak)	2	793.804	17.259	.000	*
Treatment (Ac)	2	1115.409	12.057	.000	*
Site*Treatment (S)	8	5578.756	1.429	.225	NS
Site*Treatment (Fe)	8	13.923	.923	.512	NS
Site*Treatment (Ak)	8	484.239	10.528	.000	*
Site*Treatment (Ac)	8	233.849	2.442	.036	NS

* = statistically significant (p < 0.01)
NS = Not statistically significant (p > 0.01)

Table 4.9: Bonferroni post hoc tests showing significant (p < 0.01) differences between sites for sulfate released after 22 days from rehydration The analysis uses data set (a).

	Site 2	Site 4	Site 6	Site 7	Site 9
Site 2					
Site 4	NS				
Site 6	*	*			
Site 7	*	*	*		
Site 9	NS	*	NS	*	

* = statistically significant (p < 0.01)
NS = Not statistically significant (p > 0.01)

Table 4.10 Bonferroni post hoc tests showing significant ($p < 0.01$) differences between sites for total acidity released after 22 days from rehydration. The analysis uses data set (a).

	Site 2	Site 4	Site 6	Site 7	Site 9
Site 2					
Site 4	NS				
Site 6	*	*			
Site 7	*	*	NS		
Site 9	NS	NS	NS	*	

* = statistically significant ($p < 0.01$)

NS = Not statistically significant ($p > 0.01$)

Table 4.11: Bonferroni post hoc tests showing significant ($p < 0.01$) differences between sites for total alkalinity released after 22 days from rehydration. The analysis uses data set (a).

	Site 2	Site 4	Site 6	Site 7	Site 9
Site 2					
Site 4	*				
Site 6	*	*			
Site 7	*	*	NS		
Site 9	*	*	NS	NS	

* = statistically significant ($p < 0.01$)

NS = Not statistically significant ($p > 0.01$)

Table 4.12: Bonferroni post hoc tests showing significant ($p < 0.01$) differences between treatments for total acidity released after 22 days from rehydration. The analysis uses data set (a).

	0 days	10 days	30 days
0 days			
10 days	*		
30 days	NS	*	

* = statistically significant ($p < 0.01$)

NS = Not statistically significant ($p > 0.01$)

Individual one way ANOVAS on each site were performed for total alkalinity, this is the standard method for dealing with interactions (Table 4.1). The results show that only site 4 had a significant ($p < 0.002$) difference between treatments.

Table 4.13: One way ANOVA for total alkalinity for sites 2,4,6,7 and 9. It shows which sites have a significant difference ($p < 0.002$) between positions and over time.

FACTOR		One way ANOVA				
		Variable = total alkalinity				
		df	Mean Square	F - Value	P - Value	
Treatment						
	Site 2	2	381.771	2.066	.208	NS
	Site 4	2	2338.397	92.842	.000	*
	Site 6	2	.521	.273	.770	NS
	Site 7	2	9.896	.564	.596	NS
	Site 9	2	.174	.333	.729	NS

* = statistically significant ($p < 0.002$)
 NS = Not statistically significant ($p > 0.002$)

Note: probability levels had been altered to $p < 0.002$. As per Underwood (1999) when individual ANOVAS are completed based on interactions the probability level should be made more stringent by dividing the number of tests by the original probability level i.e. in this case it is 0.01 divided by 5 which is the number of sites tested.

To provide detailed information on the sediment types tested, one core from each site was analysed for basic stratigraphy (Table 4.14). Sandy sediment with some iron coloring was found in sites 1, 2, 3 and 10. Sites 8 and 9 had organic/diatomaceous sediment under large clumps of $\text{Fe}(\text{OH})_3$ precipitate and sites 6 and 7 were diatomaceous with small scattered portions of $\text{Fe}(\text{OH})_3$ on the sediment surface. The sediment surface at site 8 and 9 was heavily cracked. The organic matter (loss on ignition) content of all sites and all sections ranged from 0 to 56 %. Sites 5, 6, 7, 8 and 9 had the highest organic matter content in the sediment of between 30 and 56%, while the remaining sites had less than 5% organic matter per section. In sites 6, 7, 8 and 9 the iron hydroxide layer had a similar organic matter content to the organic/diatomaceous sediment underneath.

Table 4.14: Descriptions of sediment type. The descriptions and sections were taken by removing sediment from the control cores following rehydration and measurement. (LOI = Loss on ignition for 2 hours at 500°C)

Site	Section (cm)	Description	% Organic matter (LOI)
1	0-6	Dark grey/black coarse sand. Little organic matter (o/m). A few plants roots.	2.2
	7-18	Coarse sand, dark grey/black. Fewer plant roots.	.57
2	0-3	Dark grey coarse sand with Fe mottles.	0
	3-7	Dark grey coarse sand with fewer Fe mottles than previous sections	.10
	7 - 17	Grey coarse sand with no Fe mottles	.10
3	0-3	Coarse dark grey sand with Fe Mottles	.16
	3 - 18	Coarse dark grey sand with no Fe mottles	11.76
4	0-3	Coarse light grey sand with algae scum on top. Fe mottles	1.78
	3-18	Light grey coarse sand with algae bits scattered throughout.	.21
5	0 - 20	Organic, no sand. Small amounts of plant material throughout core.	39.62
6	0 - 5	Small (<5cm) bits of Fe(OH) ₃ precipitate mixed with dark brown organic sediment. Some sand present.	42.65
	5 - 9	Similar to 0-5 but less and smaller particles of Fe(OH) ₃ . Dark brown to black organic sediment	64.95
	9 - 18	Black organic sediment. No Fe(OH) ₃ .	56.27
7	0 - 6	Dark brown/black organic sediment. Iron sludge on surface mixed with plant/algae material.	41.73
	6 - 17	Dark brown to black organic sediment. Fewer plant roots.	36.05
8	0 - 3	Fe(OH) ₃ precipitate. 80% clay/20% sand dark brown/black sediment.	34.63
	3- 17	Black organic sediment. Iron scum inside core when broken open. No sand.	35.41
9	0 - 5	Fe(OH) ₃ precipitate. Large clumps (>5 cm) Red/Brown colour	35.93
	5- 15	organic soil. Small bits of Fe(OH) ₃ in soil.	32.22
	15 - 20	White to grey sand with 5% Fe mottles	5.07
10	0 - 2	Light grey coarse sand with some red colouring indicating iron	1.60
	2 - 18	Light grey coarse sand with algae in core. Iron colouring in small amounts.	2.94

Chapter Summary

The following point form summary provides the major findings of the laboratory study.

- i. Dried sediment taken from diatomaceous areas at Lake Jandabup produced the lowest pH values (< 4.0) upon drying and rehydration.
- ii. Longer drying times generally did not appear to affect pH, sulfate, total iron or total alkalinity release, however longer dried sediment usually had a higher total acidity.
- iii. Upon drying and rehydration water that had low pH also had low total alkalinity and high sulfate.

CHAPTER 5: FIELD STUDY RESULTS

The field study showed that Lake Jandabup has a high short-term temporal and spatial variability in pH and other physico-chemical variables (e.g. conductivity and temperature). An SSH ordination for all physico-chemical variables (pH, dissolved oxygen, conductivity, temperature and redox) for all sites and all times found a large spread between sites, with many outliers (Figure 5.1). There is a general trend for sites 1, 4, 7 and 10 to group together and for 5, 6 and 8 and 9 to group together. Site 2 is spread across these groupings and site 3 is clustered individually, but is closer to site 8 than site 1.

Sites are plotted individually in the ordination. It appears that there are 3 distinct time groupings within each site (weeks 1, weeks 2-9 and weeks 10-18) and that inside values are usually separated from outside values (Figure 5.2).

Box plots were constructed (combining inside and outside data) for each individual variable for the three time periods to attempt to determine the variables influencing the observed groupings. The variables that changed the most over the 3 time periods were pH, conductivity, temperature and depth (Figure 5.3). For redox and dissolved oxygen the change was minimal. This suggests that it is probably these variables (i.e. pH, conductivity, temperature and depth) that are driving the groupings. These graphs also highlight that the spread of scores within each time period is high and there are many outliers indicating high spatial variability.

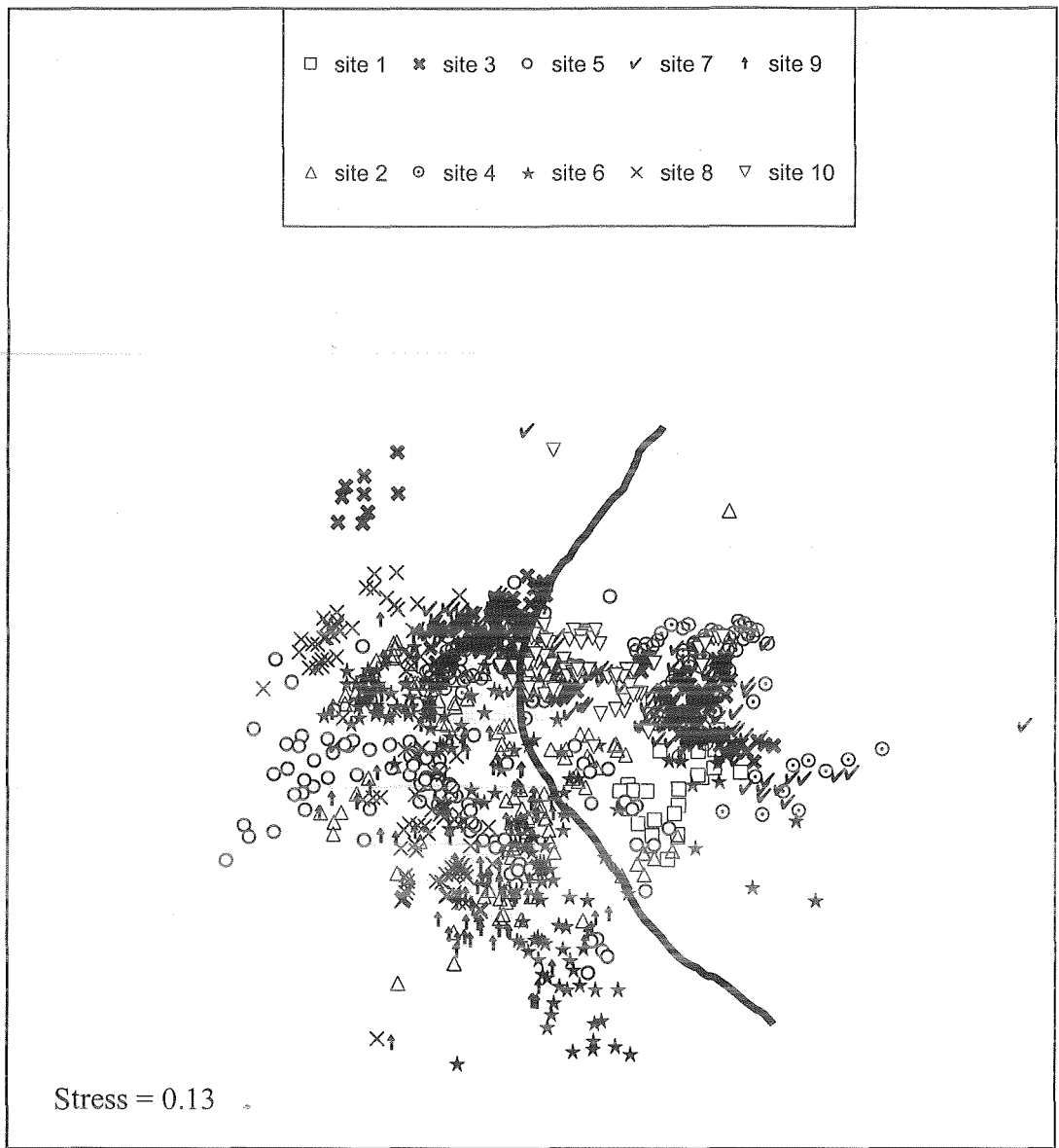


Figure 5.1: Ordination using all physico-chemical variables for all sites for all times at Lake Jandabup between April and August 2000. The solid line represents the approximate boundary between the grouping of sites 1, 4, 7 and 10 and the grouping of sites 5, 6, 8 and 9.

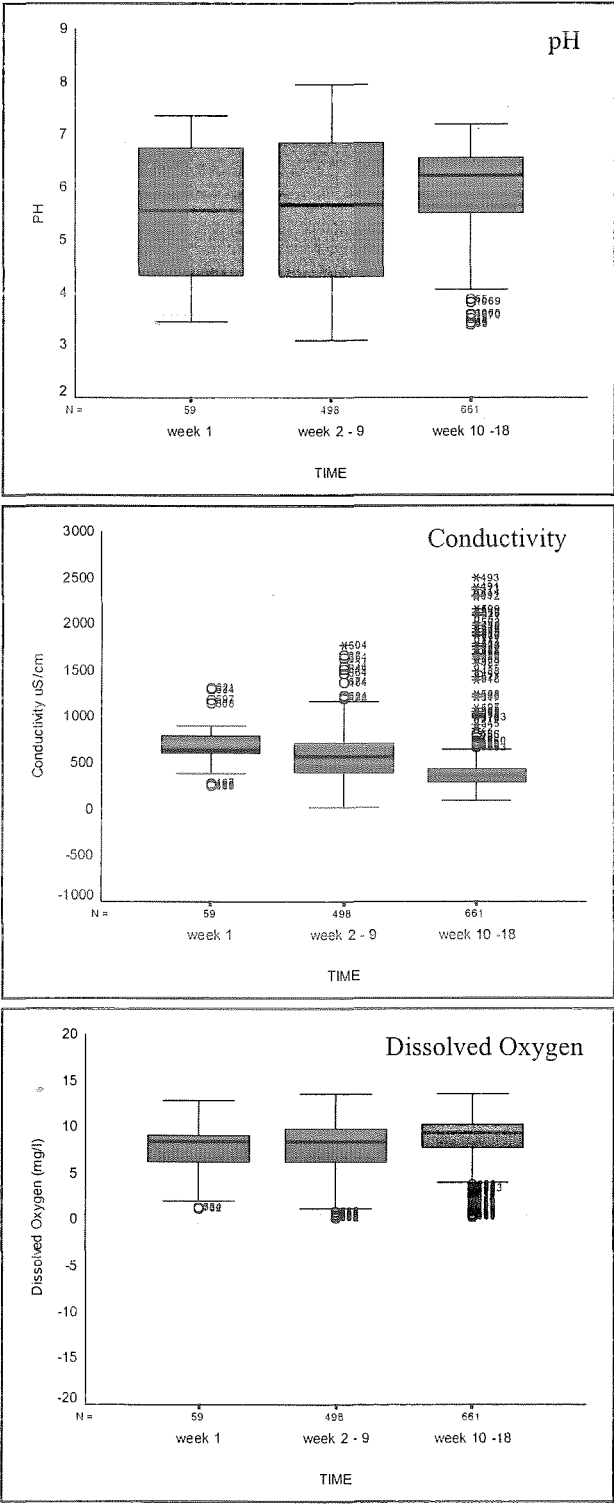


Figure 5.3 : Box plots of physical chemical variables (as indicated on graph) over 3 time periods as identified in the individual site ordination. Numbers above and below each box are outliers. It is not important to read their exact value as they are only present to indicate the spread of data. CONTINUED NEXT PAGE.

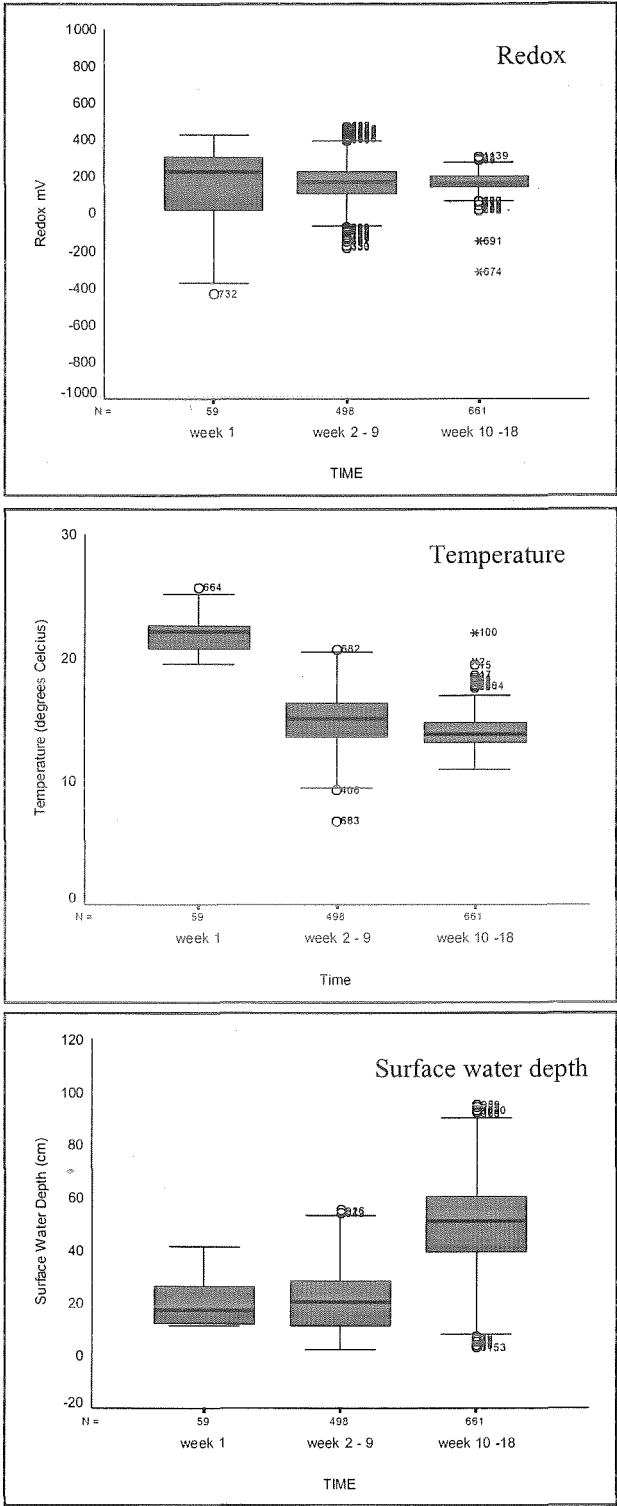


Figure 5.3 CONTINUED: Box plots of physical chemical variables (as indicated on graph) over 3 time periods as identified in the individual site ordination. Numbers above and below each box are outliers. It is not important to read their exact value as they are only present to indicate the spread of data.

