Seasonal hydrology and its influence on acidity and trace element mobilisation in a coastal wetland

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Abstract

Trace element mobilisation from sediments can affect adjacent surface and marine water quality and the health of aquatic ecosystems. Mobilisation in wetlands or acid sulfate soil landscapes has historically been related to variations in acidity or oxidation-reduction (redox) potential in sediments.

Seasonally inundated wetlands exhibit a dynamic water level, which has implications for contaminant solubility. For example, during winter, acidity products are dissolved and anaerobic conditions may develop at the sediment-water interface. Low pH and Eh conditions can release previously sediment-bound trace elements into the water column, which may be washed into adjacent streams during large stormflow events. Evaporation of surface water in summer concentrates contaminants as salts in surface sediments.

There are more than 9600 wetlands on the Swan Coastal Plain (SCP) of Western Australia. An estimated 70 – 80% of these wetlands have been disturbed through drainage, infilling or vegetation clearing, and many are underlain by acid sulfate soils. Muddy Lake (ML) is a small (~30 ha), seasonally inundated coastal wetland near Bunbury on the SCP. Agricultural drainage was installed at ML prior to the 1930s, which may have been responsible for the oxidation of subsurface sulfidic sediments. The wetland is now severely degraded and exhibits seasonal significantly acidic and trace element-enriched surface water discharge via a main drain.

Ground and surface water has been monitored at ML since September 2008, and results have been combined with meteorological data to calculate a water balance for ML. The water balance results elucidate the seasonal dominance of hydrologic components for the wetland. Rainfall and evaporation dominate the water balance in winter and summer, but groundwater and surface water discharge are important in spring and autumn. Soil and water from the surface and subsurface of ML have been analysed for trace element concentrations: mobilisation is seasonally dependent and responds to variations in pH and Eh. Results indicate that the degree of mobilisation is affected by the soil composition and its exposure to seasonally variable conditions, driven by wetland hydrology. Peak water levels in the wetland coincide with peak contaminant concentrations due to dissolution of accumulated salts in surface sediments. The results of a laboratory incubation experiment on three sediments from ML suggest that subsurface wetland sediments are a significant store of contaminants in the system.

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Acronyms

AMD	Acid mine drainage
CLASS	Coastal lowland acid sulfate soil
DOM	Dissolved organic matter
LOI	Loss on ignition
MC	Moisture content
ML	Muddy Lake
OM	Organic matter
XRF	X-ray diffraction

1 Introduction

Acid sulfate soils contain iron sulfide minerals, which when exposed to air through drainage or excavation, can lead to the formation of sulfuric acid and the release of trace metals and metalloids from oxide or silicate surfaces. Metals bound to iron oxyhydroxides can be mobilised by reductive dissolution under reducing (anaerobic) conditions. Contamination of environmental waters with metals such as aluminium, copper and zinc can have toxic effects on aquatic ecosystems. In waterlogged wetland sediments, anaerobic conditions are common due to high concentrations of organic matter and limited diffusive mixing of oxygen. Seasonal hydrology of wetlands controls the periodic variability of oxidation-reduction conditions and associated contaminant and mineral cycling. Hydrology also affects the transport of acidity and contaminants from groundwater to wetlands and eventually downstream.

The current study combined field investigations of an acid sulfate soil wetland on the Swan Coastal Plain of Western Australia over a 16-month period with a laboratory experiment and analyses. A wetland water balance was developed in order to elucidate the seasonal dominance of the hydrologic components and their affect on the wetland geochemistry. The project had the following aims:

- Elucidate the seasonal hydrology of the wetland with a water balance
- Gain an understanding of the seasonal changes in acidity and oxidation-reduction conditions experienced on site and their relation to hydrology
- Calculate acidity and metal export from the wetland
- Determine sources of acidity and metals onsite
- Relate acidity and chemical concentrations of ground and surface water to sediment-water interactions and relate differences between 2008 and 2009 water quality to hydrology and geochemical processes

The achievement of these research aims may provide appropriate site knowledge to allow an effective remediation strategy to be developed. Furthermore, elucidation of acidity generation and trace element mobilisation mechanisms may inform the development of management plans for other coastal areas at risk of contamination.

2 Literature Review

Trace elements are technically defined as those that are present in a natural system in trace amounts. This dissertation is focused on the behaviour of metals (such as aluminium, iron and zinc), and metalloids (such as arsenic) when exposed to seasonal changes in water and soil chemistry. The terms trace element, trace metal, or metal may be used interchangeably here to refer to metals or metalloids that may be vital for ecosystem health at low concentrations, but are toxic and cause environmental damage at elevated levels.

2.1 Trace metal behaviour in wetland sediments

Wetland sediments have historically been known for their ability to capture pollutants from waterways that flow through them, and protect downstream ecosystems from contamination (Olivie-Lauquet et al. 2001). However, scientific research has also investigated the potential for wetland sediments to act as sources for contaminants (Salomons et al. 1987; Olivie-Lauquet et al. 2001), particularly when perturbed as a result of human activities. Du Laing et al. (2009) discuss the various factors and processes that impact on trace metal sorption or mobilisation in sediments. The behaviour of trace metals is governed by the nature of their occurrence in wetlands, and the conditions to which they are exposed. General forms of metals in sediments include:

- water soluble metals, as free ions or complexes;
- exchangeable metals;
- metals precipitated as inorganic compounds, including insoluble sulfides;
- metals complexed with humic substances;
- metals adsorbed to Fe or Mn oxyhydroxides; and
- metals bound within the lattice of primary minerals (Du Laing et al. 2009).

Wetland soils are influenced by dynamic conditions; including changes in water level, oxidation-reduction (redox) potential, pH, dissolved organic matter and plant growth (Du Laing et al. 2009). Seasonal variability in these factors can affect the mobilisation of trace metals (Olivie-Lauquet et al. 2001).

Increased salinity in wetland soils may mobilise metals from sediments through the formation of soluble chloride complexes, such as $CdCl_2$ (Du Laing et al. 2009). Saline conditions also cause high concentrations of major cations such as Na, K, Ca and Mg, which compete with trace metals for sorption sites on sediment particles (Du Laing et al. 2009). Increased salinity can be a result of evapo-concentration of salts in ponds or by tidal effects in wetlands hydraulically connected to the ocean.

Solid organic matter in the form of plant detritus on wetland beds can bind metals by adsorption, complexation and chelation (Du Laing et al. 2009). However, the presence of dissolved organics in the overlying water, such as carboxylic, amino or fulvic acids, can form soluble metal complexes (Du Laing et al. 2009). Therefore, the ability of organic matter to bind metals in wetland sediments appears to be related to the fractions of labile and refractory compounds present. The charge on humic and fulvic acids is pH dependent, and this affects their ability to complex with metal cations, however the effect is much less than for oxide minerals (Appelo & Postma 2007). Humic acids contain many acid groups, and pH changes cause selective deprotonation and protonation of these groups due to their differing acidity constants (Appelo & Postma 2007).

Wetland plants can accumulate metals through uptake, microbial activity in the rhizosphere, or the formation of "iron plaque" on the roots (Du Laing et al. 2009). Oxygen is transported into the anoxic zone in the soil by the root systems of wetland plants, and this may cause the oxidation of reduced metals, particularly Fe and Mn, which then co-precipitate with other metals and are concentrated around the roots (Du Laing et al. 2009; Keon 2002).

Anaerobic conditions may lead to the reduction of sulfates to sulfides, which can bind metals through the formation of metal sulfide precipitates. Sulfate reduction is catalysed by microbes at low redox potentials, and results in the formation of sulfides:

$$SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O \tag{1}$$

Iron is usually present as dissolved ferrous ions, following iron oxide and oxyhydroxide reduction, and reacts with H_2S to form amorphous or crystallised forms of iron sulfides, such as mackinawite and greigite (Du Laing et al. 2009). In their study on the iron geochemistry of acidic drains in coastal lowlands, Burton, Bush and Sullivan (2006b) propose a model for iron transformations in sediments. The species involved in the model included schwertmannite, goethite, mackinawite, siderite and pyrite. The formation of iron sulfide minerals is a potential sink for trace elements, which may be bound in the mineral structure.

Wetland sediments are particularly vulnerable to changing redox conditions due to the dynamic water levels they often exhibit (Du Laing et al. 2009; Olivie-Lauquet et al. 2001). Waterlogging or flooding of sediments rich in organic matter can lead to the formation of anoxic conditions as part of the ecological redox sequence of reactions (Du Laing et al. 2009; Hemond & Fechner-Levy 2000). Once established in organic-rich environments, bacteria in the soil use oxidants in a preferential fashion to convert organic matter (OM) to energy, as shown in Figure 1. If the supply of oxygen becomes depleted, due to aerobic respiration in waterlogged sediments for example, the sequence of reactions will begin to occur from left to right, and the redox scale (Eh) decreases. Measuring the redox potential of water and sediments with a reference electrode allows for an estimation of the level of reduction. The redox electrode measures more negative potentials where electron activities are higher, such as in reducing conditions (Hemond & Fechner-Levy 2000); however, the exact relationship between Eh and redox potential (or oxidation-reduction potential, ORP) varies between electrodes and conditions, and measurements of redox potential should be interpreted with caution (Olivie-Lauquet et al. 2001). A shift in redox conditions can affect the mobility of trace metals by altering the adsorption capacity of species such as humic materials and Fe and Mn oxyhydroxides (Du Laing et al. 2009).

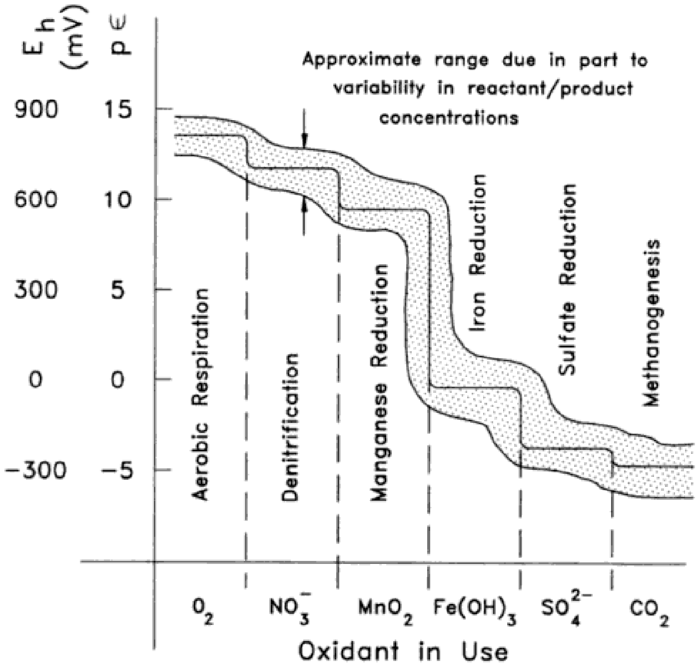


Figure 1. The ecological redox sequence (Hemond & Fechner-Levy 2000)

During reduction, protons are consumed and pH tends to increase (Grybos et al. 2007), while oxidation is associated with increased acidity (Du Laing et al. 2009). Changes in pH condition also affect metal mobility in sediments, with low pH leading to metal release by desorption from sediments. Low pH conditions result in a reduction of the negative surface charge of OM, clay particles, and Fe and Al oxides and carbonates. Furthermore, the solubility of sulfides increases, and thus metal adsorption is inhibited by a range of factors (Du Laing et al. 2009; Salomons et al. 1987).

The hydrology of wetlands may also influence trace metal fate, due to a shift in redox conditions. Du Laing et al. (2009) focus on the effect of oxidation of previously reduced sediments, which may occur as a result of the artificial drainage of wetlands to lower the water table. Exposure to air can cause sulfides to oxidise, and metals that are co-precipitated or adsorbed to, for example, FeS, are solubilised. Seasonal lowering of the groundwater table in summer has also been linked to sulfide oxidation and increased metal concentrations (Du Laing et al. 2009). In contrast, flooding conditions can lead to anoxia in sediments and metal mobilisation, as discussed previously. Reducing conditions also have the potential to initiate sulfate reduction and the sequestration of metals through the formation of insoluble sulfides (Du Laing et al. 2009; White et al. 1997).

The dynamic nature of wetland hydrology, particularly in seasonally inundated wetlands, suggests that seasonal and inter-annual variability in hydrological regimes and the resultant alternation between oxic and anoxic conditions (Olivie-Lauquet et al. 2001) have the potential to be a dominant control on trace metal mobilisation and transport to downstream ecosystems.

2.2 Coastal lowland acid sulfate soils

On a global scale, many coastal lowlands have been drained for urban development, agriculture or mining, and acidic discharges from oxidised sulfidic sediments are commonplace, particularly in Australia (Appleyard et al. 2004; White et al. 1997; Green et al. 2006), Vietnam’s Mekong Delta (Hanhart et al. 1997; Minh et al. 1997), and Scandinavia (Astrom & Astrom 1997; Nordmyr, Astrom & Peltola 2008). Studies of coastal lowland acid sulfate soils (CLASS) are sometimes coupled with investigations into elevated metal concentrations in associated natural waters (Nordmyr, Astrom & Peltola 2008; Burton, Bush & Sullivan 2006a; Burton et al. 2008).

In the heavily developed coastal areas of eastern Australia, CLASS are a significant problem and have resulted from extensive deep drainage for agriculture, particularly sugarcane production (White et al. 1997). The severity and widespread-nature of CLASS on the east coast has led to a proliferation of research in the region (e.g. van Oploo et al. 2008; White et al. 1997; Burton et al. 2008).

2.2.1 Oxidation of sulfidic sediments and the production of acid

Metal-sulfide minerals such as pyrite can produce acid when exposed to air and water due to the process of oxidation, shown by the following reaction.

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (2)$$

This equation highlights the potential for acid generation: for every mole of pyrite oxidised, four moles of protons are produced. The reaction may occur directly or following the dissolution and dissociation of pyrite into Fe(II) and disulfide (Appelo & Postma 2007). In either case, the reaction kinetics associated with pyrite oxidation mean that the process occurs slowly (Appelo & Postma 2007). The overall process is in fact the product of a number of reactions, as shown in Figure 2.

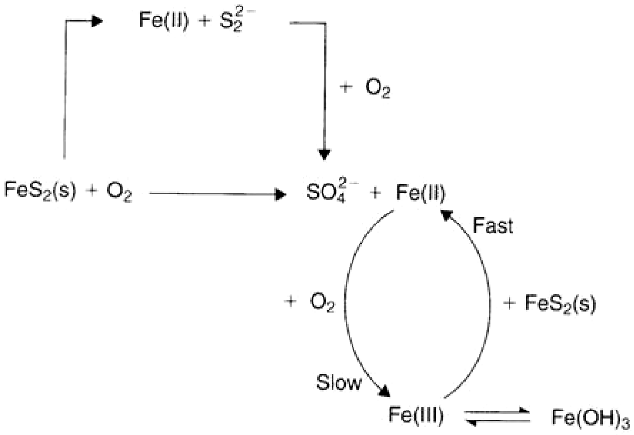


Figure 2. Pyrite oxidation reaction pathways (Stumm & Morgan, cited in Appelo & Postma 2007)

Initially, disulfide is oxidised to the sulfate ion, either directly or following dissolution (Appelo & Postma 2007):

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (3)$$

Then Fe^{2+} is oxidised to Fe^{3+}:

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (4)$$

Dissolved Fe(III) is unstable if pH is greater than 4, and so will be precipitated as an oxide (White et al. 1997):

$$Fe^{3+} + H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (5)$$

If pH is less than 4, Fe(III) remains in solution (White et al. 1997) and additional pyrite can be oxidised via a second pathway:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (6)$$

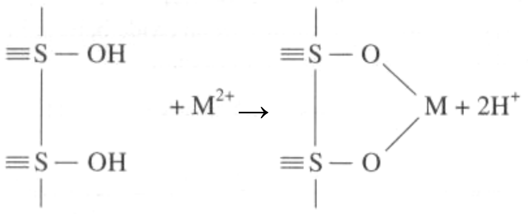
The Fe(II) produced in this reaction may be oxidised by oxygen to reform Fe(III). Although the kinetics of the oxidation are slow at low pH, iron-oxidising bacteria catalyse the reaction, resulting in high reaction rates (Appelo & Postma 2007). Thus at low pH, bacterial catalysis allows rapid pyrite oxidation by cycling between Fe(II) and Fe(III), as highlighted in Figure 2. At higher pH, pyrite oxidation by O_2 dominates due to low Fe(III) solubility, although this process occurs slowly (Appelo & Postma 2007).

2.2.2 Effect of pyrite oxidation and acidity on trace metal mobilisation

Abraitis et al. (2004) conducted a literature review on the variability of natural pyrite composition, and found that minor elements within the pyrite lattice or within discrete mineral inclusions included As, Co, Sb, Au, Ni, Cu, Ag and Sn. Trace elements included Ag, Bi, Cd, Hg, Mo, Pb, Pd, Pt, Ru, Sb, Se, Te, Tl and Zn. In a study of acid sulfate soils from Sweden and Finland, Ni, Co, Mn, Mo and Cu were mobilised during pyrite oxidation because they were bound in pyrite in trace amounts (Sohlenius & Öborn 2004). Increased weathering of soils (which were mostly clays) due to the low pH in acid sulfate soils was found to cause mobilisation of Cd, Ni, Mn, Co, Zn and Cu (Sohlenius & Öborn 2004). The authors suggest that mobilisation of trace metals from pyrite oxidation was not as quantitatively important as increased weathering when considering the processes which cause trace element leaching.

Adsorption of trace metals on the surfaces of iron and manganese oxides and hydroxides is strongly pH dependent. This relationship can be seen in Figure 3. Below a certain pH, which varies between metals, there is no adsorption, and at some slightly higher pH there is complete adsorption (Drever 1997). The sharp transition between no adsorption and complete adsorption is why metal release often occurs suddenly when pH decreases. The way in which metals adsorb to oxide surfaces may be conceptualised by regarding the surface as a plane of hydroxyl groups (Drever 1997). These hydroxyl groups act as mono- or bidentate ligands, adsorbing metal cations as shown in equations (7) and (8) respectively, where S represents an oxide surface, and M represents a metal.

$$\equiv S—OH + M^{2+} \rightarrow \equiv S—OM^+ + H^+ \qquad (7)$$



(8)

Given that metal cations compete with hydrogen ions for surface sites, it follows that the adsorption of metal cations by oxides is strongly pH dependent, as seen in Figure 3. As the acidity of a solution increases, the equilibrium of reactions (7) and (8) can be pushed to the left, resulting in desorption of metal cations from the mineral surface.

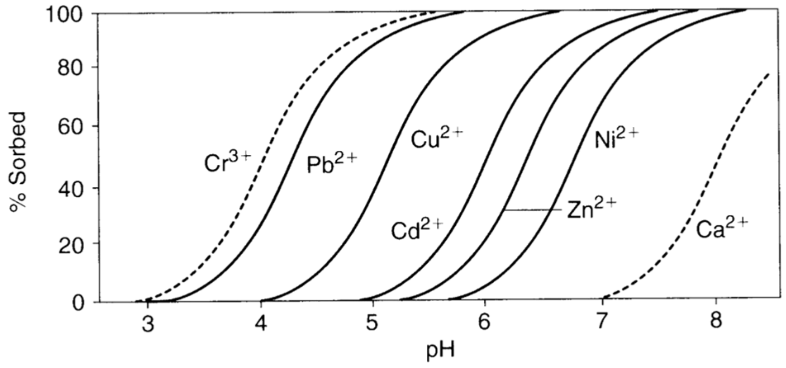


Figure 3. Dependence of pH on adsorption of metal cations on ferrihydrite (Appelo & Postma 2007)

Anions may also be adsorbed onto surface sites of, for example, oxyhydroxides. In this case, the anion acts as a ligand and competes with hydroxide ions for surface sites (Drever 1997). The relationship of adsorption and pH is complicated by changes in speciation, as shown by the isotherms for the organic arsenic and selenium species in Figure 4.

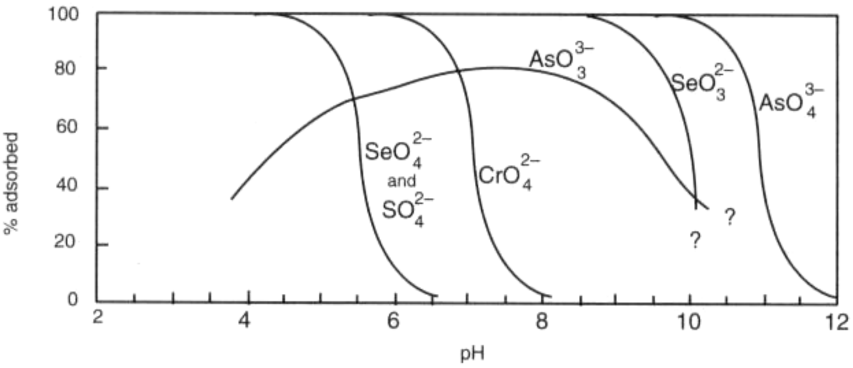


Figure 4. Dependence of pH on adsorption of anions on iron oxyhydroxide (Drever 1997)

The release of trace metals due to pyrite oxidation may be affected by a fluctuating water table in the subsurface. In dry conditions, the water table is low and sulfide oxidation occurs, releasing sulfate ions. When the water table rises in the wet season, the soil becomes waterlogged and reducing conditions develop, and mackinawite (FeS) may be formed (Sohlenius & Öborn 2004), in which trace metals may be bound. The cycling of Fe between various species in sediments can affect the pH and flux of Fe to surface waters (Burton, Bush & Sullivan 2006b). This has been studied intensively in acid mine drainage (AMD) settings, but less is known about Fe cycling in CLASS settings (Burton, Bush & Sullivan 2006b). Unlike AMD environments, CLASS drains and landscapes typically contain high concentrations of organic matter due to the growth of aquatic macrophytes (Burton, Bush & Sullivan 2006b). These organic rich sediments have been found to host different Fe cycling and geochemical regimes than AMD environments (Burton, Bush & Sullivan 2006b) and management plans for treating AMD discharges may be inappropriate for treating acidic drainage of CLASS landscapes. The effect of seasonal hydrology on sediment-water chemistry is thought to be a major factor in controlling water quality in these areas (White et al. 1997).

2.3 Oxidation and reduction

Changing redox conditions affect the sorption of trace metals to humic materials and Fe/Mn oxyhydroxides, and can lead to the formation or oxidation of insoluble metal sulfides (Du Laing et al. 2009). Oxidation of pyrite can release associated metals, as discussed in the previous section. Reducing conditions can also lead to the release of trace metals via Fe oxyhydroxide dissolution, but can immobilise metals with the formation of insoluble sulfides (Jimenez-Carceles, Alvarez-Rogel & Conesa Alcaraz 2008). Therefore, variations in soil redox potential have implications for trace metal mobility (Jimenez-Carceles, Alvarez-Rogel & Conesa Alcaraz 2008; Du Laing et al. 2009; Salomons et al. 1987).

Hydrous iron and manganese oxides may occur in the environment as coatings around silicate grains and as isolated minerals (Drever 1982). Oxyhydroxides have large surface areas, they are often amorphous, and have a high affinity for metals (Drever 1982). The adsorption of metals on oxyhydroxide surfaces is sensitive to changes in pH or redox potential. As pH increases, the negative surface charge of oxyhydroxide increases, and metals are strongly adsorbed (Drever 1982). At low pH, this affinity may be reversed. Additionally, oxyhydroxides may be dissolved by reduction under anoxic conditions, leading to the release of previously sorbed metals (Drever

1982). Trace metal mobilisation under reducing conditions associated with increased Fe and Mn in solution has shown that the stability of Fe and Mn oxyhydroxides is a key factor in controlling trace metal release from sediments (Olivie-Lauquet et al. 2001).

Wetlands exhibit seasonal oxidation and reduction patterns, causing the periodic release of trace elements from sediments. During wetland inundation, the organic-rich environment may lead to reducing conditions in the sediment, while dry conditions can cause sediments to oxidise when the water level falls to below the surface. Additionally, the growth of wetland plants can cause the localised oxidation of sediments around root systems. Blute et al. (2009) studied a contaminated wetland in Massachusetts and found that As speciation varied seasonally. Arsenic species investigated in this study included As(III)-sulfides, and As(III) and As(V) adsorbed on Fe oxyhydroxides, carbonates, and silicates. The periodic saturation and desaturation of wetland surface soils produced seasonally-changing redox conditions, which in turn caused cyclic precipitation and dissolution of Fe oxyhydroxides (Blute et al. 2009). The resulting redox conditions controlled the mobility of As in these wetland sediments (Blute et al. 2009).

Under some environmental conditions, such as the start of the winter flooding season, surface sediments may be oxic and metals are mobilised by an alternative mechanism. In oxic conditions, organic matter is decomposed and this leads to a release of metals that were sorbed to the solid organic phase (Salomons et al. 1987). Organic matter may also be dissolved under reducing conditions due to the pH rise associated with a consumption of protons during reduction reactions (Grybos et al. 2007; Du Laing et al. 2009). Sediment-bound OM is released due to electrostatic repulsion between electronegative OM and deprotonated mineral surfaces, which become less electropositive as reducing conditions develop (Grybos et al. 2007). The presence of dissolved organic matter (DOM) in the surface waters may cause metal-DOM complexes to form and enhance the solubility of trace metals, and even result in their desorption from sediments (Salomons et al. 1987; Grybos et al. 2007). The laboratory study conducted by Grybos et al. (2007) concluded that reducing conditions caused mobilisation of trace metals into solution, via Fe oxyhydroxide dissolution and/or DOM release. Given that OM released from sediments under reducing conditions is caused by a pH increase, Grybos et al. (2007) suggest that for metals such as Pb, Ni and the rare earth elements, which were mobilised due to OM dissolution, pH is a crucial factor, whatever redox conditions prevail.

The oxic-anoxic interface and its position in the soil profile controls the flux of trace metals from the sediments to surface water (Salomons et al. 1987; Du Laing et al. 2009), and from anoxic soil layers to oxic surface soils (Du Laing et al. 2009). Around the oxic-anoxic interface, redox-driven processes can lead to precipitation of metals or their dissolution (Du Laing et al. 2009). Due to the dynamic water levels experienced in wetlands, particularly those that are seasonally inundated, the cyclical rise and fall of the oxic-anoxic interface may cause seasonal mobilisation of trace metals. The kinetics of such mobilisation are restricted by the size and period of the water level fluctuation (Du Laing et al. 2009). Therefore, seasonal and inter-annual variations in hydrology are likely to be a major factor in trace metal release from wetland sediments.