The pH across the lake can vary by up to 4 pH units on any one sampling day, usually ranging between 3.5 and 7.5 pH units, although there are the occasional values outside this range.

Sites 1, 3, 4, 7 and 10 had a pH between 6.0 and 7.5 pH units for the majority of the study period (Figure 5.4). A decreasing trend was observed between week 0 and week 18. With the exception of site 1, these sites also had similar values between inside and outside the core, and little within site variability.

Sites 2, 5, 6, 8 and 9 had a pH range between 3.0 and 6.5 indicating that they were acid producing for some time during the study (Figure 5.4). Sites 6 and 8 had an initial pH between 3.5 and 4.5, then increased throughout the study to no higher than 6.5 pH units. At site 2 the pH started at around 6.5 then dropped to a low of 4.0 at week 3 before increasing. Sites 5 (inside only) and 9 started with a pH around 5.5, which decreased to a low of 3.5 before increasing. In general these sites (2,5,6,8 and 9) had relatively high within site variation of up to 1 pH unit, but usually for inside the core only. At sites 5, 6 and 9 there was a difference between inside and outside the core for almost all weeks tested. In some cases the difference was up to 2 pH units, but generally remained around 1 unit. At site 5 and 6 the outside of the core had lower pH than inside, while at site 9 inside was lower than outside. Also at site 9, for outside the core, the pH fluctuated weekly by up to 1 unit, but at sites 5 and 6 the pH remained fairly constant. At site 8 a difference (inside ~ 1 pH units lower than outside) only started to occur after week 7. For site 2 there was only a difference (inside ~ 1.5 pH units lower than outside) in positions between weeks 6 and 12.

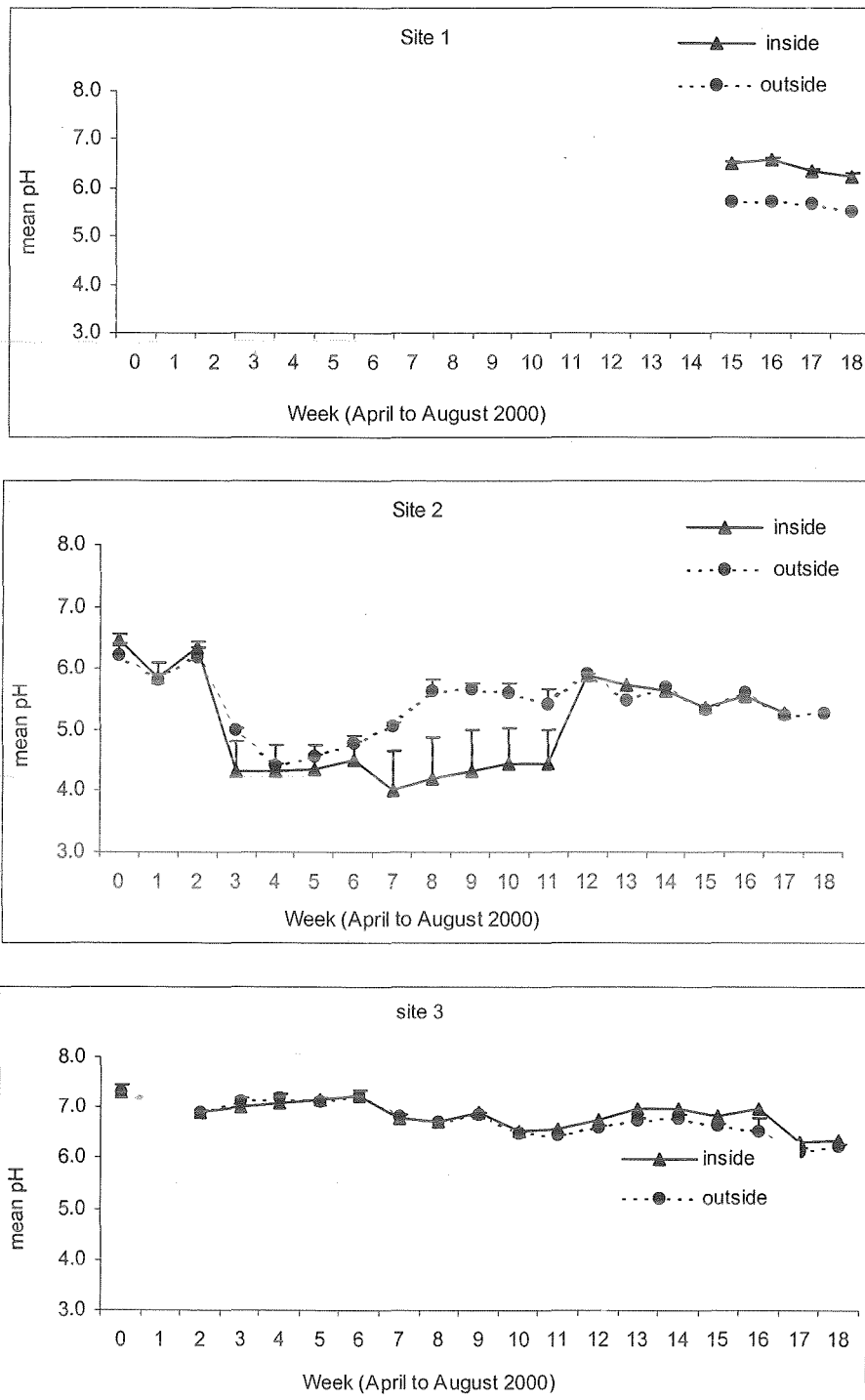


Figure 5.4: Mean and Standard Error ($n = 5$) for pH at Lake Jandabup between April and August 2000. Inside refers to inside the in situ core and outside refers to outside the in situ core. Site number is indicated on graph. Note: Site 1, 5 and 10 were dry at the beginning of the study therefore no data is available for this time. Incomplete data sets after week 12 is due to missing cores or inside cores being underwater. CONTINUED NEXT PAGE

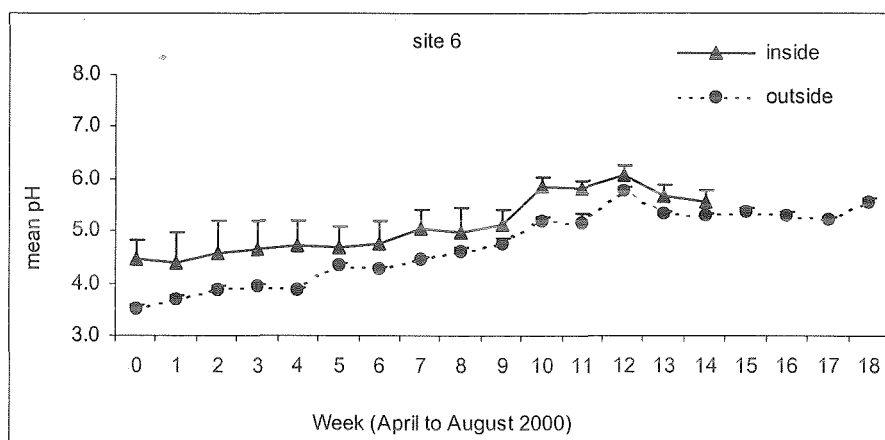
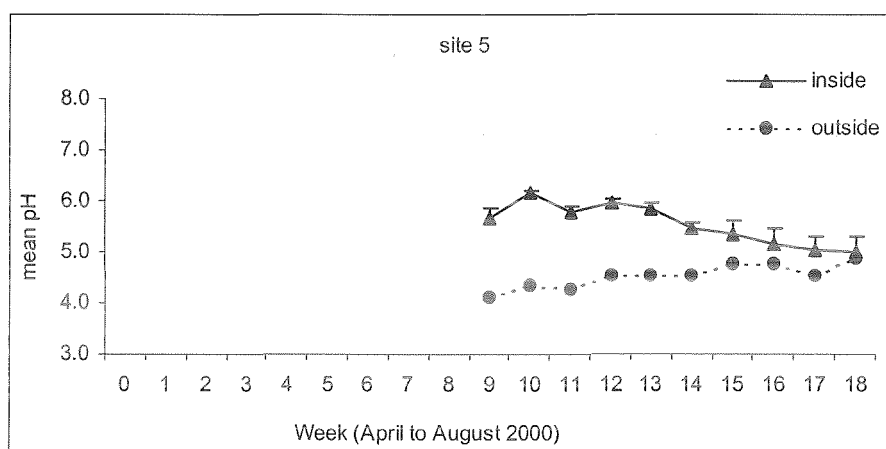
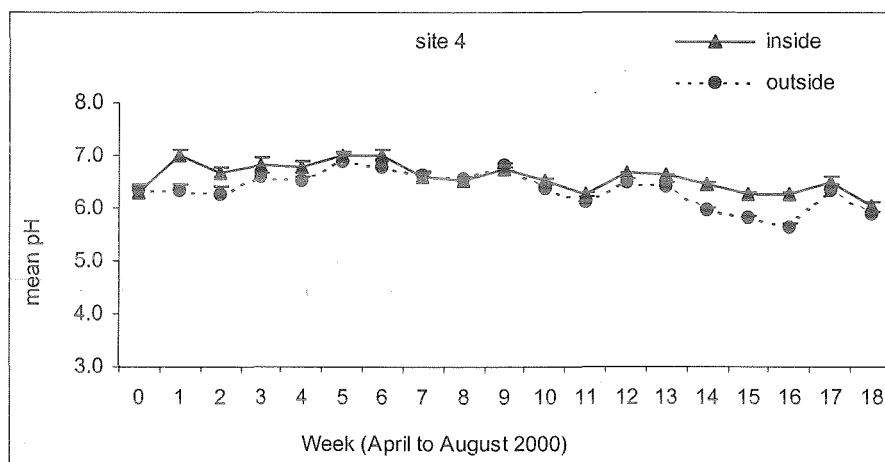


Figure 5.4 CONTINUED: Mean and Standard Error ($n = 5$) for pH at Lake Jandabup between April and August 2000. Inside refers to inside the in situ core and outside refers to outside the in situ core. Site number is indicated on graph. Note: Site 1, 5 and 10 were dry at the beginning of the study therefore no data is available for this time. Incomplete data sets after week 12 is due to missing cores or inside cores being underwater. CONTINUED NEXT PAGE.

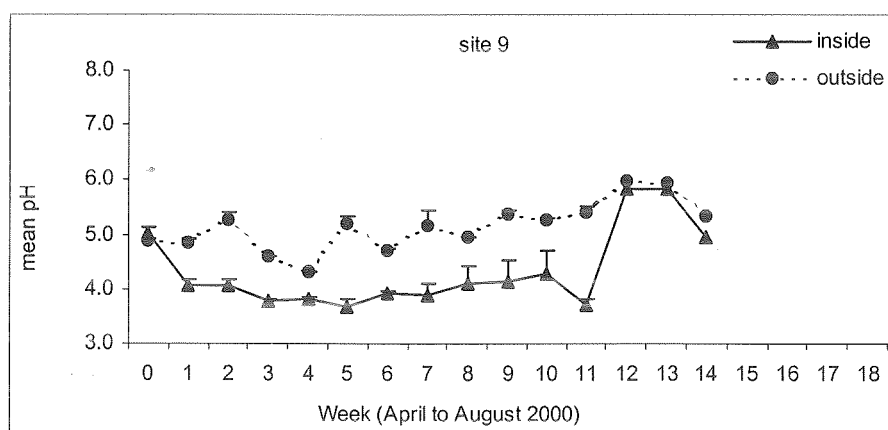
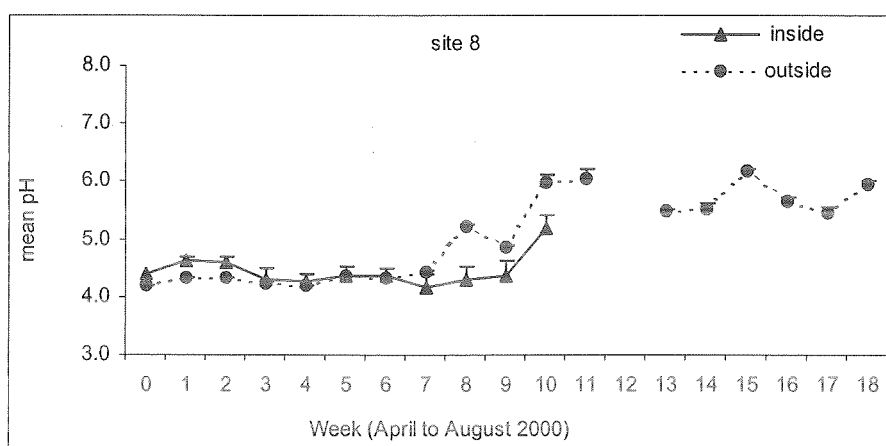
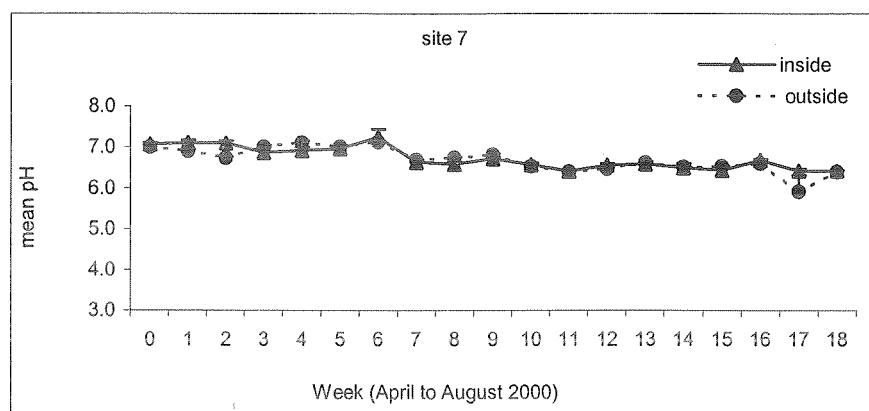


Figure 5.4 CONTINUED: Mean and Standard Error ($n = 5$) for pH at Lake Jandabup between April and August 2000. Inside refers to inside the in situ core and outside refers to outside the in situ core. Site number is indicated on graph. Note: Site 1, 5 and 10 were dry at the beginning of the study therefore no data is available for this time. Incomplete data sets after week 12 is due to missing cores or inside cores being underwater. CONTINUED NEXT PAGE

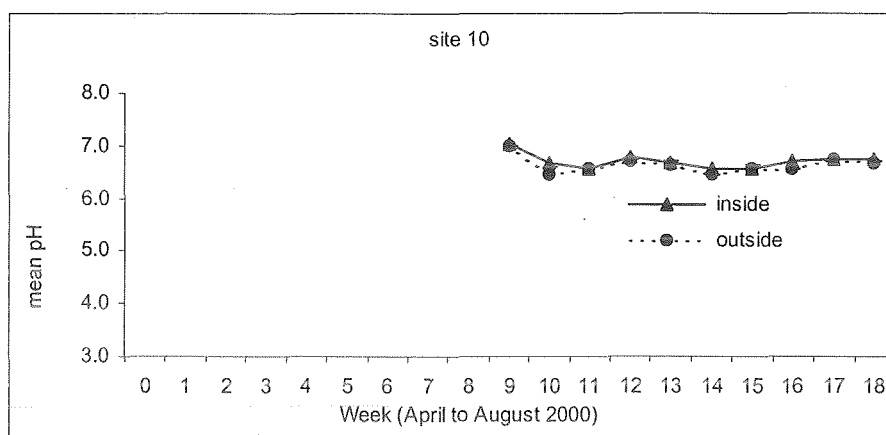


Figure 5.4: Mean and Standard Error for pH at Lake Jandabup between April and August 2000. Inside refers to inside the in situ core and outside refers to outside the in situ core. Site number is indicated on graph. Note: Site 1,5 and 10 were dry at the beginning of the study therefore no data is available for this time. Incomplete data sets after week 12 is due to missing cores inside cores being underwater.

A three way repeated analysis of variance (ANOVA) was performed on pH data using weeks 3 to 10 and sites 2,3,4,6,7,8 and 9. The nature of the analysis required that there were no missing data, therefore:

- i. Sites 1,5 and 10 were excluded because data were only available for them from week 9 due to the site being dry and
- ii. Weeks 11 to 18 had to be discarded due to incomplete data sets. At some sites inside measurements were no longer taken after week 10 due to the cores being under water, and some cores had been lost.

In addition, weeks 0, 1 and 2 were excluded, as it was decided no isolation effects (if present) would have been detected because inside water would have been very similar to outside water. All interactions were significant ($p < 0.05$) showing that each site is behaving differently over time and between positions (Table 5.1). As a result no confidence can be found for the significance of any single factor (Underwood, 1999).

Table 5.1: Three way repeated measures ANOVA for pH showing significant ($p < 0.05$) differences between sites, position (i.e. inside and outside the in situ core) and over time. Data uses sites 2,3,4,6,7,8 and 9 and weeks 3 – 10 ($n = 3$).

FACTOR	3 way repeated measures ANOVA				
	Variable = pH				
	df	Mean square	F - Value	P - Value	
Site	3.577	186.392	70.151	.000	*
Position	1	4.696	5.711	.075	NS
Week	7	1.119	20.437	.000	*
Site*Position	3.542	8.982	4.218	.021	*
Site*Week	20.402	1.844	11.196	.000	*
Site*Position*Week	31.483	.217	2.762	.000	*

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

As per Underwood (1999) Bonferroni post hoc tests were used for pairwise comparisons of sites and times to examine the interactions. Although the main effects are not valid these comparisons highlight the site and time variations. Generally the sites with low pH (2,6,8 and 9) as identified earlier, were not significantly different from each other but they were different from the sites with $pH > 6.0$ (Table 5.2). There were very few weeks that were significantly different from each other, however, weeks 3 and 4 tended to be different from weeks 9 and 10 indicating that pH is showing some short term variability across the lake (Table 5.3).

Table 5.2: Bonferroni post hoc tests showing which sites were significantly different ($p < 0.05$) from one another for pH. This analysis used data from 7 sites and weeks 3 to 10 of the study ($n = 5$)

	Site 2	Site 3	Site 4	Site 6	Site 7	Site 8	Site 9
Site 2							
Site 3	*						
Site 4	*	*					
Site 6	NS	*	*				
Site 7	NS	NS	NS	*			
Site 8	NS	*	*	NS	*		
Site 9	NS	*	*	NS	*	NS	

* = statistically significant ($p < 0.05$)
 NS = Not statistically significant ($p > 0.05$)

Table 5.3: Bonferroni post hoc tests showing which sites were significantly different ($p < 0.05$) from one another for pH. This analysis used data from 7 sites and weeks 3 to 10 of the study ($n = 5$)

	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10
Week 3								
Week 4	NS							
Week 5	NS	NS						
Week 6	NS	*	NS					
Week 7	NS	NS	NS	NS				
Week 8	NS	NS	NS	NS	NS			
Week 9	*	*	NS	NS	NS	NS		
Week 10	NS	*	NS	NS	NS	NS	NS	

* = statistically significant ($p < 0.05$)
 NS = Not statistically significant ($p > 0.05$)

As intersite variability appears to be the major source of the significant interaction (for pH between site*time*position). This was eliminated by completing individual 2 way repeated measures ANOVAS on each site. For sites 3 and 8 there was a significant ($p < 0.007$) interaction between position and time indicating that each site was behaving differently over weeks and between positions (Table 5.4). For sites 4,6 and 7 there was no significant interaction meaning that the nonsignificant position and significant position main effects are valid and that the difference between weeks is independent of position. For site 9 there was no significant ($p < 0.007$) interaction indicating that the significant position and nonsignificant time main effects are valid. At site 2 the interaction was not significant, nor was there a significant difference between positions and over time.

Table 5.4: Individual 2 way repeated measures (ANOVA) for sites 2,3,4,6,7,8 and 9. It shows which sites have a significant differences ($p < 0.007$) in pH over time and between positions (inside and outside the in situ core)

FACTOR		2 way repeated measures ANOVA				
		Variable = pH				
		df	Mean Square	F - Value	P - Value	
Position						
	Site 2	1	8.719	1.839	.247	NS
	Site 3	1	0.01326	1.272	.322	NS
	Site 4	1	.194	.5304	.083	NS
	Site 6	1	7.302	3.189	.149	NS
	Site 7	1	.0732	2.332	.201	NS
	Site 8	1	1.458	1.943	.236	NS
	Site 9	1	18.750	37.057	.004	*
Week						
	Site 2	2	2.359	7.212	.012	NS
	Site 3	3.66	1.180	17.611	.000	*
	Site 4	3.25	.685	.632	.007	*
	Site 6	7	1.519	9.539	.000	*
	Site 7	2.90	1.146	17.772	.000	*
	Site 8	2.51	5.083	55.618	.000	*
	Site 9	2.73	1.860	6.028	.012	NS
Week*Position						
	Site 2	1.806	2.318	8.958	.012	NS
	Site 3	7	0.00988	7.557	.000	*
	Site 4	3.033	.101	2.050	.160	NS
	Site 6	5.647	.118	.631	.696	NS
	Site 7	3.986	0.04579	1.317	.306	NS
	Site 8	4.42	.644	29.484	.000	*
	Site 9	3.747	.499	2.444	.095	NS

* = statistically significant ($p < 0.007$)

NS = Not statistically significant ($p > 0.007$)

Note: probability levels had been altered to $p < 0.007$. As per Underwood (1999) when individual ANOVAS are completed based on interactions the probability level should be made more stringent by dividing the number of tests by the original probability level, in this case it is 0.05 divided by 7 which is the number of sites tested.

Over the study period the surface water depth of Lake Jandabup increased from 44.32 to 44.87 mAHD (Figure 5.5). The water depth at all sites between weeks 0 and 9 was fairly constant, then increased rapidly until week 14 where it climbed slowly up to week 18. From shallowest to deepest the order of sites was site 1 < 5 < 10 < 3 < 6 < 4 < 9 < 2 < 8 (Figure 5.6). The depth at the wettest time of the study period ranges from 0.5m to 0.8m, this range excludes site 1 because it only started to become wet at week 15 and was never more than 0.05m deep. Water levels reflect rainfall patterns as it increased over the study period (Figure 5.7)

The conductivity of the lake on any one day of sampling varied between $300 \mu\text{S cm}^{-1}$ and $700 \mu\text{S cm}^{-1}$ for outside the core, and $300 \mu\text{S cm}^{-1}$ and $2000 \mu\text{S cm}^{-1}$ for inside the core (Figure 5.8). There was a downward trend for conductivity for all sites over the study period as waters became more diluted following winter rainfall. The exception was site 5 inside the core where the conductivity continued to increase between week 9 (when the site first became wet) and week 18 (end of study). Sites 1, 3, 4 and 10 had conductivities generally below $500 \mu\text{S cm}^{-1}$ for the entire study period. They had little temporal and within site variation. Generally the conductivity remained constant throughout the study, changing by less than $100 \mu\text{S cm}^{-1}$ between week 0 and week 18. At site 1 outside the core had a conductivity on average $500 \mu\text{S cm}^{-1}$ higher than inside the core. Sites 2, 7, 6, 8 and 9 all had similar conductivities of between $500 \mu\text{S cm}^{-1}$ and $1000 \mu\text{S cm}^{-1}$ over the study period. At these sites the difference between position was more noticeable. Generally on the inside of the core, conductivity was approximately $200 - 300 \mu\text{S cm}^{-1}$ higher than outside.

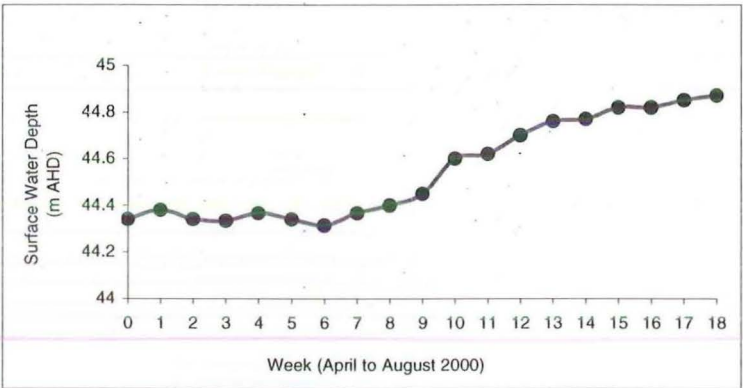


Figure 5.5: Surface water depth at Lake Jandabup in mAHD (meters Australian Height Datum) between April and August 2000.

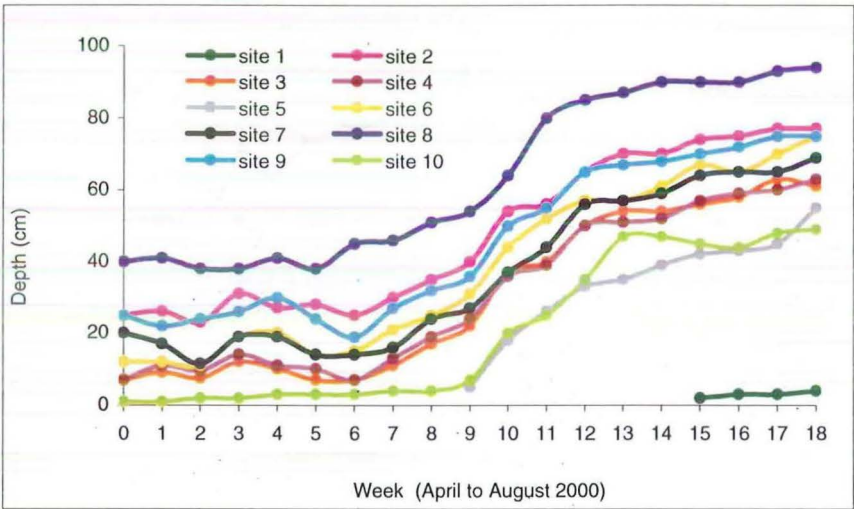


Figure 5.6: Surface water depth at Lake Jandabup for each site between April and August 2000.

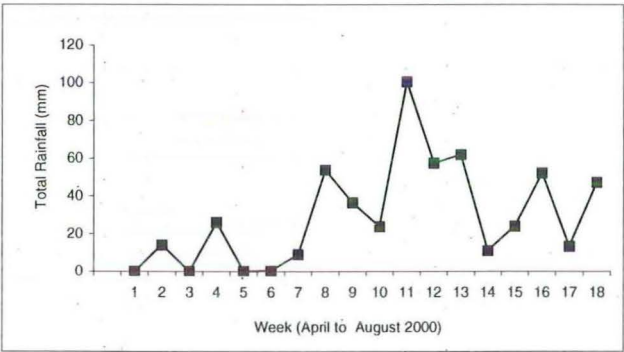


Figure 5.7: Total rainfall for each week of the study. (Source: Bureau of Meteorology, 2000)

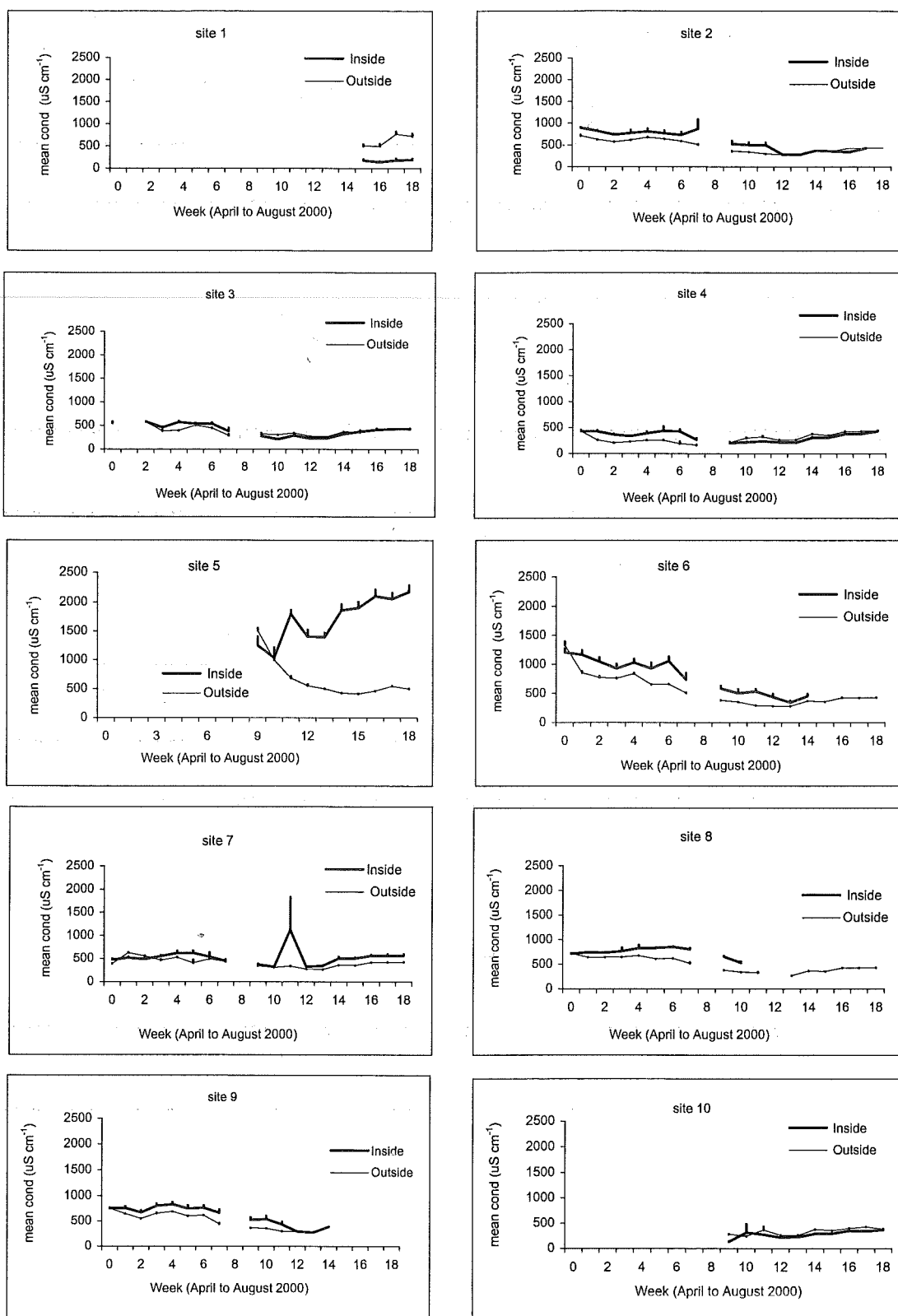


Figure 5.8: Mean and Standard Error for conductivity (cond) at each site (as indicated on graph) over the study period. Note the conductivity meter was unoperational in week 8; sites 1, 5 and 10 were dry at the commencement of the study and any missing values after week 10 are due to missing cores or cores being underwater.

Dissolved oxygen at most sites fluctuated slightly every week but overall did not change greatly between week 0 and week 18 (Figure 5.9). Generally inside the core had lower dissolved oxygen than outside. At sites 5,6 and 7 dissolved oxygen levels were below 5 mg L⁻¹ inside the core, while outside it was usually above 5 mg L⁻¹. Sites 1,2,3,4,8,9 and 10 generally had dissolved oxygen for both positions between 5 mg L⁻¹ and 10 mg L⁻¹, but, for some weeks sites 2,3 and 4 had oxygen higher than 10 mg L⁻¹.

Over the entire lake redox potential varied between -100 mV to 400 mV for inside the core and 0 to 400 for outside the core on one sampling day and also for the entire study period (Figure 5.10). At sites 1,2,4,5 and 10 redox remained fairly constant over the 18 weeks generally between 100 mV and 300 mV. Sites 3,6,8 and 9 had a trend for decreasing redox over the study, but the total decrease was less than 200 mV. Site 7 had an increasing redox trend: it was negative until week 9 where it increased into the positive zone. For most sites, with the exception of 5 and 6 there was little difference between positions. For all sites there was little within site variation.

Over the entire study period the average temperature of the lake varied between 13°C and 22°C (Figure 5.11). For most sites temperature rose and fell weekly, but there was a general decreasing trend. Spatially temperature varied by 5-10 °C on any occasion. No difference between positions was found.

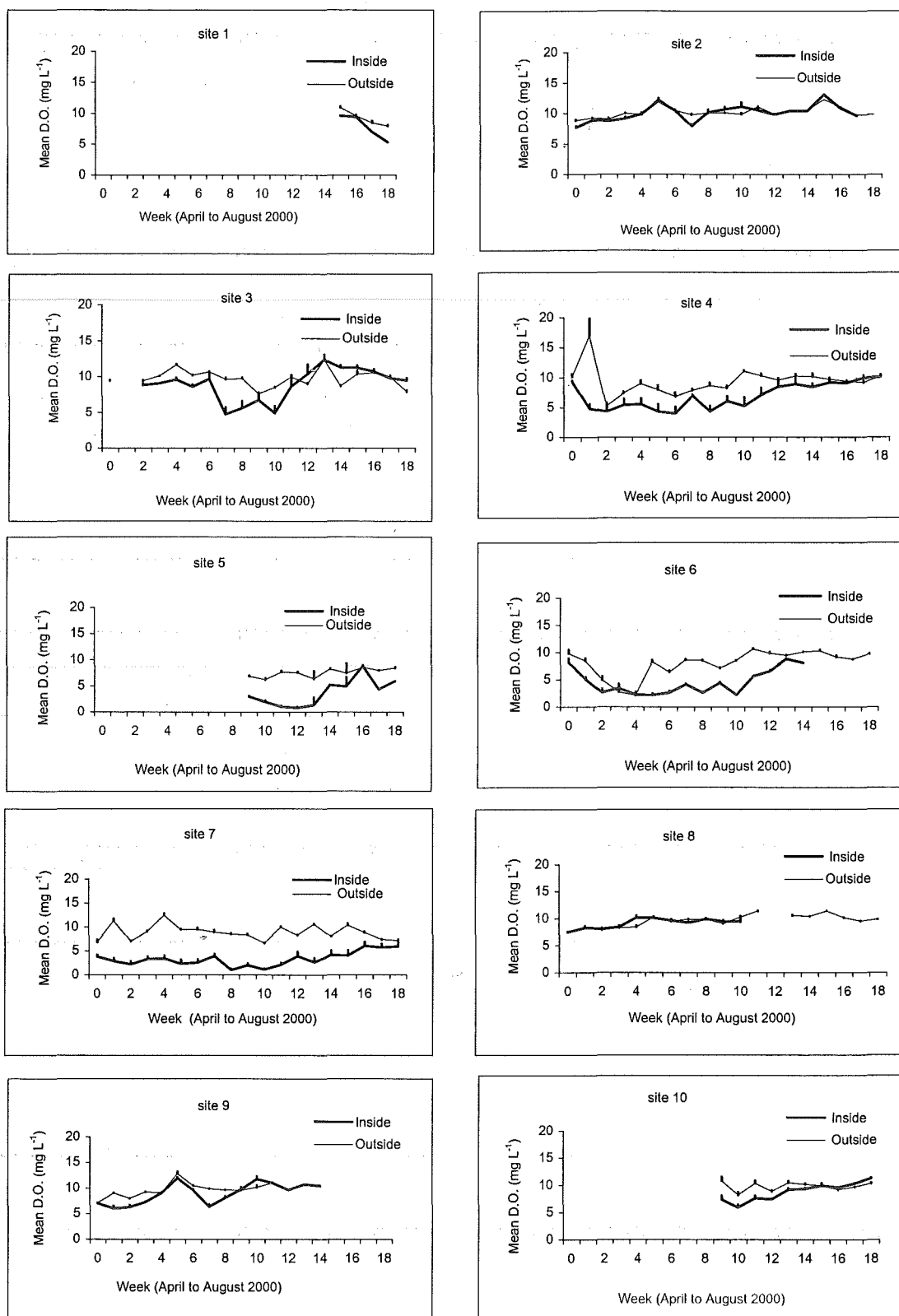


Figure 5.9: Mean and Standard Error for dissolved oxygen at each site) over the study period. Note: sites 1, 5 and 10 were dry at the commencement of the study and any missing values after week 10 are due to missing cores or cores being underwater.