2.4 Influence of hydrology on processes affecting metal mobility

Flooding of wetland sediments associated with seasonal water inputs from groundwater, rainfall, runoff or streamflow can cause a release of trace metals, which are then transported to downstream ecosystems as water continues to be added over the wet season. During the dry season, evapotranspiration dominates and contaminants precipitate onto surface soils as surface water evaporates. As the oxic-anoxic interface falls below ground level, surface sediments become oxidised. The water table in the surrounding landscape is also affected, and changes in soil chemistry result from oxidation of previously waterlogged soil layers. The seasonal alternation between oxic and anoxic conditions in wetland sediments can also prevent the formation of insoluble metal sulfides (Olivie-Lauquet et al. 2001). Wetland hydrology and the relative importance of hydrological inputs and outputs can be determined using a water balance.

2.4.1 Water balance

Water balances can be combined with water quality data to estimate the rate of export of acid (White et al. 1997) or metals mobilised from coastal lowlands. Hydrologic modelling of wetlands can elucidate the dominant flow regimes in these systems (Blute et al. 2009; Townley et al. 1993), and variability of pH and redox conditions can be related to wetland hydrology.

Ferone and Devito (2004) used a water balance to determine the shallow groundwater and surface water interactions in pond-peatland complexes in Canada. The interaction of groundwater and surface water was found to vary seasonally, and was affected by large rainfall events (Ferone & Devito 2004). Hydrometric measurements were taken at study locations and used to calculate hydrologic budgets:

$$\pm r = P_r + S_i + G_i - E - G_o - D_o - \Delta V \tag{9}$$

where:

P_r	is precipitation
S_i	is surface flow inputs
G_i	is shallow groundwater inputs
E	is pond evaporation
G_o	is shallow groundwater outputs
D_o	is deep vertical groundwater recharge through the pond bottom
ΔV	is the change in pond volume, and
r	is the residual, representing uncertainty in flux measurement.

Groundwater fluxes, estimated to be accurate within 70%, were estimated using hydraulic gradients between ground and surface water, and saturated hydraulic conductivity (determined by Hvorslev water recovery method) (Ferone & Devito 2004). Results of the water balance indicated that P_r and E dominated the inputs and outputs, and that the D_o term was negligible. The storage in the ponds decreased in summer because E exceeded P_r (Ferone & Devito 2004). Results allowed for discussion of dominant water fluxes and hydrological response to extreme conditions, such as large rainfall events or extended dry periods. The residual term was found to be within the error of instrumentation and approaches used for measurement. Although groundwater fluxes were estimated with a large degree of uncertainty, their relatively small magnitude compared with atmospheric fluxes meant that the water balance could be achieved (Ferone & Devito 2004).

A conceptual wetland water balance model was developed by Krasnostein and Oldham (2004) and applied to the Loch McNess wetland on the Swan Coastal Plain of Western Australia. The numerical model is based on an equation that determines the change in storage per unit area:

$$\frac{ds(t)}{dt} = i(t) - e_v(s,t) - e_b(s,t) - q_{ss}(s,t) - q_{se}(s,t) \tag{10}$$

where:

i	is precipitation
e_V	is evapotranspiration
e_b	is bare soil evaporation

q_{ss} is subsurface runoff, and

q_{se} is surface runoff

and the model is solved explicitly on a daily timestep. The model was validated by comparing the result to changes in storage measured by wetland water depth or groundwater bores (Krasnostein & Oldham 2004). If the model was not accurately predicting storage changes, it could be adapted by adding or subtracting extra water balance components, or “buckets” which feed the basic system (Krasnostein & Oldham 2004). For example, a local and regional groundwater component, and a subsurface overflow term, were added to the Loch McNess model for extra complexity. The authors suggest that seasonally inundated wetlands may be modelled using a bare soil evaporation term for times when the wetland is dry.

2.5 Swan Coastal Plain

As discussed previously, pH and redox variability caused by the seasonal hydrology of wetlands can cause mobilisation of trace elements from wetland sediments. The Swan Coastal Plain (SCP) lies to the west of the Darling Scarp in the southwest of Western Australia (WA). The SCP is abundant with wetlands, with over 9600 seasonal or permanent water bodies, including sumplands, damplands, floodplains and lakes (Balla 1994). An estimated 70 – 80% of these have been disturbed through drainage, infilling or vegetation clearing (Balla 1994). The distribution of wetlands and acid sulfate soils is shown in Figure 5. The spatial distribution of wetlands and high-risk acid sulfate soils close to the coast suggests that the area has the potential to cause trace element contamination of coastal areas. The Perth average annual rainfall has been 20 – 30% below the long-term average since the mid-1970s, and groundwater resources have been increasingly pumped for metropolitan drinking water supplies (Hinwood et al. 2006). Thus, a combination of factors has caused oxidation of sulfidic sediments and groundwater acidification in the region (Appleyard et al. 2004; Appleyard, Angeloni & Watkins 2006; Hinwood et al. 2006). The proximity of the SCP to the capital city of Perth may lead to a requirement for further drainage or groundwater extraction as urban sprawl occurs along the WA coastline. Although the potential for contamination of groundwater and receiving water bodies due to CLASS disturbance in WA is relatively unstudied, the issue was brought to public attention following the arsenic contamination of a number of domestic groundwater bores in the Perth suburb of Stirling in 2002 (Appleyard et al. 2004; Appleyard, Angeloni & Watkins 2006).

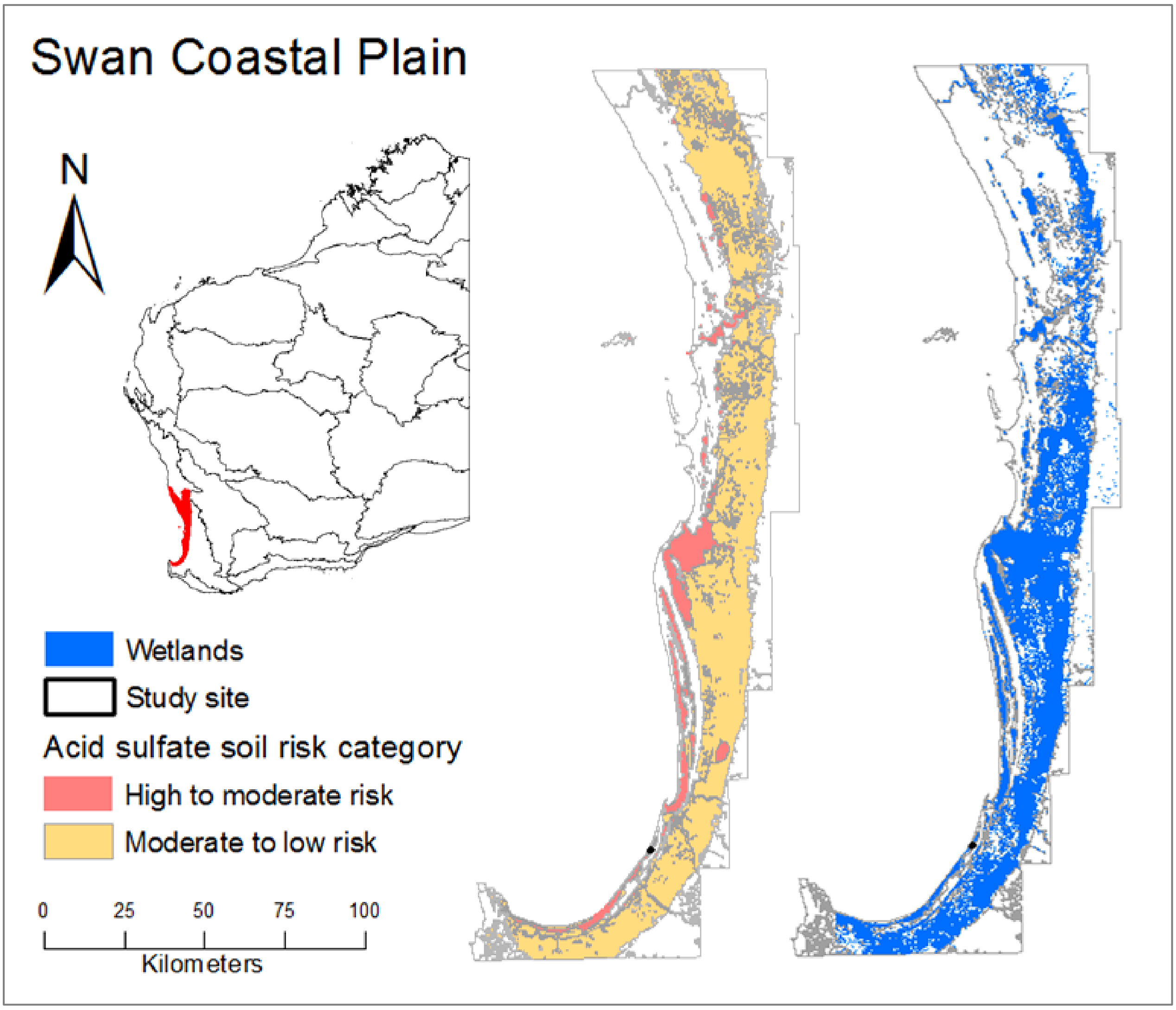


Figure 5. The location of the Swan Coastal Plain in Western Australia and the distribution of acid sulfate soil risk and wetlands (GIS data from Department of Environment and Conservation)

2.6 Study motivation

In the current study, the Muddy Lake wetland on the SCP was used as a model system for the investigation of factors that cause seasonal mobilisation of trace metals and their transport offsite via agricultural drainage. Metal and trace element contamination of wetlands from acidic and redox variations on the SCP has received little attention in the literature. The current study has the potential to extend the current scientific knowledge of the mobilisation of trace elements in wetland sediments affected by CLASS. Trace metal mobilisation in wetland sediments and CLASS have been studied independently elsewhere (e.g. Olivie-Lauquet et al. 2001; Sohlenius & Öborn 2004; Green et al. 2006), as have wetlands contaminated by upstream pollution from industry or AMD (Blute et al. 2009; Jimenez-Carceles, Alvarez-Rogel & Conesa Alcaraz 2008). This study fits in somewhat of a niche in recent environmental research, combining field and laboratory study to examine how changes in acidity, oxidation-reduction potential and other factors led to metal mobilisation in a natural wetland affected by CLASS. An improved understanding of the metal mobilisation processes in the Muddy Lake wetland may assist in the evolution of sustainable land development policies for coastal areas, and informed remediation of this and other contaminated sites. Indeed, the National Working Party on Acid Sulfate Soils (2000) have formally recognised the need for scientific research into the soil solution and leachate chemistry of Australian acid sulfate soils.

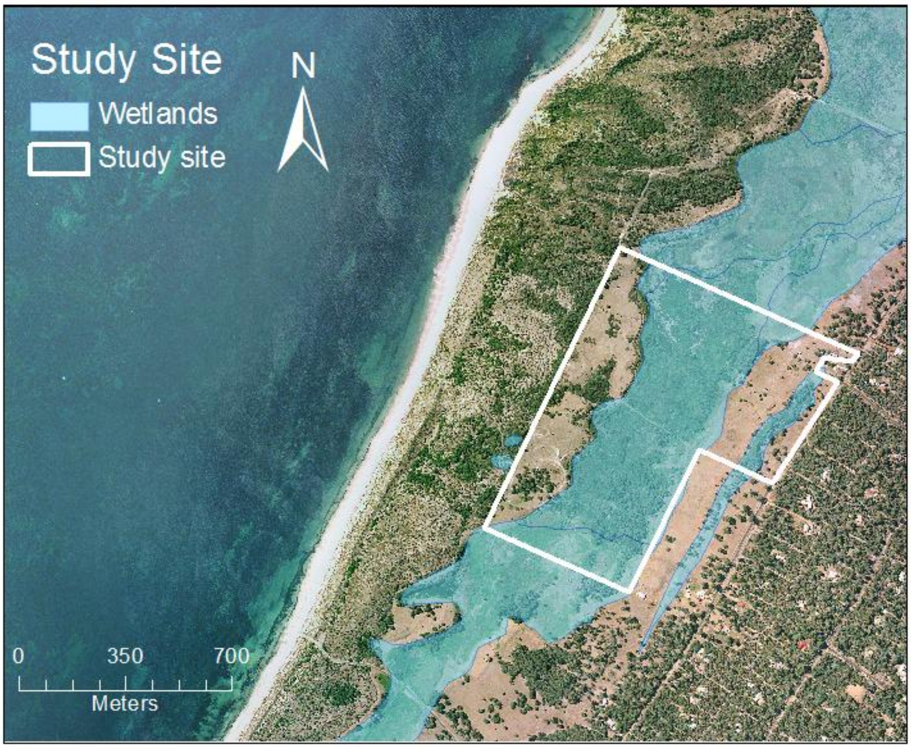


Figure 6. Map of the study site: Muddy Lake is part of a system of coastal wetlands

3 Study Site

3.1 Environmental setting

3.1.1 Geography

Muddy Lake (ML) is a coastal wetland situated approximately 14 km south of Bunbury on the SCP. It sits within a study site (Figure 6, hereafter referred to as “the site”) acquired by the Western Australian Planning Commission. The ML wetland (hereafter referred to as “ML” or “the wetland”) is listed as regionally significant and the site earmarked for rehabilitation as regional open space under the Greater Bunbury Region Scheme (Western Australian Planning Commission 2003). Approximately 30 ha in area, ML lies just inland from the first dune system and is aligned with the coast, northeast to south-west. It is long (length ~1000 m) and narrow (width ~300 m), and an access road crosses over the centre of the wetland.