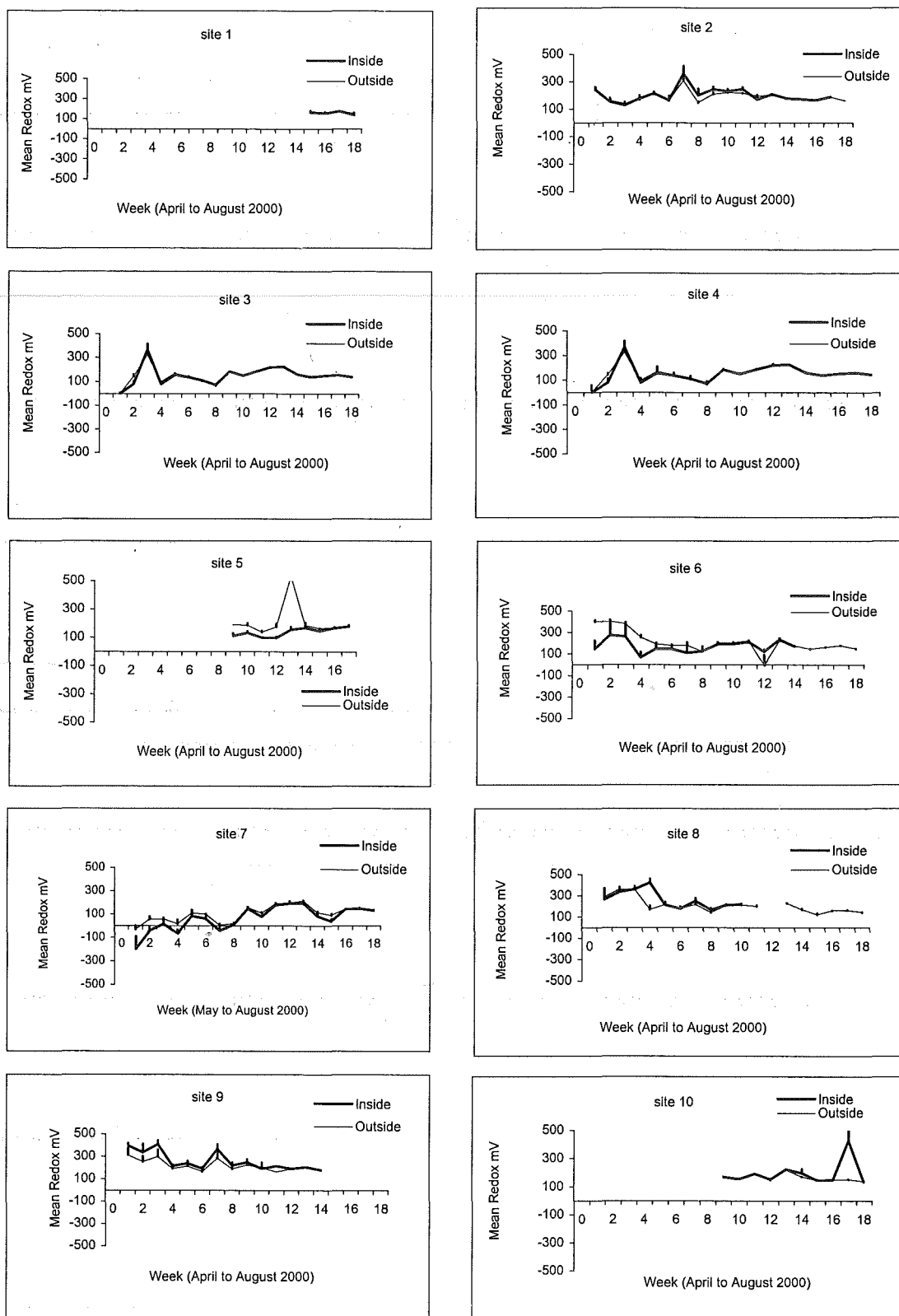


Figure 5.10: Mean and Standard Error for redox at each site (as indicated on graph) over the study period. Note: sites 1, 5 and 10 were dry at the commencement of the study and any missing values after week 10 are due to missing cores or cores being underwater.

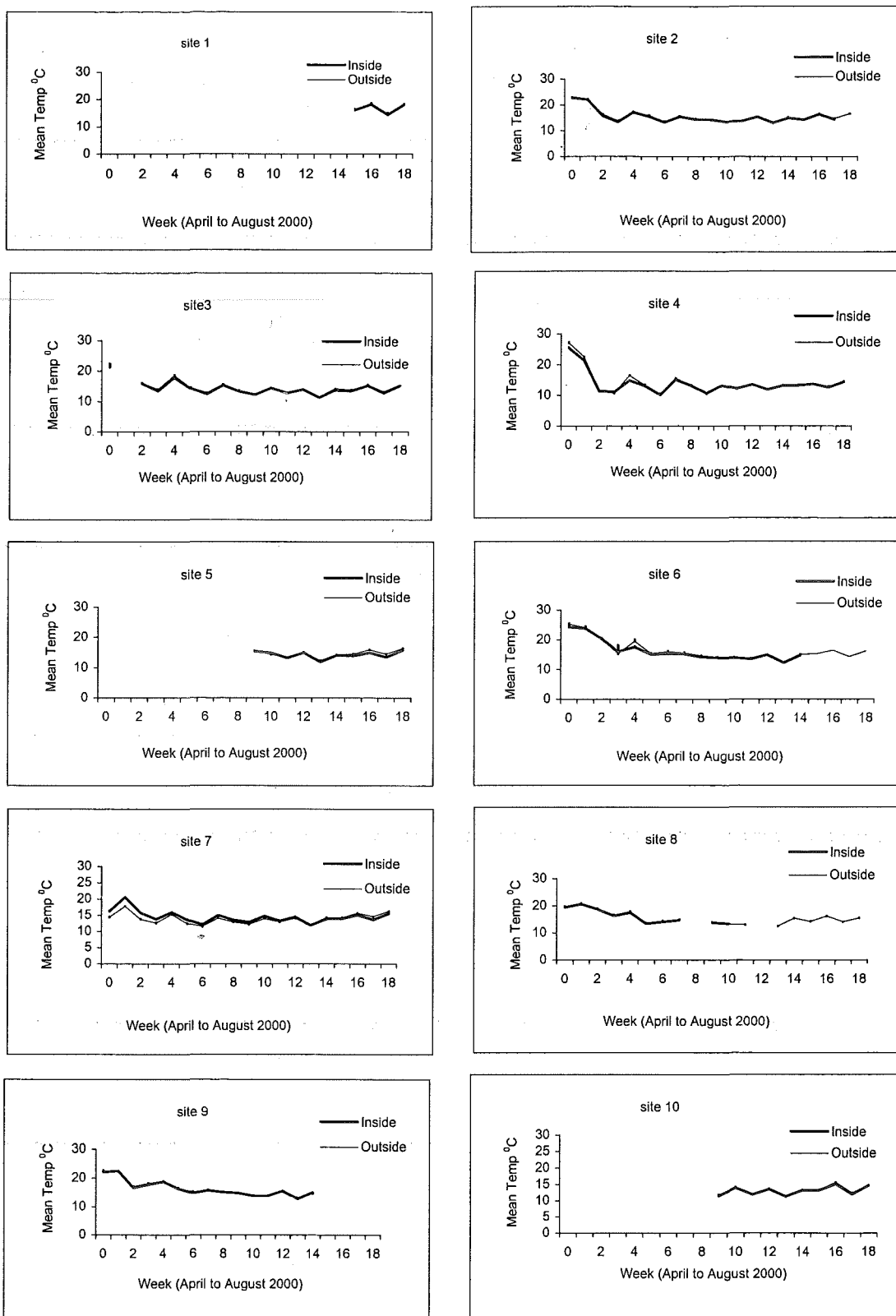


Figure 5.11: Mean and Standard Error for temperature at each site (as indicated on graph) over the study period. Note: sites 1,5 and 10 were dry at the commencement of the study and any missing values after week 10 are due to missing cores or cores being underwater.

All variables (i.e. physico-chemical properties, total acidity, total alkalinity, sulfate and total iron) were ordinated (Figure 5.12). There was a large scatter between sites and over time, generally sites 7 and 4 group together and sites 2, 6 and 9 group. Strong separation was found between inside and outside positions. These groupings are similar to those seen in previous ordinations. The ordination data support the results of the ANOVA in Table 5.2

Sulfate levels inside the core at the acidic group (sites 2,6 and 9) were considerably higher (up to 100 mg L^{-1}) than the neutral group (sites 4 and 7) which had levels below 20 mg L^{-1} (Figure 5.13a and 5.13b). Between May and August sulfate levels generally decreased for all sites, the exceptions were sites 4 and 7. At site 4 inside and outside the core there was a general increase in sulfate between May and August. For site 7 there was a difference for outside the core only. At sites 2, 6 and 9 inside the core had between 10 and 40 mg L^{-1} more sulfate than outside, while at sites 4 and 7 inside the core had between 15 and 40 mg L^{-1} more sulfate than outside.

Inside the cores at all sites during all months, total iron was usually below 20 mg L^{-1} , however, there were three extreme exceptions (Figure 5.14 a and 5.14b). Total iron peaked in May at sites 4, 6 and 7 with on average 50 mg L^{-1} more iron than other months, but within site variability was high. Site 4, in particular, ranged from 18 mg L^{-1} to 254 mg L^{-1} . Another interesting anomaly is that site 4, at this time, had low sulfate, but high total iron. Outside the core, at all sites and all months, levels were generally below 10 mg L^{-1} . There were no extreme values and almost no within site variability.

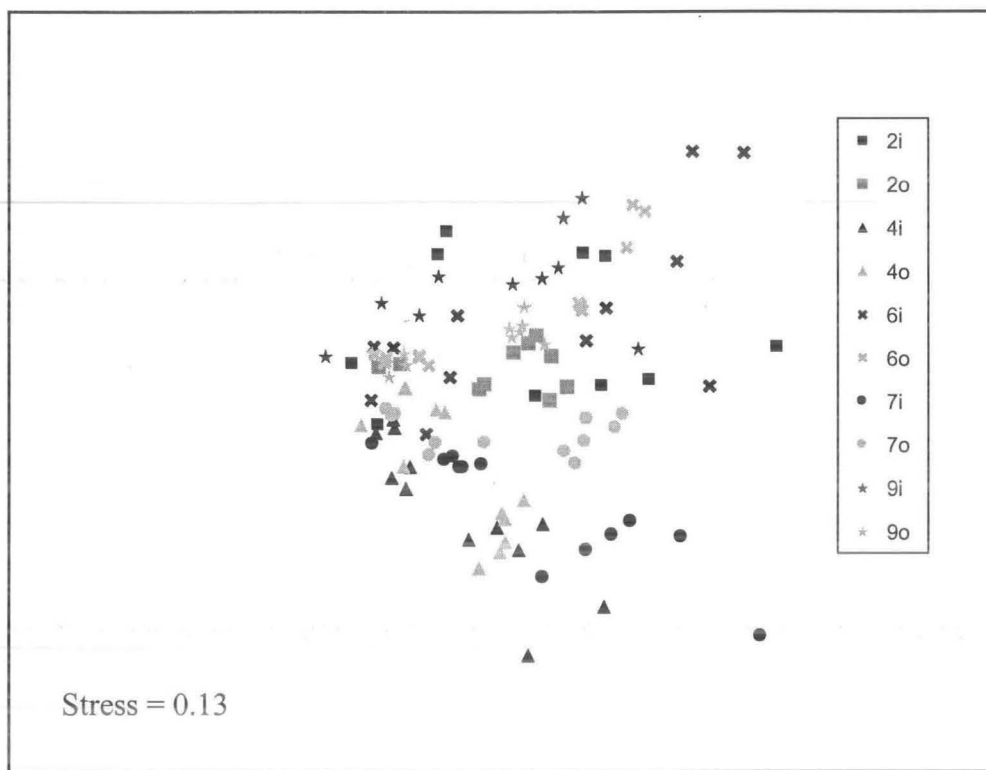


Figure 5.12: Ordination using all variables (physico- chemical, sulfate, total iron, total alkalinity and total acidity,) at Lake Jandabup between May and August 2000.

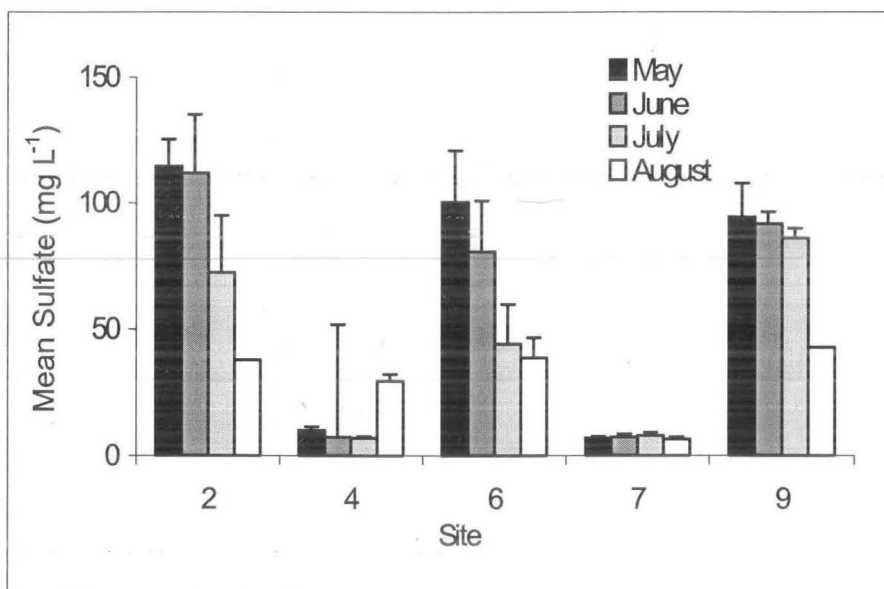


Figure 5.13a: Mean and Standard Error ($n = 3$) for sulfate inside the in situ core at each site between May and August 2000.

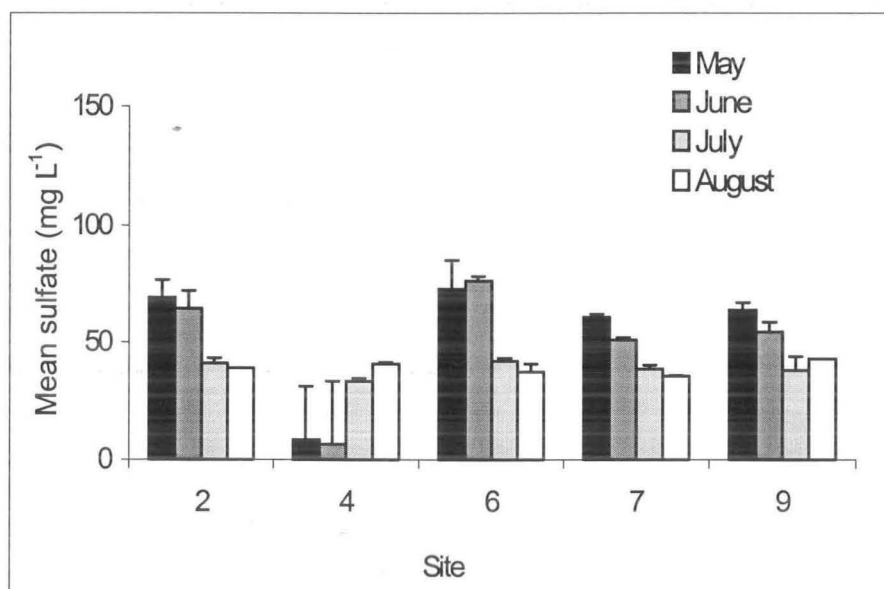


Figure 5.13b: Mean and Standard Error ($n = 3$) for sulfate for outside the in situ core at each site between May and August 2000.