Figure 7. Hydrologic map of Muddy Lake: blue shaded region shows extent of seasonal waterlogging or inundation; the main drain, shown in light blue, runs along the eastern edge of the wetland and flows south (Google Earth 5.0)

3.1.2 Hydrology

Muddy Lake is part of a greater system of wetlands, known as the Minninup Lakes. The wetland system is aligned parallel to the coast and is situated in the low-lying area just inland from the beach dunes. The wetlands are seasonally inundated depressions in the landscape, and are therefore sumplands using the classification provided by Semeniuk (2007). Drainage was installed in the area prior to the 1930s to prevent flooding and increase the land area available for agricultural development. The “main drain” runs parallel to the coast on the eastern fringe of the wetlands (Figure 7) and is fed by runoff, groundwater, and connected farm drains. Water in the main drain flows primarily north to south in the study site. At the southern property boundary, water flowing southward in the drain is “discharged offsite”. The main drain continues for approximately 3 km south of ML before water discharges into Geographe Bay, Indian Ocean. Drain and surface water flow is prevented over the northern boundary by a dirt road along the fence-line of the neighbouring property. Before the road was constructed, it is probable that water flowed in the drain between the two properties; however, without an accurate elevation model or drain survey information, the historic flow direction in the northern part of the main drain is uncertain. Land to the north of the site may be more low-lying than ML and it is possible that subsurface seepage occurs through the northern boundary when there is standing water in the wetland. Similarly, the road that crosses over the centre of ML also inhibits surface water flow between the northern and southern halves of the wetland. However, culverts under the roads at the centre and south of ML allow water to flow through the entire length of the drain. The wetland is seasonally inundated, drying up in mid-summer and drain starting to flow again in the in late autumn. The exact period of inundation each year is a dependent on the annual wetland water balance. The wetland is topographically complex and in this dissertation it is modelled as a shallow basin of depth ~2 m and length and width dimensions as stated above. In reality, the ML area consists of many low-lying “pockets” of land that collect water. It is only toward the end of a wet winter season or during periods of prolonged rainfall that they may become connected. In addition to the ML wetland, there is also a seasonally inundated pond and waterlogged area near the eastern boundary of the site. Unconfined groundwater in the Geographe Bay region is known to discharge over a salt wedge to the ocean (Hirschberg 1987), but this study suggests that ML exhibits a local, seasonally variable groundwater regime.

3.1.3 Geology

The sediments of ML and the surrounding land are superficial formations of Pliocene to Holocene-aged deposits (Hirschberg 1987). The sources of this coastal formation are littoral, alluvial, eolian and lacustrine (Hirschberg 1987). The sand dunes to the west of ML are Safety Bay Sands, consisting of fine wind-blown sands with calcified root channels (Hirschberg 1987). A belt of swamp deposits are identified as occurring parallel to the coastline, a short distance inland. These swamp deposits form the subsurface of ML. Alluvium of Holocene age occurs in valleys in these areas (Hirschberg 1987). Holocene-aged sediments were laid down during the last 10 000 years and sulfides such as pyrite may have formed in them during the last sea-level rise (White et al. 1997).

3.1.4 Meteorology

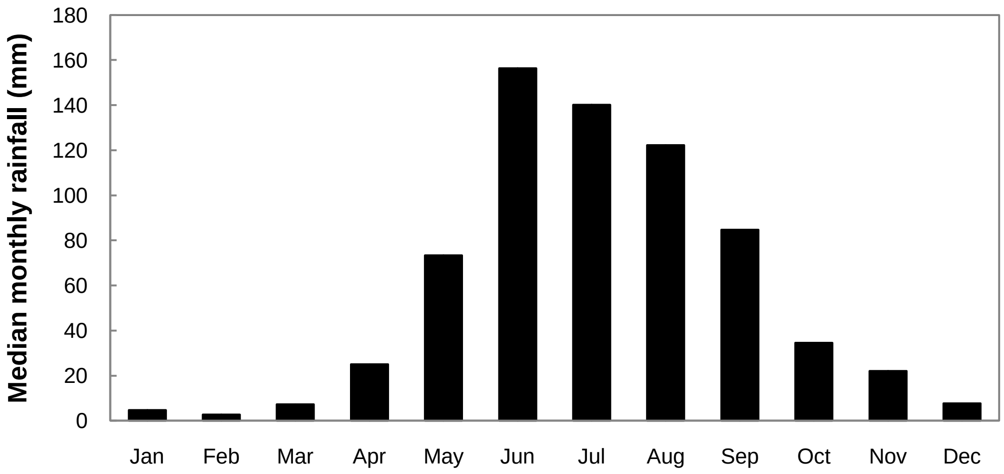


Figure 8. Monthly rainfall at Bunbury, site number 009965

Bureau of Meteorology (BOM) data was examined for Bunbury station number 009965. The station has records from 1995-2009. Median annual rainfall is 753.6 mm (Bureau of Meteorology 2009), with 56% falling in winter (June-August inclusive). Figure 8 shows median monthly rainfall at Bunbury. An older BOM station, Bunbury PO, station number 009514, recorded data from 1877 to 1985. This site had median annual rainfall 847.9 mm (Bureau of Meteorology 2009). The difference between the two stations' average annual rainfall can be attributed to the general observation that the south west of WA has experienced a decline in rainfall since the mid-1970s. Evaporation averages were not available from BOM, but Hirschberg (1987) reported annual evaporation at Busselton of 1,100 mm.

3.2 Previous work

Work by the current study's research group began at ML in July 2008 with the installation of piezometers and autosamplers. Autosamplers installed at the northern and southern ends of the drain are referred to as Minni N and Minni S. Ground and surface waters have been monitored continuously since July 2008 to determine the hydrological drivers of acidity and geochemical change. Work over the July 2008 to March 2009 period has been presented by Boland (2009). Soil cores from the bore installation were used to assess the subsurface for the presence of actual and potential acid sulfate soils, and Boland reported that both were identified onsite, and acidic ground and surface waters were present at some locations. Surface and ground waters are reported to have elevated metal and arsenic concentrations. A site survey undertaken in March 2009 established the relative elevations of the monitoring infrastructure on site. Hydraulic conductivities were assessed at groundwater monitoring bores using slug tests. This data was used in the calculation of groundwater fluxes by the water balance developed by Boland and in the current study.

Hydrologic data collected has been presented by Boland (2009) in the form of a conceptual water balance model, which aimed to determine the dominant hydrological processes causing acidity export from the Muddy Lake wetland. Boland (2009) used the drain as a control volume and solved the water balance on a daily timestep:

$$\Delta V = S_{in} + GW_{in} - GW_{out} - Q_{out} - E \tag{11}$$

where:

ΔV	is the change in the volume of water stored in the drain
S_{in}	is the volume of water entering the drain as surface water, always unknown in this equation
GW_{in}, GW_{out}	are the volume of groundwater entering and leaving the drain
Q_{out}	is the daily net flow out of the drain
E	is the volume removed by evaporation of drain water

The drain water balance is illustrated in Figure 9. Boland (2009) combined the S_{in}, GW_{in} and GW_{out} terms to calculate the daily change in water storage in the drain and compared the results to daily rainfall estimates, taken from BOM data (Figure 10). The peaks in the water balance result aligned with rainfall events, as expected. When groundwater data was available, the water balance was solved for surface inputs, and a comparison of the relative dominance of groundwater discharge and surface runoff could then be made (Figure 11). Results indicate that groundwater is not an important water source for the drain, and that water instead comes from surface runoff. The water balance used by Boland mirrors those by CLASS researchers from NSW, where deep drainage for sugarcane cultivation is commonplace (e.g. Sammut, White & Melville 1996; White et al. 1997). The drain water balance does not consider the hydrologic regime of the wetland, which is considered in light of the literature reviewed for the current study to be a major factor in both hydrology and trace element mobilisation.

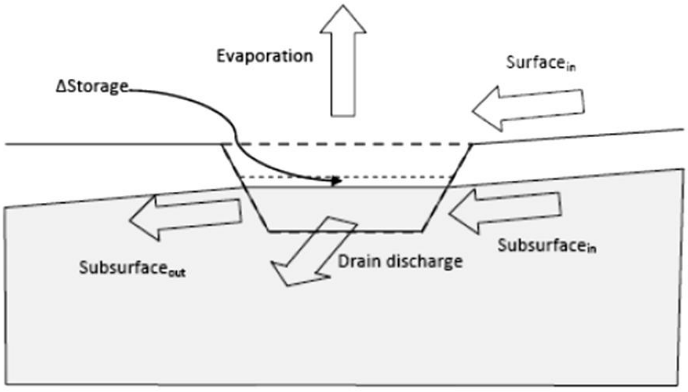


Figure 9. Drain water balance (Boland 2009)

The water balance used by Boland did not consider groundwater discharge to be a dominant hydrologic component, but it was identified as the source of acidity. However, the hydrologic model of the ML system reported by Boland may not be adequate to describe the natural system. The presence of the ML wetland is not considered important in the water balance, which disregards the large storage capacity of the basin. Groundwater discharge into the wetland may result in surface flows into the drain as the wetland store fills up over the wet season, which would be considered as “surface flow” by the drain water balance, although the water came from the ground. The drain has not been surveyed and nor has the wetland, and no reliable digital elevation model is currently available. The fact that the drain was not flowing for most of its length and for most of the wet season in 2009 may suggest that it is no longer functional (in a drainage engineering sense) and indeed the wetland is acting as a basin and collecting rain and groundwater over the wet season.

An alternative conceptual hydrologic model for the site, based on extensive field study over a nine month period (February – October 2009), is presented in this dissertation. To assess the interaction of acidic groundwater with organic wetland sediments, the current study attempts to provide a water balance for the entire wetland. All hydrologic components are estimated and the water balance is solved for the change in storage term (after Krasnostein & Oldham 2004), which can be compared to variations in drain water level. The current study focuses on the wetland hydrology as a driver for variability of pH and redox conditions, which cause trace element mobilisation.

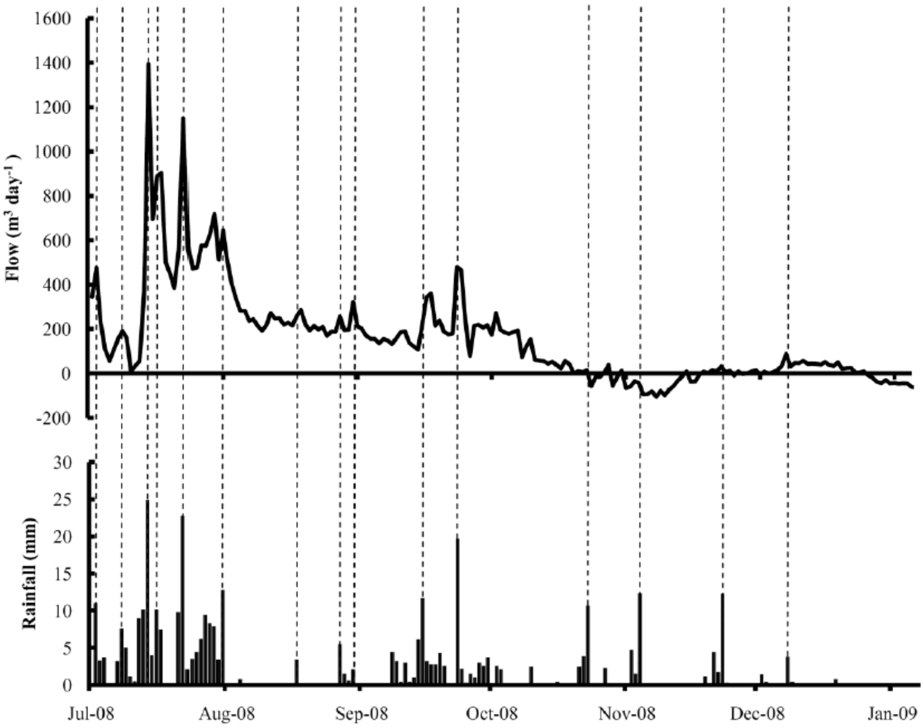


Figure 10. Net surface and subsurface flow into the drain (top) and daily rainfall (bottom) (Boland 2009)

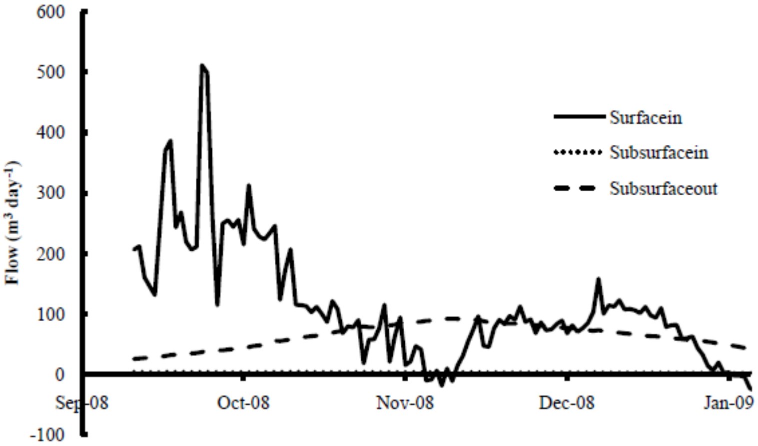


Figure 11. Surface and subsurface components of the drain water balance (Boland 2009)

4 Methodology

4.1 Monitoring and sampling

Field trips to the site were conducted approximately every three to five weeks between July 2008 and October 2009. The author was present on all field trips from February 2009 until October 2009; however, this thesis uses data from the entire study period. Field notes are provided as an appendix to this dissertation (Appendix A).

Figure 12. Study site monitoring map (Google Earth 5.0)

4.1.1 Groundwater

Eight bores were monitored, the locations of which are shown in Figure 12. Groundwater height at each of the bores below the top of the casing was measured using a measuring tape and “plopper”, a hollow device that makes a sound when it makes contact with the water in a bore. Groundwater was sampled using a bailer. Each bore was bailed three times before a sample was taken and placed into a high density polyethylene (PE) container that had been rinsed with the water to be sampled. The water was analysed onsite for physical properties (pH, electrical conductivity (EC), temperature and oxidation-reduction potential (ORP)) using a calibrated TPS 90-FLMV meter. Water to be sampled was filtered within 48 hours of sampling using a Millipore vacuum filtration kit and hand pump with 0.2 µm filter paper before it was placed into two low density PE bottles. Whatman cellulose nitrate filter papers were used until August 2, 2009, thereafter Whatman mixed cellulose ester papers were used. One sample from each bore was acidified onsite with concentrated HNO_3 for the preservation of metals in solution. Samples were transferred to the laboratory in an esky and thereafter stored in the dark at 4 degrees until being sent to external laboratories for analysis (section 4.1.4).

4.1.2 Drain water

The locations of the drain gauging stations Minni N and Minni S are shown in Figure 12. At each station, continuous monitoring was enabled by an ISCO automatic water sampler (autosampler) and pH, temperature and conductivity probes (YSI 6583). Water level and velocity measurements was automatically recorded with an area-velocity (AV) module (ISCO 750), which uses a pressure transducer to measure water depth and calculates velocity using a Doppler method. Measurements were taken every 15 minutes, and a 200 mL water sample was taken every six hours so that an 800 mL bottle was filled in one day. Bottles were acid-washed and rinsed with de-ionised water three times before installation in the autosamplers onsite. The autosamplers hold 24 bottles, so field trips were conducted at least every 24 days during drain sampling periods, and data was downloaded onto a laptop computer using the program Flowlink 4.15. A grab sample was taken from the drain at each of the stations using the manual function on the autosampler. This enabled the pump and measurements of physical parameters to be tested in the field: pH, EC, temperature and ORP of grab-sampled water were measured using a calibrated TPS 90-FLMV meter. Grab samples were treated in the same way as groundwater samples to preserve them for laboratory analysis. Autosampler samples were taken to the laboratory and manually analysed for pH, temperature and EC within two weeks using a calibrated TPS 90-FLMV meter. The purpose of these manual measurements was to detect any drift in the Flowlink data recorded by the probes. Drift was recorded in the pH measurements at Minni N in the last two months of sampling. Additionally, EC data was either incorrectly recorded or downloaded by the autosamplers and could not be used. Manual measurements taken using grab samples in the field were used as a secondary data source.

4.1.3 Surface water

On August 1, 2009, a surface water survey of the site was conducted to assess the spatial variability of acidity in ponded water. The approximate locations of sampling points (S1 to S9) are shown in Figure 13. All locations had standing water present, from which a grab sample was taken and analysed onsite (S1 to S3) or in the laboratory the following day (S4 to S9) for physical parameters (pH, EC and temperature) using the TPS 90-FLMV and the method used for ground and drain water samples.

Figure 13. Surface water monitoring map (Google Earth 5.0)

4.1.4 Laboratory analysis of water samples

Selected water samples were analysed by the Chemistry Centre of Western Australia (CCWA), or the Advanced Analytical Centre (AAC) or Australian Centre for Tropical Freshwater Research (ACTFR) at James Cook University, Townsville. Samples collected before May 23, 2009 were analysed by CCWA, those collected on or after that date were analysed by AAC or ACTFR.

Table 1 shows analyses conducted and methods used by each laboratory. Notes on chemical analyses by AAC are provided in Appendix B.

Table 1. Analytes and methods for water sample analyses

Analyte	Laboratory: method	Note
Physicals		
Acidity	CCWA: Acidity by titration with 0.01M NaOH to pH 8.3 ACTFR: APHA 2310 B	ACTFR: acidity as $CaCO_3$
Alkalinity	CCWA: Alkalinity, HCO3, CO3, OH by acid titration using 0.05M HCl to pH 8.3 and 4.5 ACTFR: APHA 2320 B	ACTFR: total alkalinity as $CaCO_3$
EC	CCWA: Conductivity at 25 degrees C	Electrical conductivity
Hardness	CCWA: Hardness calculated from Ca and Mg	CCWA: expressed as mg $CaCO_3$ L^{-1}
TDS	CCWA: Total soluble salts calculated from conductivity (EC * 5.5)	CCWA: Total soluble salts estimated from EC
Major anions		
Cl	CCWA: Colorimetric analysis by discrete analyser using mercuric thiocyanate ACTFR: APHA 4500-Cl- B Chloride Discrete analyser	
CO_3	CCWA: from alkalinity	
HCO_3	CCWA: from alkalinity	
NO_3	CCWA: flow injection analysis.	Nitrate expressed as nitrogen
SO_4	CCWA: ICP-AES, ACTFR: APHA 4500- S04-E	ACTFR: Sulfate as SO_4^{2-}
Metals		
Al	CCWA: ICP-AES, AAC: ICP-MS	
As	CCWA: ICP-MS, AAC: ICP-MS	
B	CCWA: ICP-AES	
Ba	CCWA: ICP-AES	
Ca	CCWA: ICP-AES, AAC: ICP-AES	
Cd	CCWA: ICP-MS, AAC: ICP-MS	
Co	CCWA: ICP-AES	
Cr	CCWA: ICP-AES	
Cu	CCWA: ICP-AES	

Fe	CCWA: ICP-AES, AAC: ICP-AES	
K	CCWA: ICP-AES, AAC: ICP-AES	
Mg	CCWA: ICP-AES, AAC: ICP-MS	
Mn	CCWA: ICP-AES, AAC: ICP-MS	
Mo	CCWA: ICP-MS	
Na	CCWA: ICP-AES, AAC: ICP-AES	
Ni	CCWA: ICP-MS, AAC: ICP-MS	
Pb	CCWA: ICP-MS, AAC: ICP-MS	
V	CCWA: ICP-AES, AAC: ICP-MS	
Zn	CCWA: ICP-AES, AAC: ICP-MS	

4.1.5 Soil sampling

Surface soil samples were collected on June 24, 2009, from the top 10 cm and within 3 m of each of the bores 2, 3, 4, 5, 6, and 8. Profile sampling pits were also excavated at four locations onsite. Profile sampling involved digging a hole to a certain depth and sampling soil within discrete layers, or strata. Profile ID and strata were used to identify samples. For example, the top layer from Profile 7 is identified as 7A. Details of the profile sampling are provided in Table 2, and strata descriptions in Table 3. Note that at Profile S, soil composition did not appear to change within 0.4 m, so only one sample was taken. Furthermore, the soil was completely waterlogged and there were hard lumps of (presumably Fe) mineral present, which made further exploration difficult. Figure 14 shows sampling locations, where “S” denotes surface and “P” denotes profile soil sampling. At all locations, grass and roots were removed from the surface before sampling. Each soil sample was collected into a plastic snap-lock bag using a spade. Air was removed from the bag before sealing and placing into a second bag, which was de-aired and sealed to prevent sediment oxidation. Samples were transported to the laboratory in eskies before being stored in the dark at 4 °C, except the samples from Profile N, which were frozen until analysis.

Table 2. Profile soil sampling locations, where N and S refer to North and South sampling sites

Profile ID	Location	Date sampled	Depth of profile	Number of samples
7	Within 5 m south-east of Bore 7	24/06/2009	0.9 m	3
N	In wetland, 10 m south-east of Minni N	27/03/2009	~1 m	2
1	Within 5 m of Bore 1, north side of road, in wetland	15/06/2009	0.91 m	4
S	Within 5 m of drain, 20 m north of Minni S	24/06/2009	0.4 m	1

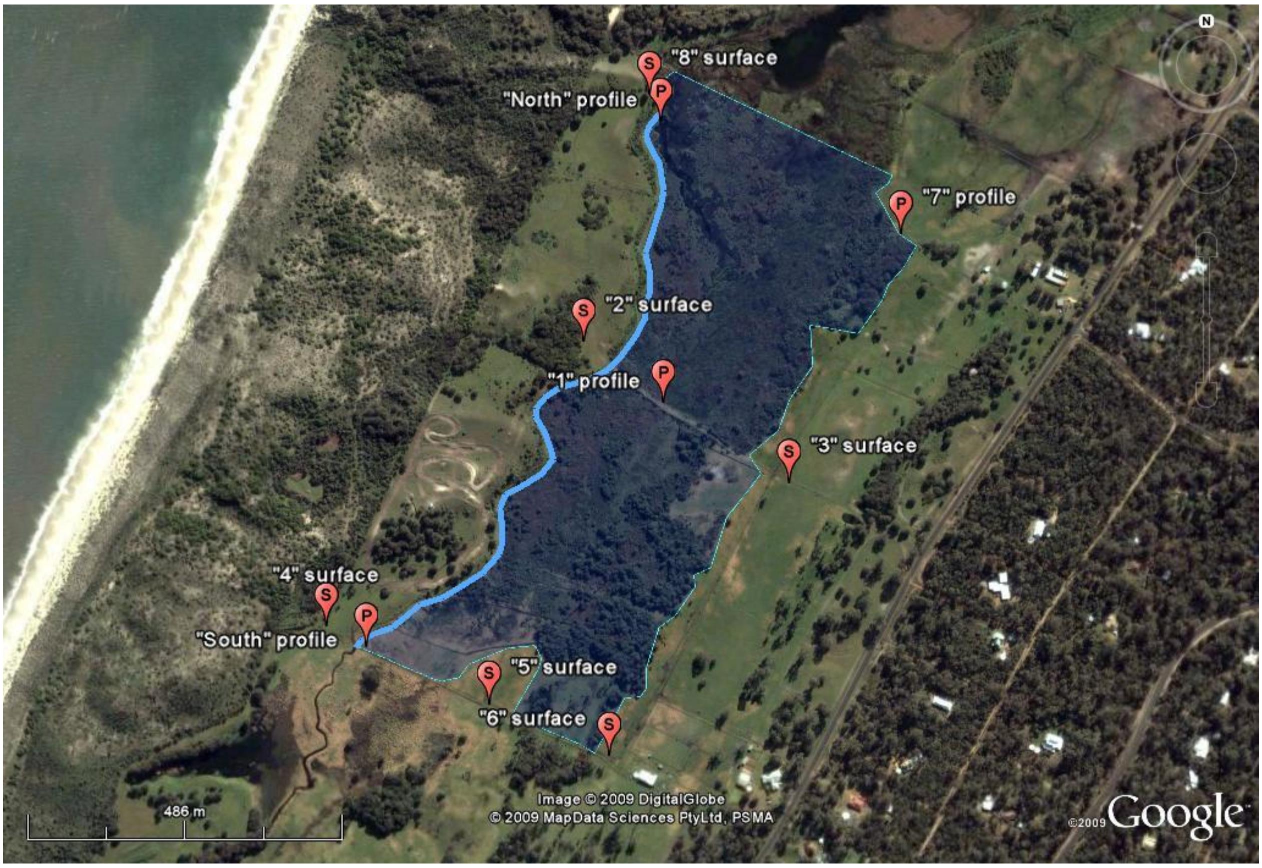


Figure 14. Soil sampling map (Google Earth 5.0)

Table 3. Profile soil strata descriptions

Profile		Strata ID	Depth	Description
7		A	10-15 cm	dark organic rich sand, root zone
		B	13 cm	dark coarse sand, roots
		C	65 cm	grey coarse sand, orange mottles
N		A	15 cm	orange precipitates (Fe) and organic rich fine sand
		B	85 cm	waterlogged very rich organic peat
1		A	8 cm	black organic rich sand
		B	6 cm	brown sand
		C	10 cm	semi-saturated dark grey, organic rich
		D	67 cm	saturated black organic rich peat
S		A	40 cm	saturated brown mud with hard lumps of orange/brown rock

4.1.6 Laboratory analysis of soil samples

Samples were analysed in the laboratory for physical parameters. Moisture content (MC) was determined by placing a small amount of sample in a crucible of known weight and drying in the oven for 24 hours at 105 °C. The crucible with sample is weighed before and after drying and the MC as a percent of the sample is given as:

$$MC\% = \frac{m(sample)_i - m(sample)_f}{m(sample)_i} \times 100 \tag{12}$$

where *i* and *f* refer to initial and final masses.

Loss on ignition (LOI) was used as semi-quantitative estimate for organic matter (OM) content. A small amount of sample was placed in a crucible of known weight and heated to 400 °C overnight. The sample was allowed to cool before being weighed. The weights before and after heating were used to determine OM, with a correction for moisture loss:

$$OM\% = \frac{m(sample)_i^{LOI} - m(sample)_f^{LOI}}{m(sample)_i^{LOI}} \times 100 - MC\% \tag{13}$$

Soil pH and conductivity were determined from soil-water slurries. Samples were combined with de-ionised water at a 1:5 ratio and mixed with a magnetic stirrer for five minutes. The TPS 90-FLMV was used for all physical measurements: pH was directly measured by insertion of the calibrated probe, while EC and temperature were measured by extracting water into a separate test tube and inserting the calibrated electrode.

Samples were prepared for X-ray fluorescence (XRF) analysis by drying in the oven at 50 °C for 48 hours. Plant material was removed and samples placed in plastic snap-lock bags before being sent to AAC for analysis. The AAC laboratory tested the samples for major and trace elements. The methods used by AAC for XRF analysis are summarised below.