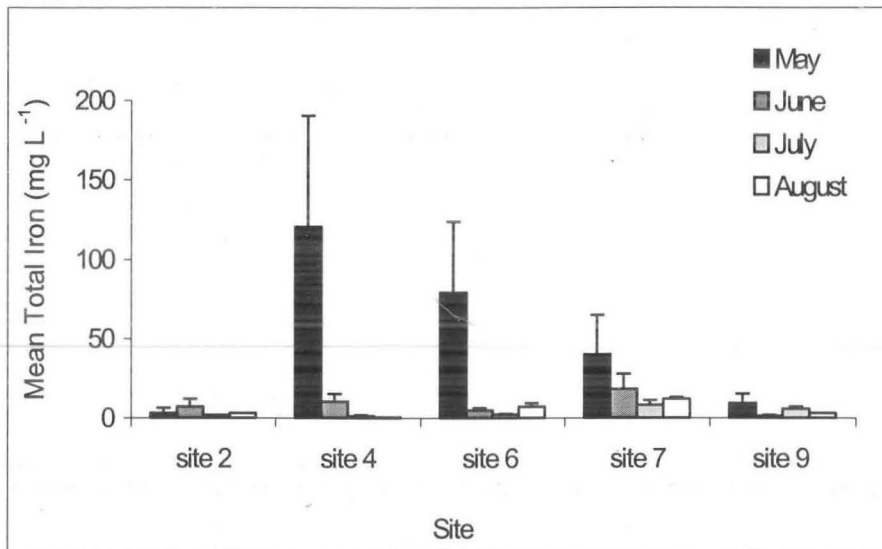


Figure 5.14a: Mean and Standard Error ($n = 3$) for total iron inside the in situ core at each site between May and August 2000.

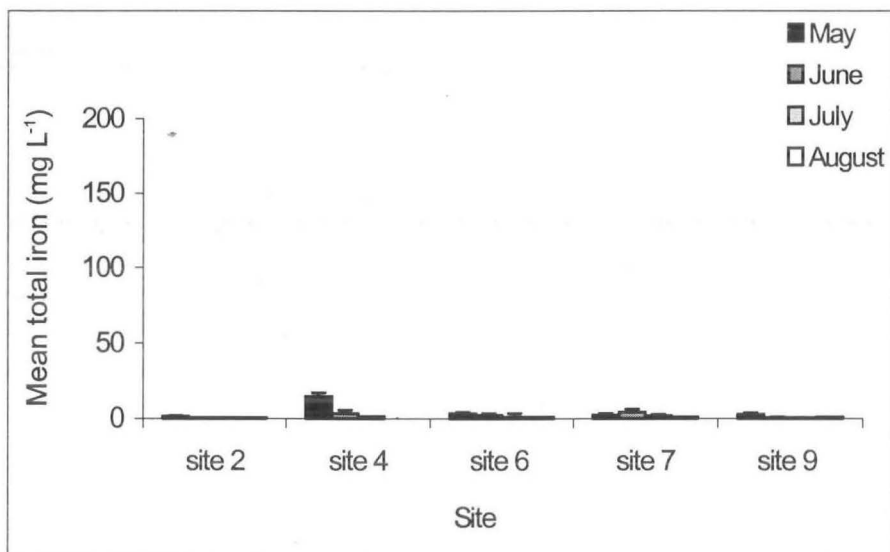


Figure 5.14b: Mean and Standard Error ($n = 3$) for total iron outside the in situ core at each site between May and August 2000.

Total Alkalinity fluctuated considerably throughout the study period. Generally inside the core had higher buffering capacity than outside e.g. at its peak (June) the highest alkalinity inside the cores was $200 \text{ mg CaCO}_3 \text{ L}^{-1}$, but outside the cores it was only $100 \text{ mg CaCO}_3 \text{ L}^{-1}$. However, generally levels were lower than this (Figure 5.15a and 5.15b). Inside the cores at sites 2, 8 and 9, alkalinity levels were lower than $25 \text{ mg CaCO}_3 \text{ L}^{-1}$ for the duration of the study while the remaining sites all had levels above $50 \text{ mg CaCO}_3 \text{ L}^{-1}$. Outside cores at all sites for all months had levels below $50 \text{ mg CaCO}_3 \text{ L}^{-1}$ with the exception of site 7 during July, when alkalinity reached a high of $100 \text{ mg CaCO}_3 \text{ L}^{-1}$.

Total acidity for all sites, all months and both positions was usually below $50 \text{ mg CaCO}_3 \text{ L}^{-1}$ (Figure 5.16a and 5.16b). The exception was in June when some replicates inside the core at sites 6 and 7 had total acidity levels up to $150 \text{ mg CaCO}_3 \text{ L}^{-1}$. The outside of the cores were less variable and ranged between 10 and $50 \text{ mg CaCO}_3 \text{ L}^{-1}$. Overall there appeared to be slight decreases in total acidity between May and August.

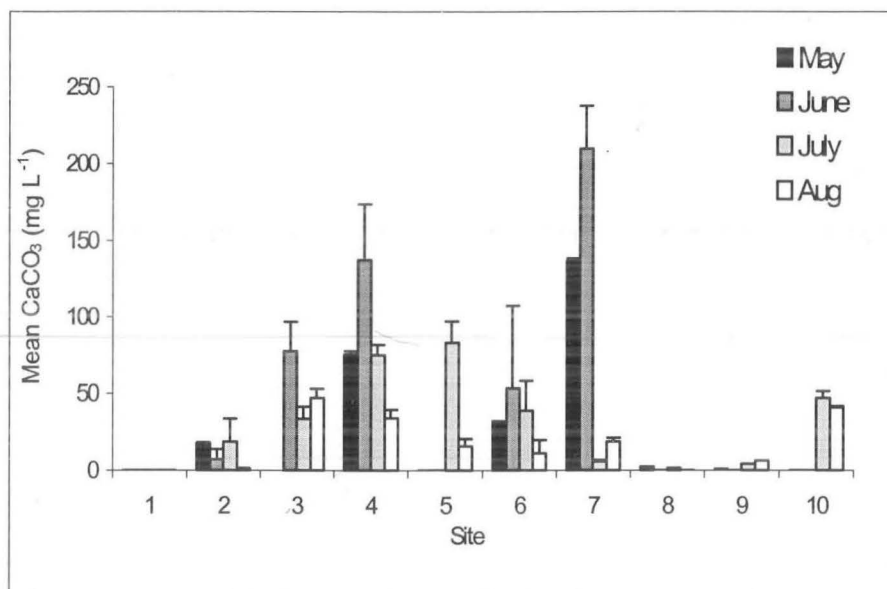


Figure 5.15a: Mean and Standard Error ($n=5$) for total alkalinity inside the in situ core for each site between May and August 2000 . Note: site 1 was dry for the entire study, site 5 and 10 were only wet in June and July and site 8 cores were underwater during August, therefore no measurements were possible, they did not have zero alkalinity

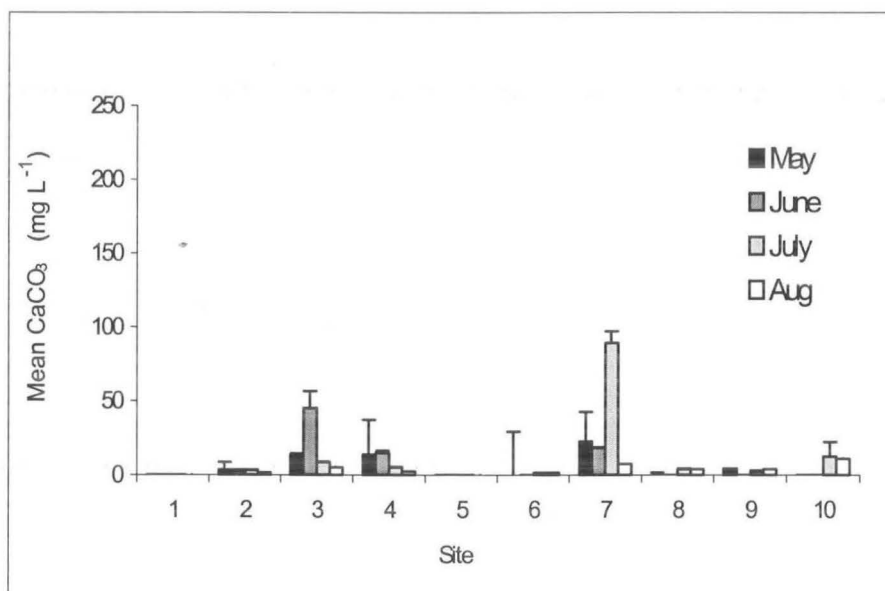


Figure 5.15b: Mean and Standard Error ($n=5$) for total alkalinity outside the in situ core for each site between May and August 2000. Note: site 1 was dry for the entire study and site 5 and 10 were only wet in June and July therefore no measurements were possible, they did not have zero alkalinity.

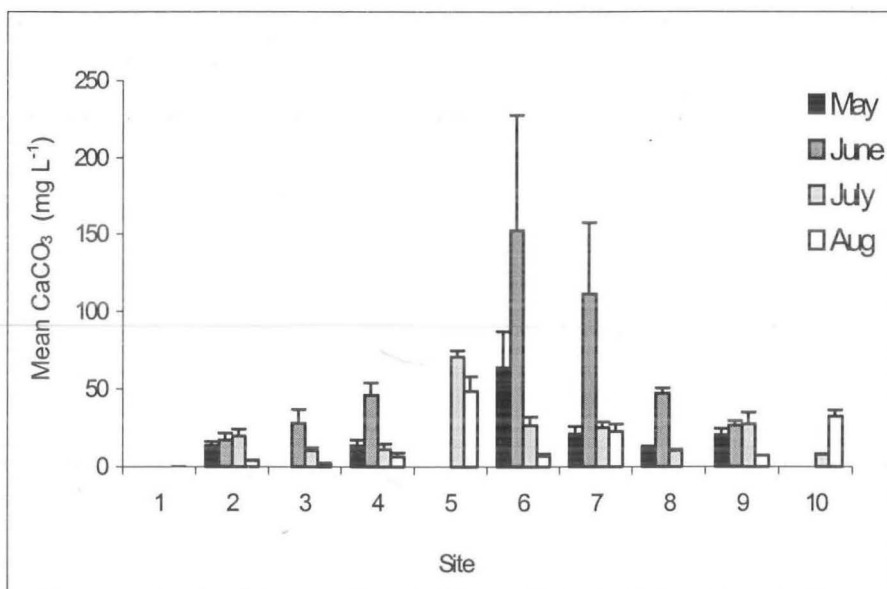


Figure 5.16a: Mean and Standard Error for total acidity ($n=5$) inside the in situ core for each site between May and August 2000.. Note: site 1 was dry for the entire study, site 5 and 10 were only wet in June and July and site 8 cores were underwater during August, therefore no measurements were possible, they did not have zero acidity

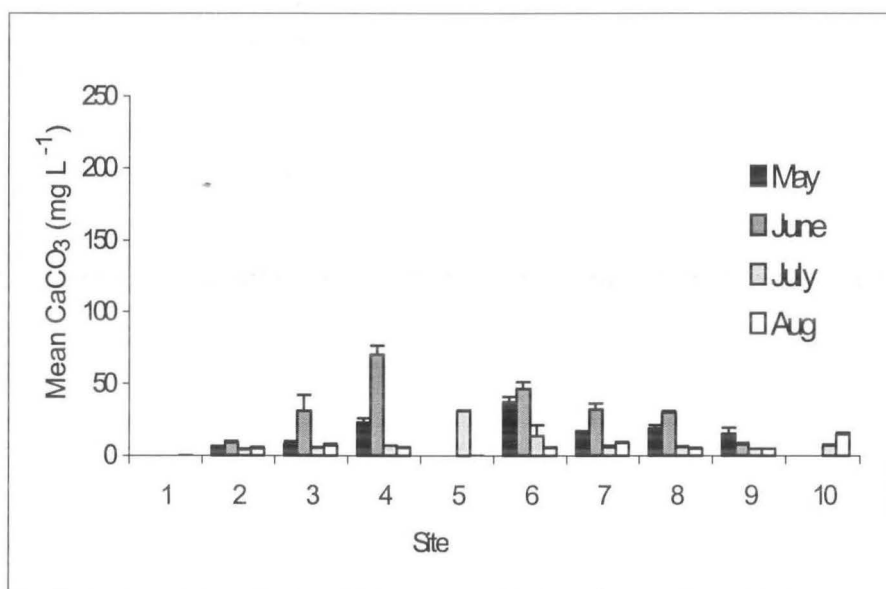


Figure 5.16b: Mean and Standard Error for total acidity ($n=5$) outside the in situ core for each site between May and August 2000. Note: site 1 was dry for the entire study and site 5 and 10 were only wet in June and July a, therefore no measurements were possible, they did not have zero acidity.

A three way repeated measures analysis of variance (ANOVA) was performed on sulfate and total iron using data from five sites (2,4,6,7 and 9) 3 replicates and 3 months (August was excluded because site 2 and 9 had missing cores during August) (Table 5.5). There were no significant differences for total iron between sites, over time and between positions. Also no significant interactions were found. All interactions for sulfate were significant, again indicating that the individual sites were behaving differently over time and between positions.

A three way repeated measures ANOVA was also conducted for total alkalinity and total acidity using data from 6 sites (2,4,6,7,8 and 9), 5 replicates and 3 months (Table 5.6). There were no significant interactions for total acidity and the only significant main effect was between months. This indicates that the monthly variation was independent of site and position. Total alkalinity had all interactions significant showing that each site is behaving differently over time and between positions.

Table 5.5: Three way repeated measures ANOVA for sulfate and total iron showing significant ($p < 0.05$) differences between sites, positions (i.e. inside and outside the in situ core) and over time. For consistency the Huynh-Feldt test was used for all significance levels. Data used 5 sites (2,4,6,7 and 9), 3 replicates and 3 months (May, June and July)

FACTOR	Three way repeated measures ANOVA				
	Variable = Sulfate (s) and Total Iron (Fe)				
	df	Mean square	F - Value	P - Value	
Site (S)	4	16110.261	28.313	.000	*
Site (Fe)	4	1578.542	2.436	.132	NS
Position (S)	1	1488.400	1.993	.293	NS
Position (Fe)	1	7454.720	4.484	.160	NS
Month (S)	1.558	11420.173	8.916	.053	NS
Month (Fe)	1.011	3723.956	4.743	.160	NS
Site*Position (S)	4	5560.782	10.018	.003	*
Site*Position (Fe)	4	969.175	1.546	.278	NS
Site*Month (S)	2.889	2360.191	7.486	.019	*
Site*Month (Fe)	8	1444.484	2.315	.073	NS
Month*Position (S)	1.027	134.843	.404	.594	NS
Month*Position (Fe)	1.016	8377.354	3.565	.198	NS
Site*Position*Month (S)	8	281.289	5.556	.002	*
Site*Position*Month (Fe)	8	1045.579	1.745	.163	NS

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

Table 5.6: Three way repeated measures ANOVA for total alkalinity and total acidity showing significant ($p < 0.05$) differences between sites, positions (i.e. inside and outside the in situ core) and over time. For consistency the Hyunh-Feldt test was used for all significance levels. Data used 6 sites (2,4,6,7,8 and 9), 5 replicates and 3 months (May, June and July).

FACTOR	Three way repeated measures ANOVA				
	Variable = Total Alkalinity (Ak) and Total Acidity (Ac)				
	df	Mean Square	F - Value	P - Value	
Site (Ak)	1.539	56727.789	71.637	.003	*
Site (Ac)	1.070	36715.499	5.319	.077	NS
Position (Ak)	1	16605.832	184.938	.005	*
Position (Ac)	1	14053.623	3.661	.128	NS
Month (Ak)	1.221	1752.986	26.947	.022	*
Month (Ac)	1.005	41876.486	15.548	.019	*
Site*Position (Ak)	1.179	22415.420	23.367	.029	*
Site*Position (Ac)	1.116	14579.044	1.822	.246	NS
Site*Month (Ak)	5.573	1854.253	8.847	.001	*
Site*Month (Ac)	1.252	21811.850	4.073	.097	NS
Month*Position (Ak)	2	4596.684	107.111	.000	*
Month*Position (Ac)	1.153	5699.278	1.632	.269	NS
Site*Position*Month (Ak)	2.587	16394.719	26.580	.002	*
Site*Position*Month (Ac)	1.289	12738.751	2.410	.182	NS

* = statistically significant ($p < 0.05$)

NS = Not statistically significant ($p > 0.05$)

Bonferroni post hoc tests used pairwise comparisons to examine interactions (Underwood, 1999). Generally all sites had similar sulfate levels; the exception was that site 4 was different from 7 and 9 (Table 5.7). This highlights observations made earlier that site 9 had considerably higher sulfate levels than site 4. However, it was also seen that site 4 and 7 had similar concentrations. One reason for the discrepancy is that this post hoc analysis combines inside and outside data, and for outside the core, site 7 had similar levels to the other sites. For total alkalinity all sites, except site 2 compared with site 8, were similar to each other (Table 5.8). The only significant difference over time was between May and July (Table 5.9) Total acidity had a significant main effect over time, it shows there was a difference between May and June (Table 5.10).

Table: 5.7 Bonferroni post hoc tests showing significant ($p < 0.05$) differences between sites for sulfate levels.

	Site 2	Site 4	Site 6	Site 7	Site 9
Site 2					
Site 4	NS				
Site 6	NS	NS			
Site 7	NS	*	NS		
Site 9	NS	*	NS	NS	

* = statistically significant ($p < 0.05$)
 NS = Not statistically significant ($p > 0.05$)

Table 5.8 Bonferroni post hoc tests showing significant ($p < 0.05$) differences between sites for total alkalinity.

	site 2	site 4	site 6	site 7	site 9	site 6
site 2						
site 4	NS					
site 6	NS	NS				
site 7	NS	NS	NS			
site 8	*	NS	NS	NS		
site 9	NS	NS	NS	NS	NS	

* = statistically significant ($p < 0.05$)
NS = Not statistically significant ($p > 0.05$)

Table 5.9: Bonferroni post hoc tests showing significant ($p < 0.05$) differences between months for total alkalinity concentration

	May	June	July
May			
June	NS		
July	*	NS	

* = statistically significant ($p < 0.05$)
NS = Not statistically significant ($p > 0.05$)

Table 5.10: Bonferroni post hoc tests showing significant ($p < 0.05$) differences between months for total acidity concentration.