Preparation for XRF Major Analysis involved igniting approximately 2 g (in duplicate) of each sample in a muffle furnace at 1000 °C for a minimum of 4 hours to determine loss on ignition (LOI). One (1.0000 ± 0.0050) gram of ignited sample was mixed with eight (8.0000 ± 0.0050) gram of Norrish Hutton flux and fused in Platinum crucible for 10 minutes at 1,100 °C. This produced a homogeneous glass bead 40 mm in diameter. Specimens were analysed in a Bruker-AXS S4 Pioneer XRF Spectrometer: data collected from various scan ranges were processed through Bruker-AXS Spectra-plus Software. The AGV-2 (silicates general) check standard was run with these samples to ensure instrument precision.

For XRF Trace Analysis, approximately 6.5 g of original (unignited) sample was mixed with 4-5 drops of binder (ethyl cellulose). This was pressed into a pellet in an aluminium cup of 32 mm diameter. Pressed pellets were analysed as above, using the BHVO-2 check standard.

4.2 Water balance calculations

The water balance of ML presented here was conceived using a mass balance approach, with the wetland as a control volume:

$$\Delta V = inputs - outputs \tag{14}$$

and considering all possible hydrological sources and sinks for ML:

$$\Delta V = P + GW_{in} + R - E_T - GW_{out} - Q_{out} - SW_{out} \tag{15}$$

where:

ΔV	is the change in the volume of water stored by Muddy Lake
P	is precipitation (rainfall) that fell directly on the wetland
GW_{in}	is groundwater entering the wetland (groundwater discharge)
R	is runoff from the surrounding catchment
E_T	is evapotranspiration of wetland water
GW_{out}	is groundwater leaving the wetland (groundwater recharge)
Q_{out}	is the net flow out of the drain, and
SW_{out}	is surface flow (sheet flow) over the banks of the wetland during flood.

The runoff term was estimated to be negligible, and thus was removed from the water balance. The soils surrounding ML are sandy, with a probable high hydraulic conductivity. In addition, the surrounding land is primarily quite flat, as ML lies on the inland side of the first beach dunes. The dunes are a potential hillslope catchment for ML, but the high hydraulic conductivity is likely to cause any rainfall to infiltrate quickly into the sand.

The E_T term was replaced with an evaporation term that was calculated differently for wet and dry periods, and is explained in detail later in this chapter.

The GW_{out} term was also estimated to be negligible, and was removed. The drain runs along the coastal side of ML, and first approximations suggest that the removal of water by conveyance in a drain would greatly outweigh groundwater seepage. The buildup of decayed organic matter on the wetland bed is likely to have a low hydraulic conductivity and therefore, inhibiting the recharge of groundwater by ponded water in ML.

The SW_{out} term was also discarded, as the wetland water height rarely reaches a level where water can flow offsite other than through the drain at Minni S. Furthermore, a valid method for estimating this term was not available. In September and October 2009, the road at Minni S was observed to be flooded, and water from ML may have been able to move offsite via overland flow at these times.

The resultant conceptual water balance for ML is shown in Figure 15.

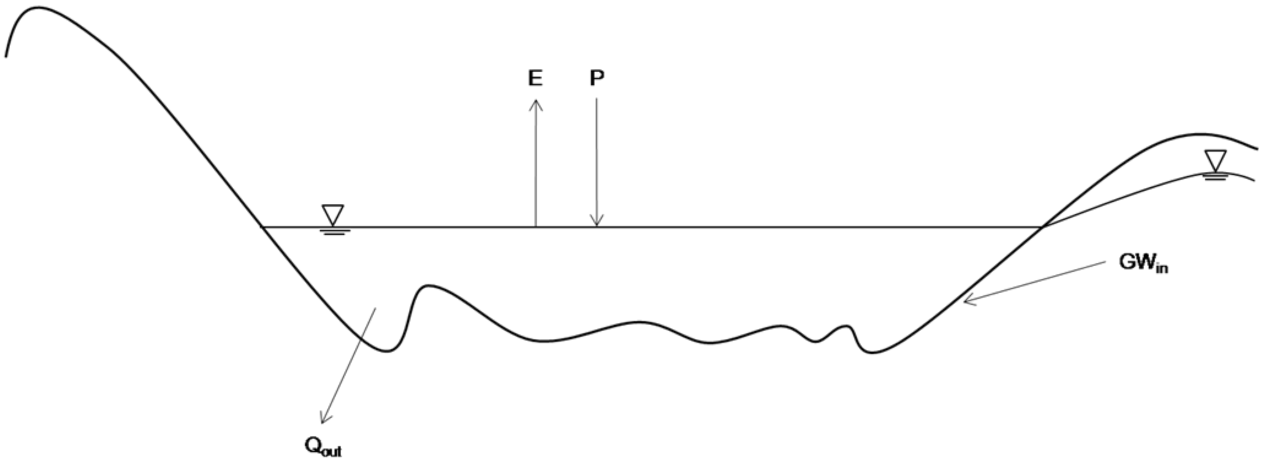


Figure 15. Conceptual water balance for ML

The water balance for ML was calculated for the period July 3, 2008 to October 2, 2009. The daily change in water storage was estimated by Equation (16,

$$\Delta V = P + GW_{in} - E - Q_{out} \tag{16}$$

where all terms have units of m^3day^{-1}.

Meteorological data was sourced from the SILO Data Drill service provided by the Queensland Department of Natural Resources. Data Drill interpolates daily observations in the surrounding region to provide estimates at specific sites (QNR&M 2009). The coordinates used for ML were 33°27’S 115°36’E.

Daily rainfall data was converted to a water volume by calculating the product of rainfall and ML surface area. The surface area of ML was estimated by importing the polygon of ML as drawn in Google Earth 5.0 and shown in Figure 12 into GE Path version 1.4.4a. GE Path (available from www.sgrillo.net) is a freeware package capable of calculating perimeters and areas of shapes drawn in Google Earth. The complete list of constants used in the water balance calculations are provided in Table 4.

Table 4. Constants used in the wetland water balance

Symbol	Description	Value
SA	ML surface area	326 384 m^2
D	Depth of the aquifer contributing to groundwater discharge, estimated as the average of the relative (to survey datum) depth of the drain at Minni N and S	1.7875 m
dl	Average distance between bores 3 and 6 and the deep part of the wetland, estimated from Google Earth imagery	282.5 m
K	Average hydraulic conductivity of the subsurface at bores 3, 6 and 7	4.74 m day^{-1}
L	Length of ML	1026 m
α	Angle made by the intersection of the seepage face and lake bottom, illustrated in Figure 19 and calculated as atan(D/210)	0.0085°

Evaporation was estimated differently for wet and dry periods. When ponded water was present in ML, Morton shallow lake evaporation data was used (after Boland 2009). When the surface soils were dry, Morton actual evaporation (over land) data was used. A comparison of the evaporation time series is shown in Figure 16, and the data used in the ML water balance is shown in Figure 17. All evaporation data was obtained from Data Drill and converted to daily volumes in the same way as rainfall data. The Morton evaporation estimates are made by the data provider using the formulae presented in 1983 by Morton in The Journal of Hydrology, vol. 66, pp. 1 – 77.

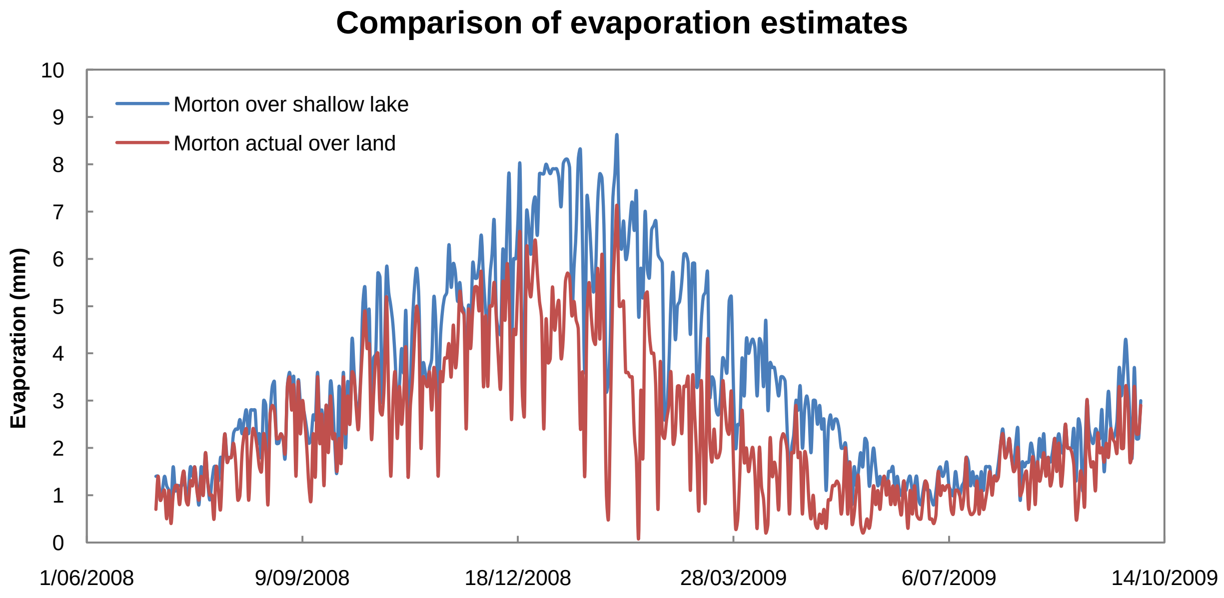


Figure 16. Comparison of Morton evaporation estimates for dry and wet periods

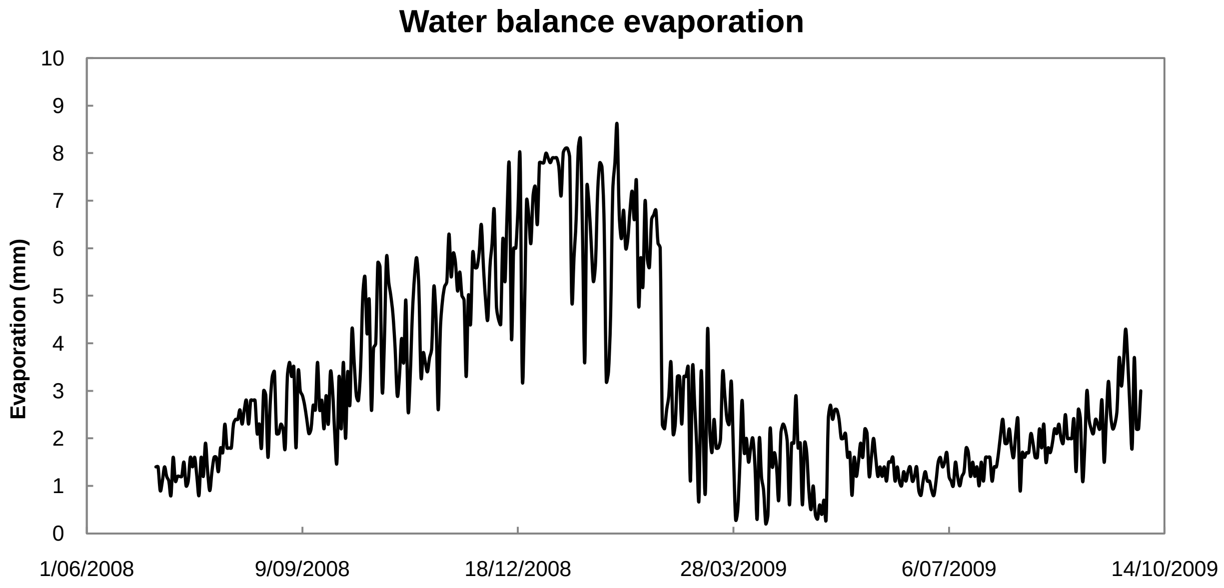


Figure 17. Evaporation data used in the water balance

A model for groundwater discharge to ML was conceptualised as shown in Figure 18 (after Li & Wang 2007).

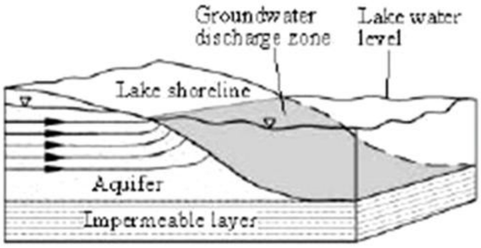


Figure 18. Conceptual model for groundwater discharge to a lake (Li & Wang 2007)

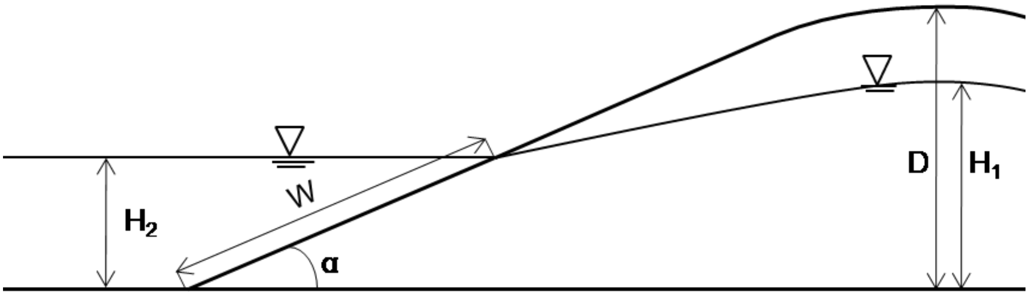


Figure 19. Schematic for discharge calculation into ML (adapted from Li & Wang 2007)

Daily discharge into ML was calculated as:

$$GW_{in} = \frac{dh}{dl} KA \tag{17}$$

where:

dh	is the difference in hydraulic head between the bores (3 and 6) and the wetland, $H_1 - H_2$ in Figure 19, where H_1 = D – relative average depth to groundwater at bores 3 and 6, H_2 = D – relative average depth to wetland water level
dl	is the average distance between the bores (3 and 6) and the wetland
K	is the average hydraulic conductivity of the subsurface at bores 3, 6 and 7, calculated by slug tests (reported by Boland 2009)
A	is the cross-sectional area of discharge, estimated as the product of L, the length of ML, and W, the width of the groundwater seepage face

and constants are defined in Table 4. Relative depths refer to measurements adjusted for differences in ground level, as estimated by survey of the study site in March 2009. Daily relative groundwater levels in bores were calculated by interpolation of data gathered on field trips. Cubic interpolation was applied using the Matlab R2008b software package. Levels between July 3, 2008 and September 11, 2008 were assumed to be constant at the level recorded on the September 11 field trip, because no groundwater data was available in the interim. The water level data recorded at Minni N and S was treated and averaged on a daily timestep. Treatment involved correction for differences between AV and actual level, observed using water level gauges at each station on field trips. Raw Minni N levels were adjusted (increased) by 3.65 cm, and Minni S levels increased by 10.3 cm, as shown in Figure 20.

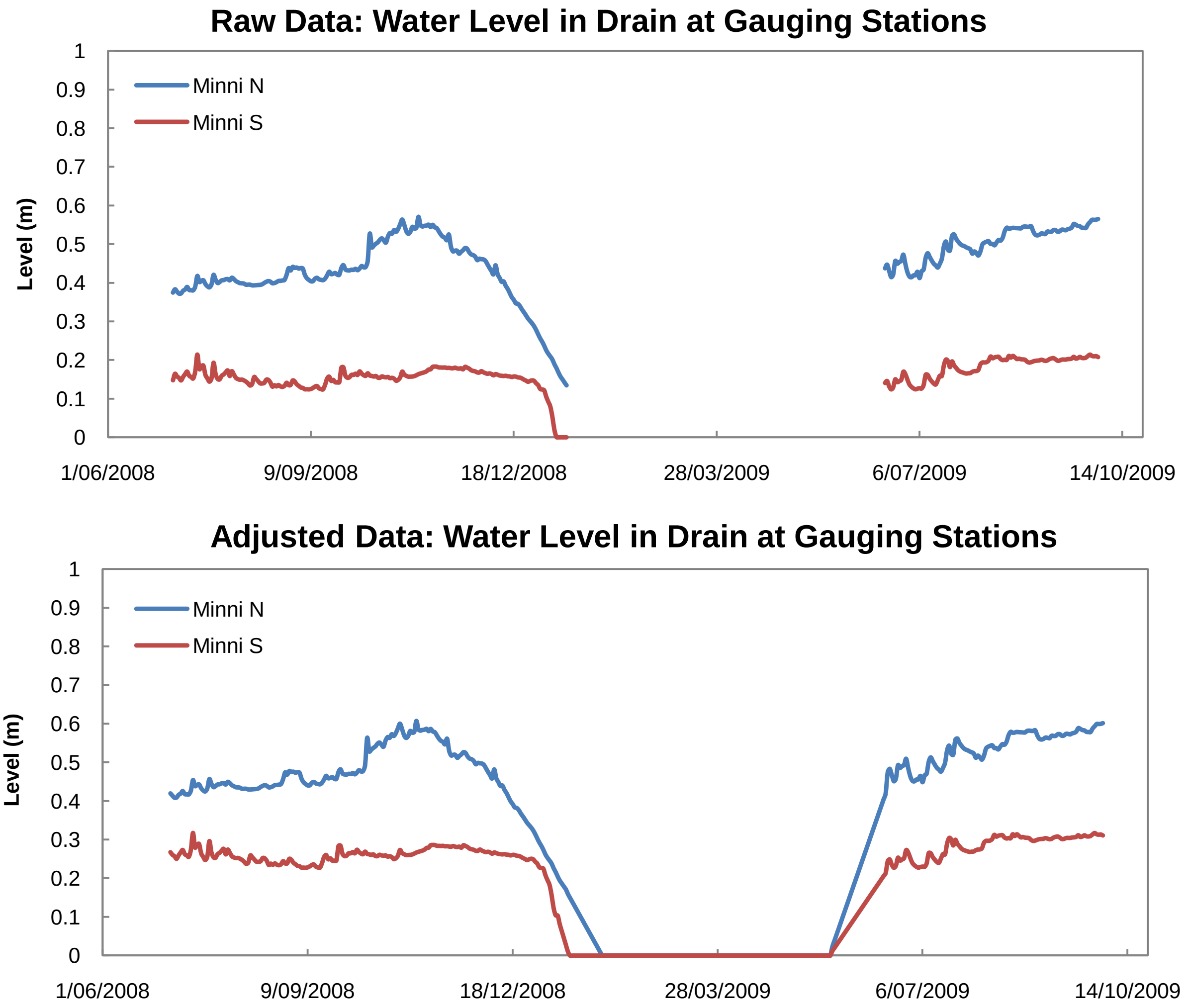


Figure 20. Treatment of water level data for use in ML water balance

The level of water in ML during periods of wetland inundation was calculated as the average of the levels at Minni N and S. During dry times, the water level at Bore 1 was used as the wetland water level, as it was located in the centre of ML and the level correlated well with Minni N level during wet times (Figure 21).

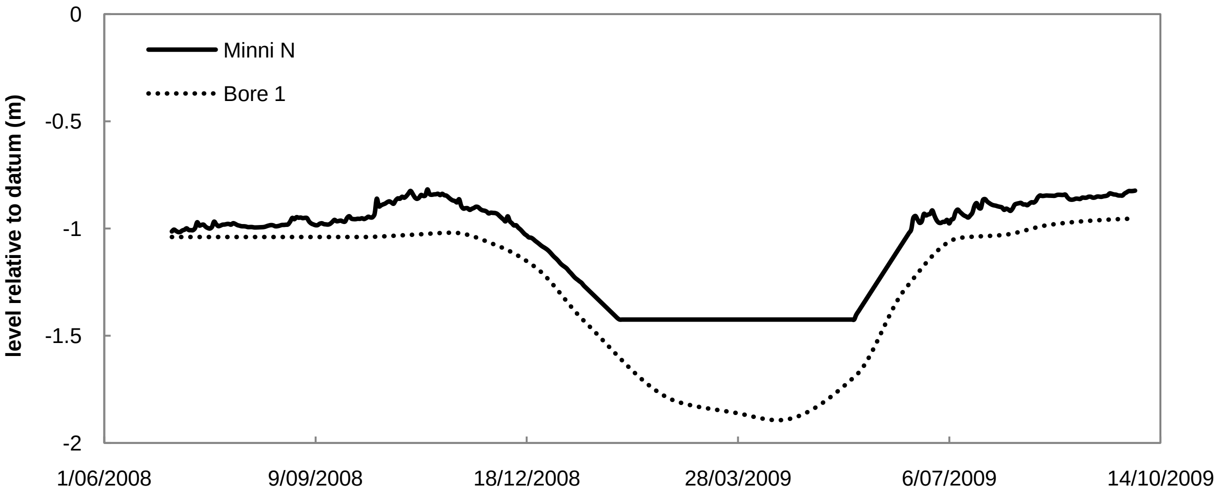


Figure 21. Comparison of Minni N and Bore 1 relative water levels

Cubic interpolation as described earlier was applied to a one-month period between wet and dry periods to smooth the level data between drain and Bore 1 data, and H_2 was calculated by subtracting relative wetland water level from D. Figure 22 shows results of the steps involved in calculating H_2.

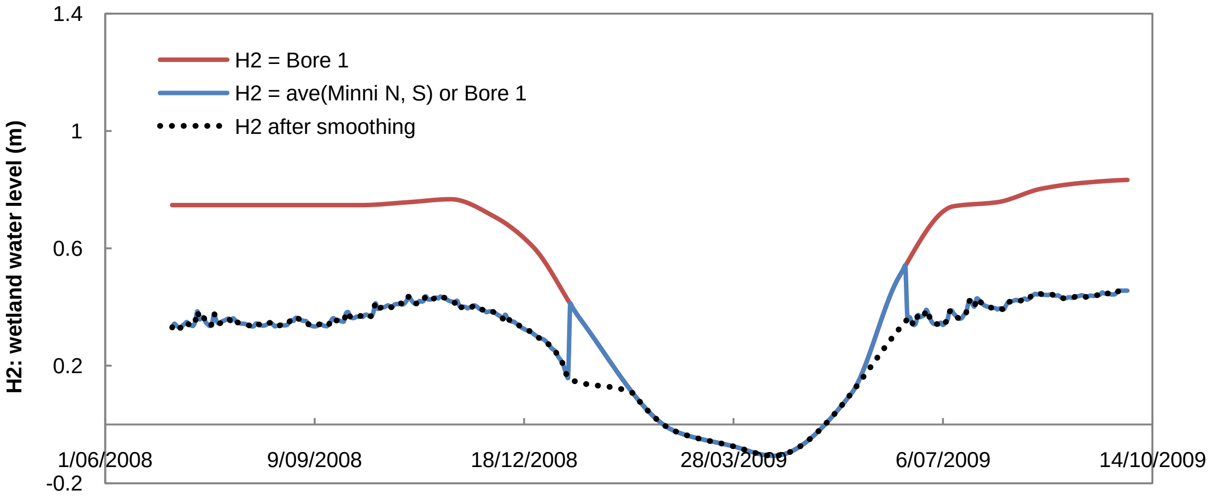


Figure 22. Data used for constructing the H_2 time series

The width of the seepage face, W as shown in Figure 19, was estimated on a daily timestep:

$$W = \frac{H_2}{sin(\alpha)} \tag{18}$$

where α is a constant (Table 4) defined as the inverse tan of the ratio of D to the average distance from bores 3 and 6 to the ML shoreline, estimated using Google Earth imagery as 210 m. The drain and ML were assumed to be free of surface water ("dry") between February 23 and May 10, 2009, where H_2 fell below zero. The groundwater discharge during this time was assumed to be zero, as the width of the seepage face became negative as defined by Equation 18.

The flow of water out of the control volume, Q_{out}, is defined as the net flow out of the drain. The velocity and level data from the gauging stations at Minni N and S was averaged for each day that the water balance was calculated. Raw data, recorded every 15 minutes by the autosamplers, was treated prior to averaging. Data was sorted according to temperature readings and null values for temperature resulted in the removal of all data recorded at that time. Freezing conditions were not known to occur and power outages or errors with the autosamplers were relatively common. Raw level data was used to determine the height of water in the culvert under the road at Minni S. The method described by Boland (2009) was used to calculate the cross-sectional area of flow at Minni S, where the culvert diameter is 0.3 m. The Flowlink data file defines velocity data as being recorded in fts^{-1}, and a conversion to ms^{-1} was applied by Boland (2009). However, in this water balance, the velocity data from the stations was taken to be in ms^{-1}, because the autosampler screen display showed units of mps and the values recorded in the field for on-screen measurements matched data downloaded into Flowlink. Interpolation was applied to velocity data at Minni S between May 22, 2009 and June 19, 2009. The probes were installed at the gauging stations on June 19, but water in the drain at Minni S was observed to be just starting to flow on a field trip on May 23. As no data was available between these dates, cubic interpolation as described previously was applied assuming that velocity at Minni S was zero on May 22. The net volume out of ML each day was defined as $Q_n + Q_s$, where Q_n and Q_s are the flow volumes out of ML at Minni N and S respectively. The volumes are defined as the average velocity of flow multiplied by the cross-sectional area, and multiplied by 86,400, the number of seconds in a day.

The daily change in volume term, ΔV, was calculated as the result of the water balance. For validation, a time series of the change in H_2, wetland water level, was then calculated. The change in level on day two is given by the level on day two minus the level on day one, and so on.

4.3 Soil incubation experiment

A batch-type soil incubation experiment was conducted on soils from the surface layers of profiles N, 1 and S. For Profile 1, soil from the top two layers (samples 1A and 1B) were combined to form sample “C”. This notation allowed samples N, C and S to refer to surface soils from the north, centre and south of the wetland. Moisture content and LOI tests were carried out on samples N, C and S, using methods described in section 4.1.6. Samples were dried at 105 °C before being crushed with a mortar and pestle until able to be passed through a 1 mm sieve to ensure that samples started the experiment in the same condition. Rainwater for the experiment was collected in Perth on July 22, 2009, as runoff from the laboratory roof. The experiment began on August 12, 2009, and was conducted in triplicate as follows: soil (8 g for sample N, 10 g sample C and S) was placed into sample jars, weighed, and rainwater added to make a slurry with water : solid ratio of 10. Slurries were stirred during this step to form homogenous mixtures. A plastic spoon was used as a stirrer and was rinsed with rainwater into the sample jar to ensure the total mass of soil and water was maintained. A sample jar containing only rainwater was incubated with the other samples as a control. The addition of water to soil marked the start of the experiment (t = 0). Samples were placed in a constant temperature room at 23 °C and incubated for two weeks. The sample jars were open to the environment, and samples were not stirred or mixed during the incubation period. The experimental set-up is pictured in Figure 23. Physical measurements of pH, EC, temperature and ORP were taken after 23, 48, 72, 126, 172 and 336 hours using a calibrated TPS 90-FLMV meter. Probes were inserted into the samples, stirred gently to mix the aqueous fraction without disturbing the settled solid, and measurements recorded after readings stabilised. After measurements were taken, samples were weighed and additional rainwater added to compensate for evaporation of sample water and maintain the water : solid ratio of 10. Rainwater was aerated before addition to samples by pushing air through the water to be added using a syringe. After the final reading was taken (t = 336 hours), the aqueous fractions were collected from each sample by syringe, and the soil fractions centrifuged at 50 rpm for 10 minutes. Supernatants were combined with the syringed aqueous fractions, and triplicate samples combined to produce four liquid samples, identified as ExptN, ExptC, ExptS and ExptR. These samples were tested for physical parameters as above, before being filtered and preserved for laboratory chemical analysis following the method used for field groundwater samples, outlined in section 4.1.1.