	May	June	July
May			
June	NS		
July	*	NS	

* = statistically significant ($p < 0.05$)
NS = Not statistically significant ($p > 0.05$)

Due to the significant three way interactions for sulfate, individual two way repeated measures ANOVA'S were performed on each site (Table 5.11) (Underwood, 1999). At site 4 and 7 there were significant differences ($p < 0.01$) between positions and also over months. The interaction was significant, indicating that these sites are behaving differently between positions and over time. At sites 2,6 and 9 there was no significant interaction nor were there any significant differences between position or over time.

For total alkalinity all interactions were significant meaning that all sites were behaving differently over time and between positions (Table 5.12). To account for this, individual two way repeated measures ANOVAS were performed for all sites (Underwood, 1999). For sites 2,4,6, 8 and 9 the interaction between month and position was nonsignificant and there were no significant differences between position or over time. At site 4 the interaction was significant ($p < 0.008$) indicating that this site is behaving different over time and between positions.

Table 5.11: Individual 2 way repeated measures ANOVA for sulfate for sites 2,4,6,7 and 9. It shows which sites have a significant difference ($p < 0.01$) over time and between positions.

FACTOR		2 way repeated measures ANOVA				
		Variable = Sulfate				
		df	Mean Square	F - Value	P - Value	
Position						
	Site 2	1	7770.889	3.801	.191	NS
	Site 4	1	280.056	66.329	.015	NS
	Site 6	1	589.389	.743	.480	NS
	Site 7	1	8363.556	581.251	.002	*
	Site 9	1	6728	61.071	.016	NS
Month						
	Site 2	2	2242.389	13.470	.017	NS
	Site 4	1.060	539.763	34.441	.024	NS
	Site 6	1.145	5574.511	7.156	.101	NS
	Site 7	1.015	289.164	150.914	.006	*
	Site 9	2	446.000	3.220	.147	NS
Month*Position						
	Site 2	2	119.056	1.388	.349	NS
	Site 4	1.309	673.388	386.976	.001	*
	Site 6	1.469	405.230	2.278	.244	NS
	Site 7	2	222.389	228.743	.004	*
	Site 9	2	114.667	.738	.533	NS

* = statistically significant ($p < 0.01$)

NS = Not statistically significant ($p > 0.01$)

Note: probability levels had been altered to $p < 0.01$. As per Underwood (1999) when individual ANOVAS are completed based on interactions the probability level should be made more stringent by dividing the number of tests by the original probability level, in this case it is 0.05 divided by 5 which is the number of sites tested.

Table 5.12: Individual 2 way repeated measures ANOVA for total alkalinity for sites 2,3,4,6,7,8 and 9. It shows which sites have a significant difference ($p < 0.008$) over time and between positions.

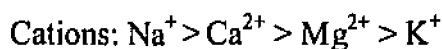
FACTOR		2 way repeated measures ANOVA				
		Variable = Total Alkalinity				
		df	Mean Square	F - Value	P - Value	
Position						
	Site 2	1	1030.774	2.575	.184	NS
	Site 4	1	48713.466	18.434	.023	NS
	Site 6	1	12743.575	1.578	.277	NS
	Site 7	1	40916.963	32.699	.005	*
	Site 8	1	0.00287	.58	.825	NS
	Site 9	1	4.532	.420	.522	NS
Month						
	Site 2	1.202	208.263	.945	.398	NS
	Site 4	1.126	4991.721	4.082	.127	NS
	Site 6	1.204	479.199	.271	.667	NS
	Site 7	2	11072.270	29.352	.000	*
	Site 8	1.640	1.640	16.547	.090	NS
	Site 9	1.048	59.526	2.199	.210	NS
Month*Position						
	Site 2	1.190	144.944	.676	.476	NS
	Site 4	1.273	2518.175	2.188	.233	NS
	Site 6	1.2	513.483	.289	.655	NS
	Site 7	1.44	69667.571	59.564	.000	*
	Site 8	1.021	26.575	4.638	.119	NS
	Site 9	1.032	50.773	1.208	.334	NS

* = Statistically significant ($p < 0.008$)

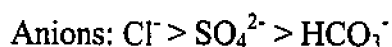
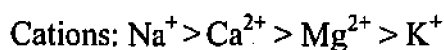
NS = Not statistically significant ($p > 0.008$)

Note: probability levels had been altered to $p < 0.008$ As per Underwood (1999) when individual ANOVAS are completed based on interactions the probability level should be made more stringent by dividing the number of tests by the original probability level i.e. in this case it is 0.05 divided by 6 which is the number of sites tested.

A total anion and cation survey was completed in June/July 2000. This was done to determine if there were any relationships of these cation and anion concentrations with acidification. In urban wetlands of the Swan Coastal Plain the relative concentration of cations and anions is as follows (Davis and Rolls, 1987; Davis et al., 1993):



In this study the relative concentrations (a total for June and July outside the core) were as follows:



It shows that for Lake Jandabup on average the buffering capacity is lower than the amount of sulfates in the wetland. These proportions were also found in a study of Lake Jandabup by Davis and Rolls *et al.* (1987).

Sites 2,8 and 9 had the lowest bicarbonate levels (tested as CaCO_3) with almost zero bicarbonate for both inside and outside the core. This indicated the low buffering capacity of those sites (Figure 5.17). At site 4,5,6,7 and 10 bicarbonate inside the core was higher than outside and ranged from 35 to 130 mg L^{-1} . Inside values ranged from 30 mg/L to 65 mg/L . Carbonate levels for all sites and all positions were below detection levels of 1 mg L^{-1} . These results are similar to tested total alkalinity levels indicating that the titration method used for total alkalinity is relatively accurate. This is

important because the buffering capacity results of the study from a vital contribution to the overall aim of the project (see conceptual model Figure 3.1) and most data are obtained are based on titration methods. Compared to the majority of other Swan Coastal Plain wetlands those on the Bassendean Dune systems (i.e. Lake Jandabup) have the lowest buffering capacities (Davis *et al.*, 1993; Davis and Rolls, 1987).

Generally calcium levels were below 30 mg L⁻¹ (Figure 5.17). The exception was site 5 with more than 50 mg L⁻¹ of calcium. Most sites, except 3 and 7, had slightly higher calcium inside the core than outside. Calcium concentrations in the present study were similar to those found by Davis and Rolls (1987). Magnesium ranged between 2 (site 10) and 40 mg L⁻¹ (site 5). Sites 2,3 and 4 had similar concentrations around 5 mg L⁻¹ while the remaining sites had levels above 10 mg L⁻¹. All sites, except 7 and 10 had slightly more magnesium inside the core than outside. Except for site 5, magnesium concentrations in the present study were similar to those found by Davis and Rolls (1987).

Chloride levels ranged between 20 mg L⁻¹ (site 10) and 240 mg L⁻¹ (site 5) but generally levels were between 50 and 150 mg L⁻¹ (Figure 5.17). All sites (except 7 and 10) had higher (~50 mg L⁻¹) chloride inside than outside. Sodium followed similar trends to chloride, levels ranged between 10 mg L⁻¹ and 140 mg L⁻¹, but generally it was between 50 and 100 mg L⁻¹ (Figure 5.17). At all sites, except 4, 7 and 10 inside cores had slightly higher levels inside than outside. These results show that outside waters are diluted, adding further evidence that the major trend over this period is dilution exacerbated by some evapoconcentration for isolated water inside the core. The cores

with the lowest sodium and chloride levels also had the lowest conductivity. In a study by Davis and Rolls (1987) sodium and chloride levels were the lowest in Jandabup of all wetlands studied (Lake Jandabup, Lake Joondalup, Lake Monger, North Lake and Thomsons Lake). In the present study sodium and chloride concentrations were below 150 mg L^{-1} in winter and in the Davis and Rolls (1987) study levels were also below 150 mg L^{-1} winter.

Potassium concentrations ranged between 2 mg L^{-1} (site 10) and 16 mg L^{-1} (site 3) (Figure 5.17). At sites 3,4,5 and 6 inside concentrations were slightly higher ($\sim 10 \text{ mg L}^{-1}$) than outside in comparison with other sites in which outside levels were generally lower than inside. These concentrations were relatively the same as those found by Davis and Rolls (1987).

Silicate was highest at sites 6 and 7 being around 10 mg L^{-1} . This is most likely related to the diatomaceous sediment at those sites (Figure 5.17). All other sites had concentrations below 5 mg L^{-1} . At sites 2, 3, 8 and 9 inside concentrations were about 2 mg L^{-1} lower than outside, but at sites 5, 6, 7 and 10 inside was higher than outside. The silicate range for the majority of Swan Coastal Plain wetlands is between 0 and 30 mg L^{-1} , with most being below 10 mg L^{-1} (Davis *et al.*, 1993).

Sulfate levels ranged between 5 mg L^{-1} (site 4) and 240 mg L^{-1} (site 5), but generally levels were between 100 mg L^{-1} and 150 mg L^{-1} (Figure 5.17). The exceptions were at sites 4, 7 and 10 where concentrations were below 50 mg L^{-1} . At all sites, except 6,10,7 and 4 inside concentrations were higher ($\sim 50 \text{ mg L}^{-1}$) than outside. These results are

relatively consistent with sulfate levels taken from individual cores. Compared to other Swan Coastal Plain wetlands sulfate levels are relatively higher, but this is not consistent for all sampling occasions (Davis *et al*, 1993; Davis and Rolls, 1987).

Figures 5.18 show for sites 2,4,6,7 and 9 the variation in these cations and anions over time. Generally for all sites the concentrations of these ions decreased between June and July. Descriptions of the differences between sites and positions has already been given above.

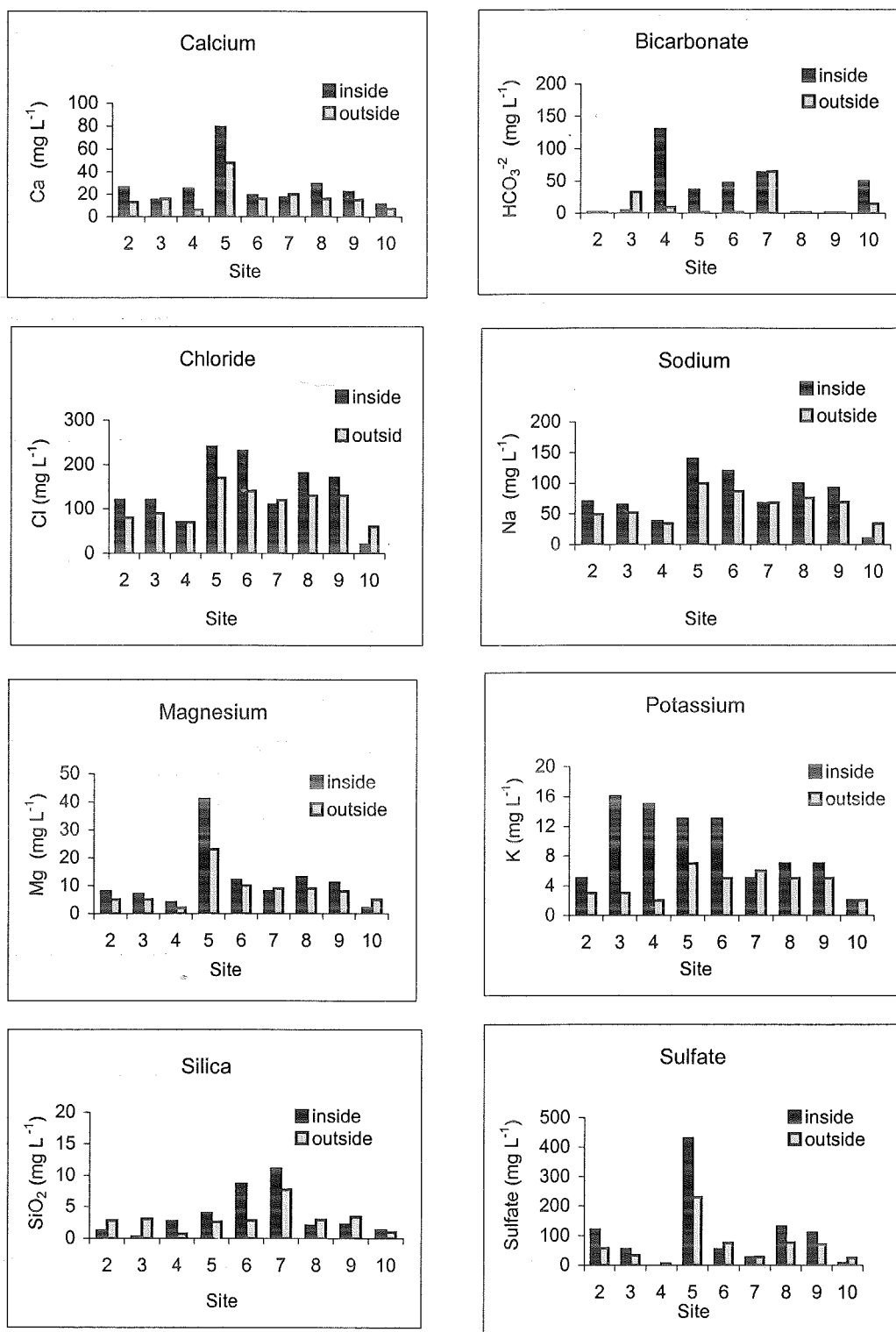


Figure 5.17: Concentrations of selected anions and cations (as indicated on graph) for each site at Lake Jandabup in June 2000. Inside refers to inside the in situ core and outside refers to outside the in situ core. One water sample was made by bulking water from randomly selected cores.

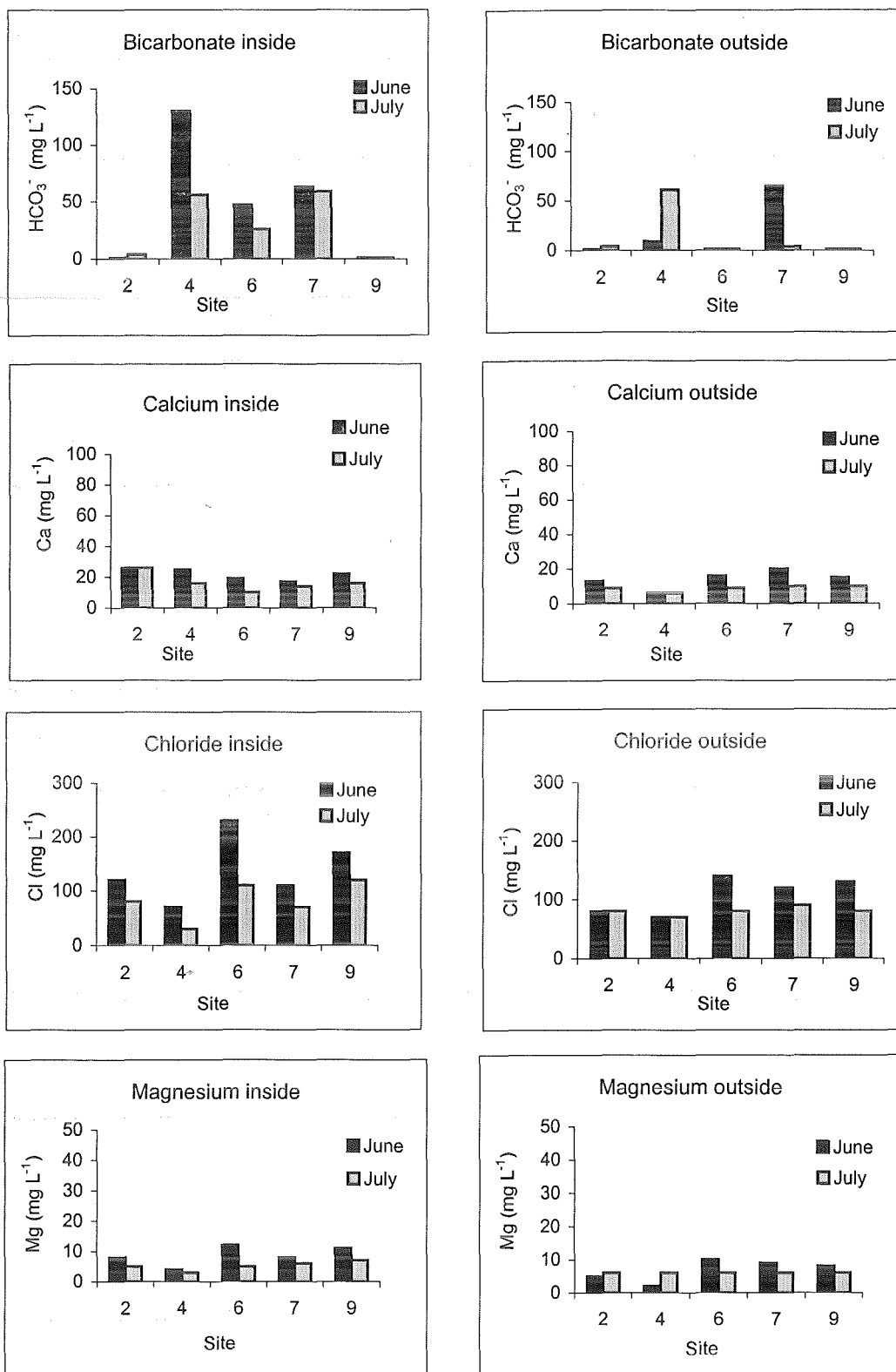


Figure 5.18: Concentration of selected anions and cations (as indicated on graph) for sites 2, 4, 6, 7 and 9 between June and July 2000. Inside indicates inside the in situ core and outside indicates outside the in situ core. CONTINUED NEXT PAGE

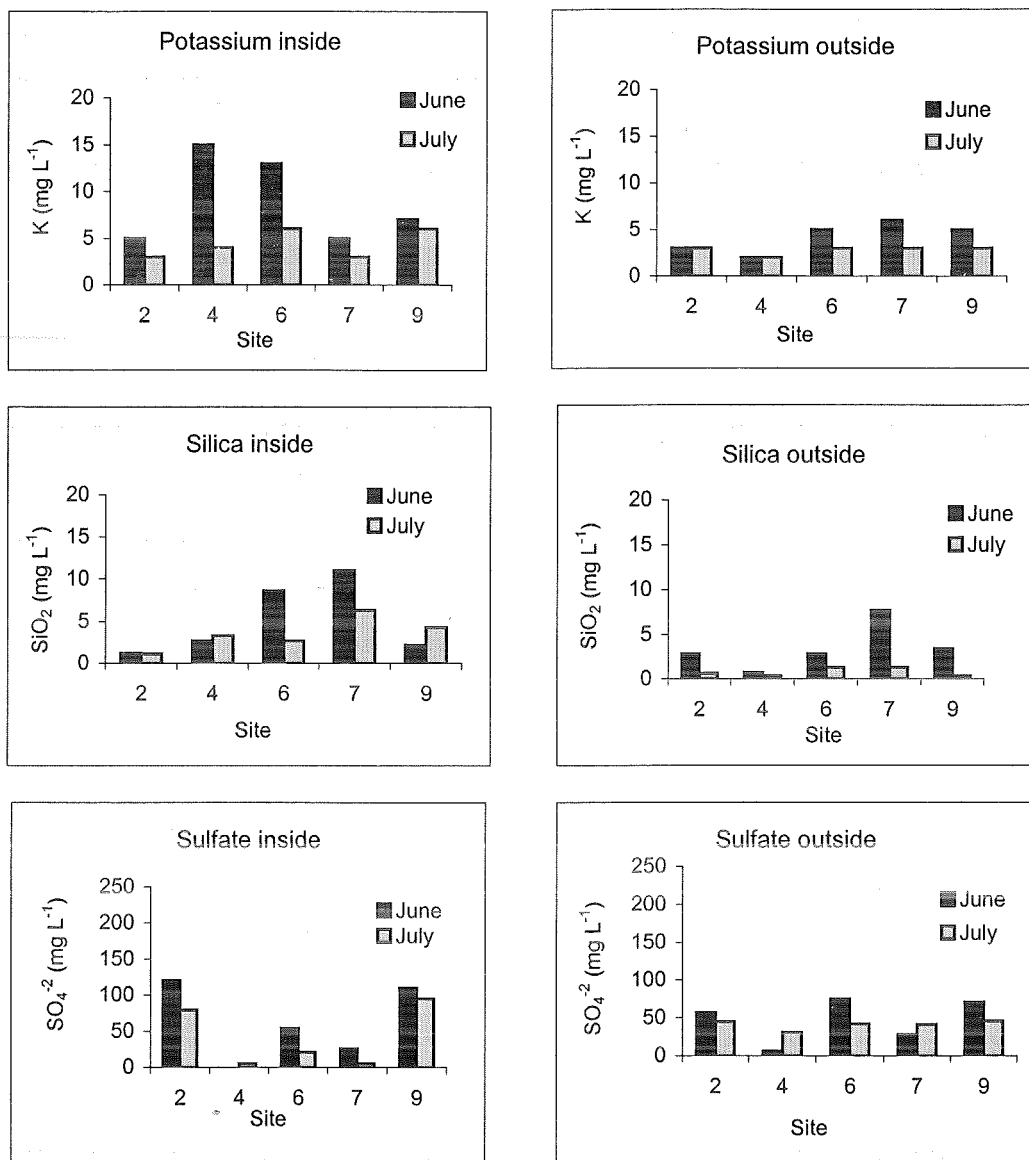


Figure 5.18 CONTINUED: Concentration of selected anions and cations (as indicated on graph) for sites 2,4,6 7 and 9 between June and July 2000. Inside indicates inside the in situ core and outside indicates outside the in situ core.

Two separate correlations were computed. One (correlation A) used pH, conductivity, oxygen , redox, temperature, depth, sulfate, total iron, total alkalinity and total acidity data collected from all sites during the monthly sampling. The other correlation (correlation B) used the cation and anion data to obtain a matching data for the other variables (i.e. pH, sulfate, total iron, total alkalinity and total acidity), where an average was taken from the two cores that the bulked water sample was made from.

In correlation A (Table 5.13) the strongest positive relationships were between: conductivity and temperature, conductivity and sulfate, pH and total alkalinity and acidity and alkalinity. The strongest negative relationships were between, pH and redox and pH and sulfate. All variables were correlated with at least 2 other variables, the exception was that total iron was only negatively related to depth.

In correlation B (Table 5.14) potassium, sodium, magnesium, chloride, calcium and sulfate were generally all strongly positively correlated with each other. Other strong positive relationships include: pH with bicarbonate and alkalinity with pH. Generally bicarbonate was poorly correlated with most variables except pH and alkalinity and silica. This could be related to the importance of alkalinity and silica in the buffering capacity of the wetland.

Table 5.13: Significant Pearson's correlations (showing *r* values) for correlation A. Numbers represent *r* values. (*n* = 122)

	pH	Cond.	Oxygen	Redox	Temp	Depth	Sulfate	Iron	Alkalinity	Acidity
pH										
Cond	-.586**									
Oxygen	NS	NS								
Redox	-.659**	.295**	NS							
Temp	-.475**	.569**	NS	.428**						
Depth	NS	-.244**	.245**	NS	NS					
Sulfate	-.562**	.709**	.286**	.459**	.496	NS				
Iron	NS	NS	NS	NS	NS	-.256**	NS			
Alkalinity	.511**	NS	-.217**	-.415**	.318**	-.279**	-.389**	.260**		
Acidity	NS	.286**	-.211*	NS	NS	-.368	NS	NS	.526**	

Key: Cond = Conductivity, Temp = Temperature

** = statistically significant at the 0.01 level

* = statistically significant at the 0.05 level

NS = Not statistically significant (*p* > 0.05)

Table 5.14: Significant Pearson's correlations (showing *r* values) for correlation B. Numbers represent *r* values (*n* = 28)

	pH	HCO ₃ ⁻	Na	K	Mg	Cl	Ca	SO ₄ ²⁻	SiO ₂	Alk	Aci
pH											
HCO ₃ ⁻	.636**										
Na	.446**	NS									
K	NS	NS	.567**								
Mg	NS	NS	.823**	.462**							
Cl	-.445**	NS	.991**	.593**	.783**						
Ca	NS	NS	.705**	.513**	.925**	.666*					
SO ₄ ²⁻	-.384*	NS	.762**	.382*	.956**	.722**	.927**				
SiO ₂	NS	.440**	.353*	NS	NS	.345*	NS	NS			
Alk	.485**	.686**	NS	.427**	NS	NS	NS	NS	.545**		
Aci	NS	NS	.514**	.490**	NS	.563**	NS	NS	.568**	.550**	

Key: Alk = Total Alkalinity, Aci = Total Acidity

Correlations could not be computed with carbonate because all variables were constant.

** = statistically significant at the 0.01 level

* = statistically significant at the 0.05 level

NS = Not statistically significant

Chapter Summary

The following point form summary is provided to give the major findings of the field study.

- i. The pH on any one sampling day at Lake Jandabup could range between 3.0 and 7.0 pH units depending on location and sediment type and time of year.
- ii. The major acidity producing area of the lake was in the south west corner that has organic sediment under $\text{Fe}(\text{OH})_3$ precipitate.
- iii. The sand areas on the eastern side generally had a pH above 6.0 pH units, except for site 2 (which had a low pH for some of the study despite being located on the eastern side in sand sediment).
- iv. Over the 18 weeks of the study the pH of the most acidic areas increased from around 3.0 – 4.0 pH units to around 6.0 pH units.
- v. Low pH, low total alkalinity, high sulfates and high total acidity were interrelated.
- vi. The concentration of anions and cations and conductivity generally decreased over the study period; their concentrations were the highest on the western side of the wetland at all times during the study.

CHAPTER 6: DISCUSSION

6.1 Acidification at Lake Jandabup

An acidification event was detected at Lake Jandabup in 1997 to 2000. The pH in the south-western section declined below 4.0 pH units, while the rest of the wetland remained between 6 and 7 pH units. It has been called an acidification 'event' because by the time this study had finished the wetland appeared to have recovered from the pH decline, where the most acidic areas had increased to above 6.0 pH units. Other acidification events may have occurred in the past. This thesis was concerned with the recent event and seeks to explain why it may have undergone an acidic change, why it may have recovered and whether it will happen again.

Previous studies on Lake Jandabup indicate that low pH (between 5 and 6) is not unusual, but extremely low pH (< 4.0) has rarely been detected, and until 1997 it has never lasted for a number of years (see Arnold, 1990; Davis *et al.*, 1993; Davis *et al.*, 1991; Davis and Rolls, 1987; Ryder, 1993; Wrigley, 1991). The few times when low pH (< 5.0) was detected it was usually in wetland areas with diatomaceous sediments and occurred immediately following drying and rehydration of the lake bed (Davis and Rolls, 1987; Ryder, 1993). Davis and Rolls (1987) detected a low pH (pH < 4.0) in February 1986 (after a unseasonal rainfall event) but noted that the pH increased to above 6.0 pH units by autumn of that year.

Studies (e.g. Davis and Rolls, 1987; Ryder, 1993) show that acidification at Lake Jandabup has the potential to occur but it appears to be seasonal and the wetland recovers that year. This project focused on a recent (1997 to present), prolonged (> 1 year) and extreme acidification ($\text{pH} < 4.0$) at Lake Jandabup. It has provided evidence for the causes of the recent acidification event and its recovery. There is cause for concern over this acidification event because monitoring (between 1996 to present) detected loss of invertebrate species at the lake. This is of great significance because Lake Jandabup is a nature reserve and the conservation status may have been compromised.

It was hypothesised that the recent acidification of Lake Jandabup was exacerbated due to increased drying of the lake bed causing greater oxidation of pyrite and/or a decreased buffering capacity of the water and sediments. This hypothesis is, as at least in part accepted. The results show that any drying of intact sediment cores taken from some areas of Lake Jandabup can produce a low pH upon rehydration. Diatomaceous sediment taken from the south-west corner produced low pH. The lowest pH was produced from sediment overlain with $\text{Fe}(\text{OH})_3$ precipitate, which is a product of pyrite oxidation. (Clarke and McConchie, 1996; Evangelou, 1998; Psenner, 1994; White *et al.*, 1989).

In conjunction with low pH, high sulfate levels provided evidence for pyrite oxidation. Research shows sulfates are released when pyrite is oxidised (see chapter 1). In the laboratory pH positively correlated with total alkalinity. Intact sediment cores taken from diatomaceous sediment had the lowest pH, while sediment from the sand area had

higher pH and higher total alkalinity. This indicates that the acidity being produced from diatomaceous sediment is not or cannot be neutralised.

The results of the laboratory study show that dried sediment will produce low pH upon rehydration, but they did not show that longer drying of up to 30 days, enhanced pyrite oxidation as there was no significant difference between treatments for pH and sulfate. There was also no significant difference between treatments for total alkalinity so it may be concluded that buffering capacity was not affected by the longer drying times. The exception was for site 4, where 30 days drying had a lower buffering capacity than 0 and 10 days drying. There was however, a significant difference between treatments for total acidity released. Total acidity is the ability of water to react with a strong base. It is an indication of how easily the water will return to the pH of a solution of sodium carbonate after acidification (~7.0 pH units) (Wetzel, 1983). Sites 1,4,3 and 10 that had the highest pH upon drying and rehydration, also had the lowest total acidity, indicating that they did not require much base or alkalinity to be present for an increase in pH to occur. Sites 5,6 7,9 and 8 had very high total acidity. It is possible that alkalinity was available for these sites, but they were unable to utilise it due to high total acidity meaning that they required large quantities of base to increase the pH. Alternatively it may just be that the sites with sandy sediment (1,4,3 and 10) have more carbonates and therefore appear to have higher lower total acidity. Generally, longer dried sediment had the highest acidity. This could indicate that when sediment is dried for longer it has a reduced ability to increase in pH after there was acid production, even if a base was added.

There could be other reasons related to the oxidation of pyrite that could be contributing to the acidity produced in cores taken from diatomaceous sediment. Iron, whether it enters a wetland as Fe^{2+} or Fe^{3+} , can oxidise and hydrolyse rapidly to form solid iron hydroxides $\text{Fe}(\text{OH})_3$. This process can remove iron from solution, generate protons and decrease the pH of the water (Cravotta, 1998; Fitzpatrick *et al.*, 1993; Vile and Wider, 1993; Zhang and Evangelou, 1998). In this study, sites (8 and 9) with organic sediment overlain with $\text{Fe}(\text{OH})_3$ generated the lowest pH. Site 9 (laboratory cores) also had the lowest iron levels; there was no more iron in the core water than there was in the initial rainwater used for rehydration, whereas all other sites sampled had an increase in iron. This could indicate that there was no iron in the sediment to be released or all of it has been precipitated as $\text{Fe}(\text{OH})_3$. These results indicate acid generating processes where $\text{Fe}(\text{OH})_3$ precipitate is found. In support of this explanation sites 8 and 9 had some of the highest organic matter levels of all sites. Organic matter is a good source of food for bacteria such as *Thiobacillus – Ferrobacillus* that catalyse these reactions and lack of organic matter can be detrimental to these organisms (Gazea *et al.*, 1996; Weider *et al.*, 1990; Zhang and Evangelou, 1998). High redox and high oxygen levels, as found in the aerated core water, can increase this reaction (Boulton and Brock, 1999).

There were limitations to the laboratory experiment that may have affected the results. It is possible that the length of drying used was not long enough to activate acid generating processes. Previously Lake Jandabup has dried for up to 20 weeks but the scope of this study did not allow these long drying times to be reproduced. It is also possible that the difference between drying length was not great enough to detect a change (i.e. 0 days' drying was too close to 10 and 30 days' drying). In addition, the

method of drying and collection of sediment may have kept sediment anaerobic and not allowed oxidation of pyrite. This could also be due to a situation where pyrite was located deeper than 20 cm (only 20 cm of sediment was collected for the study).

The laboratory experiment showed that dried sediment taken from diatomaceous areas at Lake Jandabup will produce a low pH (<4.5 pH units) upon rehydration. This experiment highlights the high spatial variability in pH and other physical and chemical variables between sites, which was also seen in the field.

The field study showed that at Lake Jandabup the high spatial heterogeneity can be related to:

- i. patterns of refilling,
- ii. location in the wetland and
- iii. sediment type and drying of the lake bed.

Overall, the results from the field study indicate that for most variables, each site is behaving differently over time and between inside and outside the core, however there are some groupings of sites that showed similar trends. One possible reason for these groupings can be attributed to the groundwater movement in the lake.

As stated in chapter 2, Lake Jandabup is a surface expression of the unconfined aquifer of the Gngangara groundwater mound with inflow occurring along the eastern margins and outflow on the western side (Allen, 1979; Davidson, 1995). Sites 1, 3, 4, and 10 lie in sandy sediment on the eastern side of the wetland. In the ordination these sites were

grouped together by physico-chemical properties. The likely reason for this grouping is that these sites being located where ground water flows in should have similar properties to that of the groundwater as it moves up through the sediment (Allen, 1979). Compared to the latest groundwater chemistry available (Chapter 2) these sites and the groundwater had similar properties e.g. conductivities were below $500 \mu\text{S cm}^{-1}$, chloride levels were below $100 \mu\text{S cm}^{-1}$, sodium below 50 mg L^{-1} , and magnesium below 10 mg L^{-1} .

Another interesting trend is that sites 1,3,4 and 10 almost always had the lowest concentration of these variables compared to the other sites. A reason for this is that the remaining sites, located near the outflow area would have higher concentrations due to evapotranspiration at the surface of the wetland (Allen, 1979). Davidson (1995) also found that chloride levels in bore water on the eastern side of the lake were less than 40 mg L^{-1} , but on the western side they were greater than 200 mg L^{-1} . In terms of pH eastern sites (i.e. 1,3,4 and 10) had near neutral pH in the field that did not alter much during the study. Also, these sites did not produce low pH in the laboratory and site 4 (the only site tested in the laboratory) had the lowest sulfate levels of all the sites. This indicates that these sites are not acid producing and therefore their water quality can be attributed to the quality of the ground water. Sites 3,4 and 10 also had very similar and low ($< 50 \text{ mg L}^{-1}$) sulfate levels in the field which is similar to that of the groundwater ($< 100 \text{ mg L}^{-1}$). These sites also had the highest buffering capacities which can be attributed to the high alkalinity of the groundwater (Davidson, 1995). These sites also generally had low total acidity, meaning that it will not take much base to neutralise and

acid being produced. It is possible that as ground water inflow brings with it carbonates and bicarbonates that are quickly utilised.

Site 5, located in the south west corner had, at time of refilling (week 10) a conductivity near $1500 \mu\text{S cm}^{-1}$ for both inside and outside the core. As the site filled over subsequent weeks the conductivity inside the core dramatically increased, while outside the core decreased. The high conductivity inside the core can be attributed to evaporation as the water slowly exits and because the water is isolated it can not be diluted by the surrounding water. Another contributing factor could be that the sediment releases large concentrations of ions upon rehydration, thus, when isolated it cannot be diluted by the surrounding water. Ferguson and Eyre (1996) state that in acidic water (as found in site 5) salinities can be high. Field data supports this idea. Analyses shows that this site generally had the highest concentrations of all the sites for cations and anions thereby giving it giving it high salinity and inside the core always had the higher concentration. In the laboratory this site was the only one that had a conductivity above $1000 \mu\text{S cm}^{-1}$.

Based on this theory of the influence of east to west movement of groundwater, site 2 being located in sandy sediment on the eastern side would be expected to have similar properties to the groundwater. However, the pH at this site, both inside and outside the core decreased from 6.5 pH units at week 2 to 3.4 at week 3. It is unlikely that this site produced acidity through oxidation of pyrite because it was never dry during this study to oxidise and the pH was not acidic when the study began. The most likely cause of the decline is that acidic water from nearby site 9, south west of site 2, (which was acidic

from week 0), was blown into this area by strong winds. In the week 2 there were consistent afternoon south westerlies (Bureau of Meteorology, 2000). However, inside water, which was isolated from mixing effects also declined. This brings up a limitation of the study, that maybe the cores were not isolating the water as well as expected; the cores were probably leaking and acid water was entering inside the core. This idea is supported by the high standard error of the inside core for pH indicating that not all cores leaked and went acidic.

The major acidity producing area of the wetland are sites 6,8 and 9. These areas had organic/diatomaceous sediment under $\text{Fe}(\text{OH})_3$ precipitate (sites 8 and 9 had much larger clumps of $\text{Fe}(\text{OH})_3$ than site 6). In the laboratory these three sites produced the lowest pH, had the highest sulfate and the lowest buffering capacity and on average over the treatments they had the lowest total iron levels. In the field these sites also had low pH, high sulfates and low buffering capacities. This evidence points to pyrite oxidation for a number of reasons (1) oxidation of pyrite gives low pH and high sulfates after rewetting; (2) a by product of acidification is precipitation of $\text{Fe}(\text{OH})_3$ therefore, there is little total iron in the water column to be measured. The exact nature of these processes are described in chapter 1.

So far site 7 had not featured in this discussion. This site provides an anomalous result between the laboratory and the field. Even though it had diatomaceous sediment with some $\text{Fe}(\text{OH})_3$ precipitate, for the entire field study it remained above pH 6.5. However, in the laboratory study it produced a pH of around ~ 5 pH and high sulfate concentrations. In the field outside the core had similar sulfate levels to the acidic sites.

It is possible that site 7, during the field experiment, was not acidic because this site did not dry in 2000 therefore oxidation of pyrite could not occur and/or there could have been alkalinity generating mechanisms at work (which will be fully explained later) that could be keeping the pH near neutral. Monitoring data (see Sommer *et al.*, 2000) indicated that in spring 1996 and 1997 the pH was near neutral in this area of the wetland and in the previous summer the lake bed dried partially for approximately 4 weeks. However, in spring 1998 an area close to site 7 located in the north of the wetland with the same sediment type had a pH of 4.18 and in the previous summer the entire lake bed dried for 16 weeks. Although based on tenuous data, it highlights that site 7 has the potential to have low pH if the lake bed dries completely.

Alternatively, sulfate rich groundwater could be entering this site as it is close to an inflow area on the eastern side. The north of the wetland, where this site is located is less wide than the south, therefore inflowing ground water will accumulate at this site relatively quickly, and compared to other diatomaceous sections of the lake, it will dry less and be wet for longer. This is in contrast to site 5, in the very south, which is the last area to become wet and the first to become dry. Since site 7 had similar sulfate levels outside the core compared to low pH sites it could indicate pyrite oxidation, however, pH was near neutral. This could show that sulfate rich waters were entering the site, but there was no oxidation of pyrite therefore no decrease in pH. Further evidence supporting this claim is that sulfate levels in the isolated inside core water remained low, thus it is probable that the cores were not leaking and were isolating inside water from the effects of mixing.

6.2 Recovery from acidification

Lake Jandabup appeared to recover from the acidification event for at least the short term, as by the end of the study the pH of the most acidic areas had increased from <4.0 pH units to ~6.0 pH units. Recovery can be defined in two ways, short term and long term recovery. In the case of Lake Jandabup short term recovery is indicated by the seasonal increase in pH, but long term recovery refers to the prevention of extremely low pH events in the future. The results of this study alone can not determine if the recovery is temporary (short term) or permanent (long term). Evidence points towards the recovery being only short term and if similar conditions such as prolonged drying of the lake bed were to occur in the future, acidification would be expected.

There was no significant difference in total alkalinity between months, despite the increase in pH. This indicates that the increase in pH is probably not due to increased buffering capacity of water and sediments. The most likely reason is that the winter rainfall and groundwater inflow filling the lake caused the pH to increase due to dilution of hydrogen ions and sulfates. This is also shown by the general decreasing trend in conductivity and other cations and anions from dilution over the study period. This seasonal variation has been described for Swan Coastal Plain wetlands by Davis *et al.* (1993) and Davis and Rolls (1987).

There are other alkalinity generating processes at work in the wetland that could be contributing to the short term increase in pH. As redox potential declines it enables bacteria to reduce sulfates to hydrogen sulfides, thus increasing the pH of the water. In

this study redox had a high negative correlation with pH indicating that as redox decreased pH increased. A good example of this is taken from site 5. At site 5 redox and oxygen levels were extremely low inside the core and the water was above 5 pH units, but outside the core redox and oxygen levels were much higher and the pH was <4.5 pH units. This could indicate sulfate reduction inside the core, but sulfide oxidation outside. Another example taken from site 7 shows that inside the cores both redox and sulfate were low, but outside the cores redox and sulfate were high. pH was the same, around 7.0 pH units both inside and outside the core. One reason for this is that the high silicate nature of the sediment (i.e. diatomaceous) is buffering the hydrogen ions being produced through sulfate oxidation (Wetzel, 1983; Hutchinson, 1975). Although as stated earlier there are other explanations for the anomaly at site 7. This example shows that similar sediment type can have both a low and high pH with low or high sulfate levels depending on redox and oxygen conditions of the water. These relationships have been described by Wetzel (1983); Wang and Morse (1996); Wendt-Potthoff and New (1998).

There were no significant correlations between iron and any other variables (except depth). However, this was expected as in acidic water, oxidation of pyrite eventually leads to formation of $\text{Fe}(\text{OH})_3$ therefore there will be little dissolved iron in the water to be measured (Gazea, *et al.*, 1996; Howard, 1998; Wetzel, 1983; Winfield, 1995). At low pH Fe^{3+} is soluble and can act as a primary oxidant for pyrite (Evangelou, 1995), but as water is diluted, as is the case for Lake Jandabup, the iron will hydrolyse as solid $\text{Fe}(\text{OH})_3$ (Abel, 1989; Boulton and Brock, 1999). Although not statistically significant, for some sites like 8 and 9 that had a large quantity of $\text{Fe}(\text{OH})_3$ precipitate on the

sediment surface, the levels of total iron were the lowest total iron levels of all the sites and generally decreased as water levels through dilution increased. Visual observations of $\text{Fe}(\text{OH})_3$ at the lake since acidification in 1997 suggest that levels and size of particles have increased.

Metal precipitation is alkalinity generating (Gazea *et al.*, 1996). Metal precipitation occurs when free metals such as Fe^{2+} combine with H_2S under reducing and high organic matter conditions (Boulton and Brock, 1999). In sites with high organic matter and low redox and oxygen (e.g. site 7 inside) there may have been metal precipitation, but no metal oxidation (metal oxidation will produce acidity). This site had neutral pH. However, at site 6 with similar conditions inside the core, the pH was low indicating metal oxidation. The cause of this anomalous relationship is unknown.

6.3 Management of Lake Jandabup

Lake Jandabup appears to have recovered temporarily from the recent acidification event, however, the permanency of the recovery is unknown. It is also unknown if extreme acidification, such as the present event will re-occur if similar conditions, such as longer drying of the lake bed were to occur in the future. Although this study did not show that longer drying enhanced pyrite oxidation there were limitations to the laboratory core experiment that may have affected the results. Other evidence, such as, increased lake drying times over the past 5 years and decreasing pH levels points to longer drying of the lake bed as being the cause of the recent acidification event.

In January to March 2000 Lake Jandabup was artificially maintained as it was thought that this would prevent further oxidation of pyrite. It appears to have been successful in preventing oxidation as most parts of the lake have temporarily recovered from the decline in pH that was detected in 1997. This relationship provides further evidence to suggest that when the lake does not dry there is no further oxidation of pyrite. The fact that some sites were still acid producing even when the lake remained wet the previous summer does not discount this idea. It is likely that some parts of the lake were caught in an acid cycle that began in summer of 1997: pyrite was oxidised by atmospheric oxygen causing pH decline below 4.5 pH units, this led to Fe^{3+} being produced which was able to continually oxidise pyrite because the pH was below 4.5. The lake was able to get out of the acid producing cycle for several possible reasons: (i) the Fe^{3+} oxidising the pyrite was diluted by the winter rains or (ii) eventually the availability of pyrite ran out, therefore there was none to be oxidised.

Management of acid sulfate soils (e.g. pyrite oxidation) requires an understanding of groundwater management and the geochemical and biological processes involved in pyrite oxidation. The most common method of preventing pyrite oxidation is keeping the pyrite in a reduced state by covering it with water (Crossland, 1996; Kelly, 1996; National Working Party on Acid Sulfate Soils, 2000; Williams and Copeland, 1996). However, management is not as simple as this especially in a natural, seasonal wetland where seasonal cycles must be retained. Several questions about the management of Lake Jandabup have arisen:

- i. Is a management response needed? Is the present acidification of Lake Jandabup a problem and will the lake recover without human intervention? Also, if

acidification is detected in the future should management intervene? In other words, are acidification events 'normal' and will they heal themselves through natural seasonal cycles?

- ii. When and what sort of a management response is needed? At what point should humans intervene. Should it be when the pH of the most acidic areas of lake Jandabup fall below a critical level and how long should the pH be allowed to remain low before management action is taken; or should it be related to when and how long the lake bed dries (as question (iii) will address). A critical pH level is not known. However, evidence from previous monitoring indicated that invertebrate species started to disappear when the pH declined to below 5 pH units for 2 consecutive years (Sommer *et al.*, 2000). The type of response used also needs investigation: how much water and from where should it be pumped into the wetland?
- iv. How long and which areas of the lake should be allowed to dry and what constitutes drying? In other words, what is the minimum water depth or moisture status of the lake for each sediment type that will prevent excessive oxidation of pyrite? It could be that only the acid producing areas need to remain wet and other (e.g. eastern sidesandy) areas can dry, thus allowing normal seasonal drying processes to occur. Also, maximum number of dry weeks per year should be set.

These questions are difficult to answer. Although Lake Jandabup appears to have at least temporarily recovered from the recent acidification event, it is unknown if it is directly related to the artificial maintenance of the lake this year or if the event is part of a cycle that does occur but has not been detected in the past due to irregular monitoring

of Lake Jandabup. Even if low pH did occur before it does not mean that management should not be concerned, as previous surveys may also have missed loss of sensitive invertebrate species which is of high management importance at the lake. Due to the high spatial heterogeneity of the lake any surveys (e.g. Arnold, 1990; Davis *et al.*, 1993; Davis *et al.*, 1991; Davis and Rolls, 1987; Ryder, 1993; Wrigley, 1991) that did occur missed detection of low pH due to not testing in acid producing areas. The patterns of low pH areas also change regularly. In 1993 the northern area had pH <5.5 during July. In 1997 this area was near neutral. In 1998 it had a low pH (<4.5 pH units) and in 2000 it was again near neutral (Ryder, 1993, Sommer, 1997; Sommer *et al.*, 2000). Although it is unlikely that the exact same sites were used in all surveys it does highlight the high spatial and temporal nature of pH at Lake Jandabup. This raises the need for regular spatial monitoring of pH at Lake Jandabup. Choosing sites based on results from previous years is inadequate as the pH spatial variability changes seasonally. This is one reason why the present study involved mapping the entire wetland for pH before study sites were selected. However, it appears for past (e.g. Ryder, 1993, Sommer, 1997 and Sommer *et al.*, 2000) and the present study that the lowest pH is almost always found in areas with diatomaceous sediment.

Artificial maintenance can be a short term solution to mitigating the pH decline at Lake Jandabup, but attention should be given to assessing why the wetland had been drying for longer recently. In addition to this, the long term effects of maintenance on other biological processes are unknown. In a study on Lake Jandabup by Ryder and Horwitz (1995) it was concluded that a seasonal water regime was needed for leaf litter processes that provided a food source for aquatic food webs and that leaf litter and

sediment must be kept moist to make sure organic soil development continues. A balance needs to be found between the seasonal processes at the lake and prevention or minimisation of acidification effects.

In the long term, acidification events at Lake Jandabup could potentially occur. This is because groundwater levels on the Swan Coastal Plain are declining leading to unseasonal and/or larger areas of the lake bed drying. Lake Jandabup in particular has become drier over the past 20 years (R. Loomes, pers. comm., September, 2000). Normal drying patterns would generally mean that the major acidity producing areas of lake (sites 8 and 9) probably had some water cover for most of the year as seasonal drying does not always mean complete drying of the lake bed.

It is possible that the recent acidification event of Lake Jandabup was prolonged and extreme due to the drying of the whole lake bed in 1998. Although the lake was acidic before 1998 it is possible the extreme drying caused cracks to form, as seen in the most acidic parts of the lake bed (diatomaceous areas) thus allowing easy access for oxygen to the pyrite. The sediment, once cracked will probably stay cracked regardless of whether it rehydrated or not, therefore even short drying or extremely low water levels could cause oxidation of pyrite. If the sediment is rewet it is unlikely that the cracks will dissipate in the short term. Horwitz *et al.* (1998) found that dried organic sediment lost moisture holding capacity. Although the study focused on the drying effects of fire, the results could be relevant to Lake Jandabup. It is possible, that following the 1998 drying, the sediment was no longer able to hold moisture and hence the sediments remained oxic, which are the conditions needed for pyrite oxidation. For long term

recovery from acidification at Lake Jandabup the possible extensive damage to the lake bed cause by cracking needs to be addressed.

Management consideration needs to be given to repairing the cracks in the lake bed and ensuring that the sediment remains wet and anoxic. However, it is unsure whether the cracks will heal or if they will remain in the lake forever. Management should primarily involve identifying and managing the cause of groundwater decline on the Swan Coastal Plain as decreasing groundwater levels are the main cause of unseasonal and prolonged drying of the lake. Artificial maintenance is probably only a temporary solution because it is unlikely that Lake Jandabup will always be able to be artificially maintained. Even if the lake can be artificially maintained the location of the inflow pipe and exact physical and chemical characteristics of the water used needs attention. Presently the inflow pipe is located on the north eastern edge of the wetland, but the sediments that need to remain moist are on the western side, therefore it may be better to maintain the lake from the western edge. Although this discussion has used groundwater quality data from a bore near Lake Jandabup it is unsure if this was the same water used to maintain the lake. Data was unavailable. Future management of Lake Jandabup should include knowing the exact quality of the water being pumped into the lake.

The following table gives scenarios of drying patterns and management options at Lake and predicted outcomes. However, it is important to note that these outcomes are purely speculative and based solely on the results of this study and previous monitoring data,

all of which had which had unavoidable limitations. The predictions are based on the assumptions:

- i. that the recovery from acidification at Lake Jandabup is only short term caused by dilution effect,
- ii. that the cracks formed in the lake bed are likely to persist into the future and
- iii. that the acidic producing area of the lake is the diatomaceous sediment.

Table 6.1: Scenarios and predicted outcomes of drying and acidification at Lake Jandabup.

Scenario	Predicted Outcomes	Reasons for predictions and/or management considerations
SCENARIO 1 In 2001 most of the lake bed dries, but the deepest areas, which are also the acidity producing areas remain wet either through artificial maintenance or high water levels	The pH may decline slightly due to an evapoconcentration effect, but the wetland will recover to similar to what it is now.	If sediments are kept anoxic by covering them with water they are unlikely to be oxidised. However, there is cause of concern for other processes that require a seasonal water regime
SCENARIO 2 In 2001 the whole lake dries, including the acidity producing areas for ~4 weeks with no management (i.e. no artificial maintenance)	Following refilling the pH in the diatomaceous areas will probably decline to around 4.0 pH units. If refilling occurs within 4 weeks of drying the wetland will recover that season. Recovery is likely to only be short term and the pH will decline if lake dries again.	In summer 1997 some parts of the wetland dried for ~4 weeks. In the following spring the spatial nature of pH was between 4.58 and 6.71 following refilling, indicating that only some areas became acidic following drying.
SCENARIO 3 The entire wetland dries for greater than 4 weeks in one year and continues to dry for greater than 4 weeks in subsequent years with no management (i.e. no artificial maintenance)	Some areas (probably diatomaceous) will become acidic (pH <4.5). These areas will remain with low pH until there is one year that the wetland does not completely dry. However, it is likely that recovery will only be only temporary.	This scenario can be compared to the present acidification event where the pH declines when the lake bed dried for > 4 weeks and stated low until the wetland was wet over the one whole year i.e. it was artificially maintained.

The acidification of Lake Jandabup is a problem. It is believed to have caused a decrease and possible extinction of some invertebrate species. This study has shown that some sediments types, when dried, can produce low pH. In the field areas with these sediment types also had low pH for some of the study period. It is thought that in the short term Lake Jandabup has recovered from the recent acidification event. Long term recovery is less certain. To aid in protecting Lake Jandabup from future acidification events careful management of water levels at the lake could be employed.

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