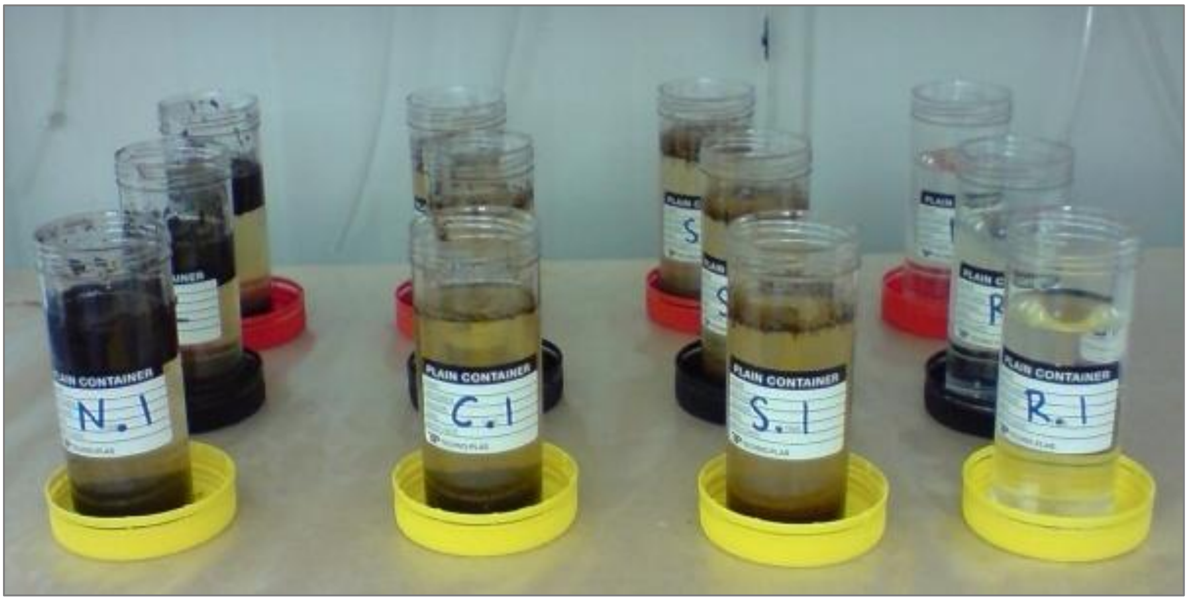


Figure 23. Soil incubation experiment, where N.1 refers to replicate number 1 of sample N

5 Results

5.1 Seasonal hydrology

5.1.1 Groundwater

Groundwater levels exhibit strong seasonal variability. In general, water levels in monitoring bores rose over the winter and fell in summer (Figure 24). The position of the water table below ground, plotted in Figure 24, is spatially variable over the study site. The difference between maximum and minimum water level is also variable, and Table 5 compares the differences between the monitoring bores. The table is sorted by ascending level difference. Bore 7 shows the smallest difference in water table height over the year, while Bore 8 has the largest. Figure 24 shows that the minimum depth to groundwater for Bore 8 occurred as a large peak in the water table in spring 2009. At this time, most other bores showed a decline in water level. Since Bore 8 is located between the Minni N gauging stations and the sand dunes, it is thought that this peak may be attributed to local groundwater flow between the ponded water at the north of ML and the dune system. If the large peak was excluded from analysis, the annual variability of depth to groundwater at Bore 8 would be only 0.82 m, the smallest difference of all bores at ML. Table 5 suggests that the range in annual water table levels is spatially auto-correlated. The bores to the south of the study site (bores 4, 5 and 6) show large fluctuations, while Bore 7 in the north shows the smallest annual variability. Bores 1, 2 and 3, in the middle of the wetland, have intermediate water level variability.

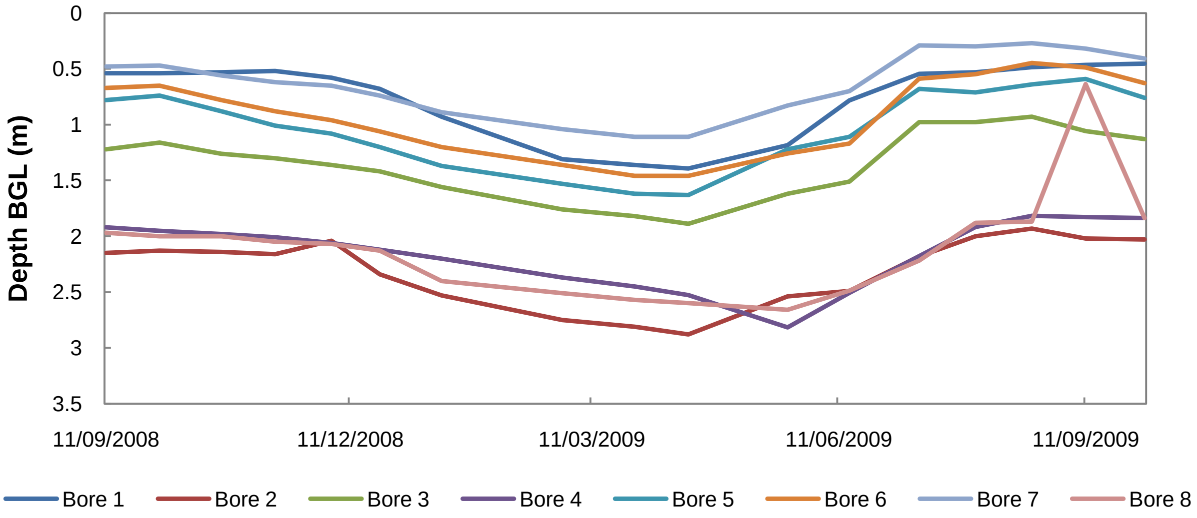


Figure 24. Depth to groundwater at ML as time series

Table 5. Difference between maximum and minimum groundwater levels

Bore	Difference between max and min water level (m)
Bore 7	0.84
Bore 1	0.94
Bore 2	0.95
Bore 3	0.96
Bore 4	1
Bore 6	1.01
Bore 5	1.04
Bore 8	2.02

The observed spatial variability of seasonal groundwater regimes on site warrants analysis of groundwater hydrology along transects through the wetland. The topography of ML and background information on regional groundwater flow directions (section 3.1.2) also supports such analysis. Transects were drawn perpendicular to the coast, between bores and gauging stations (Figure 25). Seasonal water levels at monitoring locations along these transects were plotted against “distance along the transect” on the x-axis. The levels plotted are “relative”, in that they have been adjusted to the local height datum established from site survey. The plots are shown in Figure 26, and the gradients of the lines drawn between known levels (points) allow the direction of groundwater flow to be interpreted. It should be noted that the lines connecting data points on these plots, and others in this results section, are estimations only and may not represent actual values along the line, in this case due to local topographical features. The northern transect (Bore 8 – Minni N – Bore 7) levels may be particularly inaccurate because no information was available for the water level in the centre of the wetland. The land between Minni N and Bore 7 is known to be low-lying and is inundated in winter and spring. Nevertheless, the plots (Figure 26) show interesting results. In the following discussion, “inland” refers to monitoring locations to the east of the wetland, while “coastal” refers to locations to west. Water levels are highest in winter and spring at all locations, and are spatially dependent. Levels at bores 7, 3, and 5 are highest in winter, and the difference between winter and spring levels is small for Bore 6. This suggests that groundwater is recharged earlier in the wet season for the furthest inland locations.

This perched groundwater inland may then travel coastward and discharge into the wetland, as shown by the gradients in head between Bore 7 and Minni N, Bore 3 and Bore 1, and between Bore 6 and Minni S. These gradients are particularly strong in autumn and winter. In the centre of the wetland (transect 2 – 1 – 3), the head gradients suggest that groundwater flow is toward the wetland from both the inland and coastal sides. In autumn and winter, the head gradients between Minni N and Bore 8 and between Minni S and Bore 2 suggest that groundwater flow is from the wetland towards the coast, but the gradient decreases in spring when the groundwater at the coastal locations has recharged. Recharge may occur in the form of rainfall infiltration through the sand or groundwater flow from the wetland.

Figure 25. Transects, shown as pink lines, connect monitoring bores and gauging stations and are used to analyse seasonal groundwater variability at ML

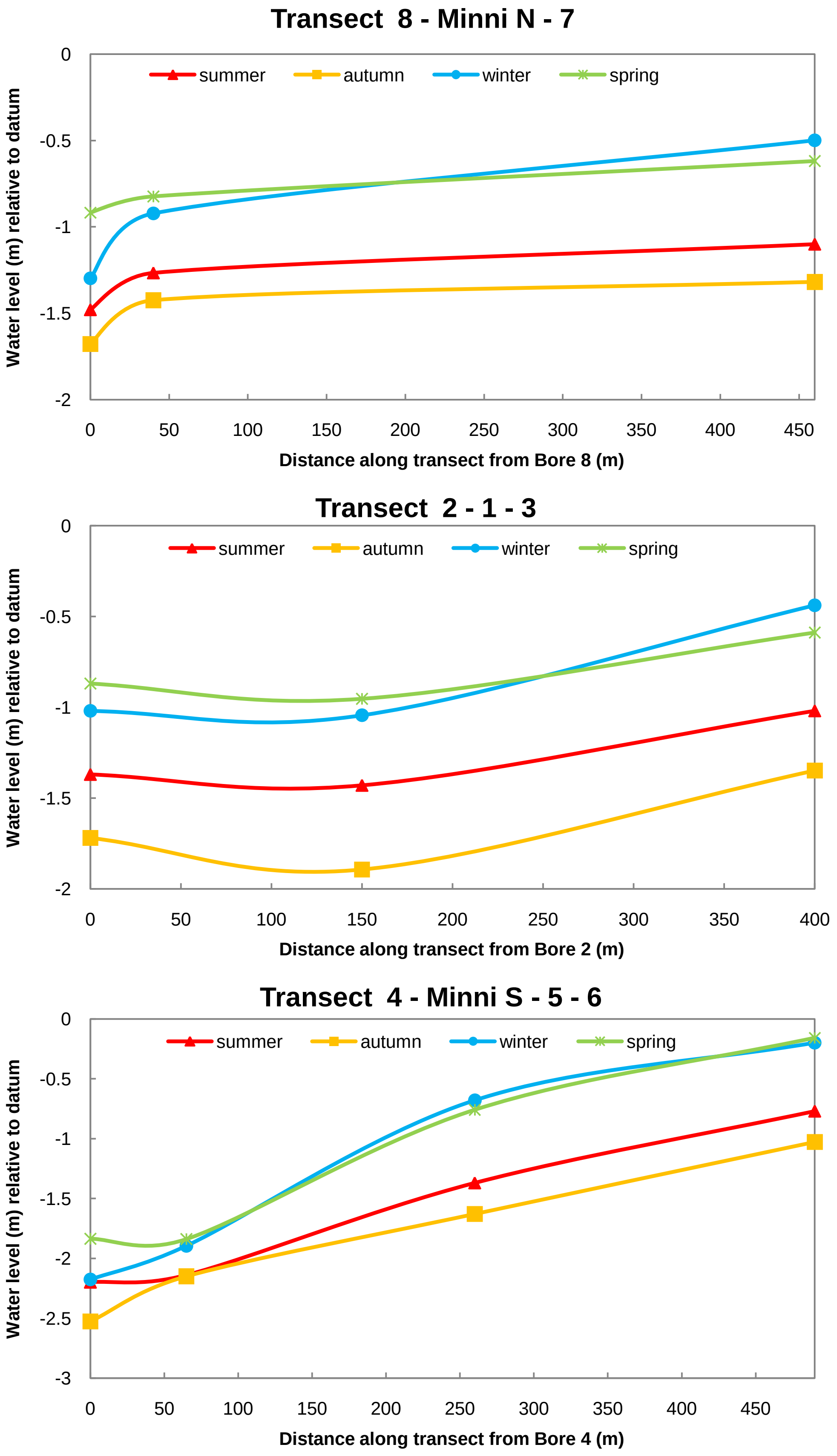


Figure 26. Seasonal variability of water levels along transects through ML

5.1.2 Drain water

Drain water levels and daily flow volumes, adjusted for use in the water balance, are plotted as time series in Figure 27. Peak water levels occur in spring at Minni N in both 2008 and 2009. Water level at Minni S is relatively stable over the wet season. Small-scale water level fluctuations (of the order of centimetres and days) occur at both gauging stations. During some periods, the fluctuations appear to occur in phase at Minni N and Minni S, such as during early winter 2009. At other times, fluctuations are independent. These small-scale fluctuations could occur because of varying atmospheric pressure associated with passing weather systems, or individual rainfall events. During periods of wetland inundation, the drain water at Minni N was hydraulically connected with wetland surface water. Flow through the Minni N gauging station was negligible, and the water at Minni N appeared to be quite stagnant.

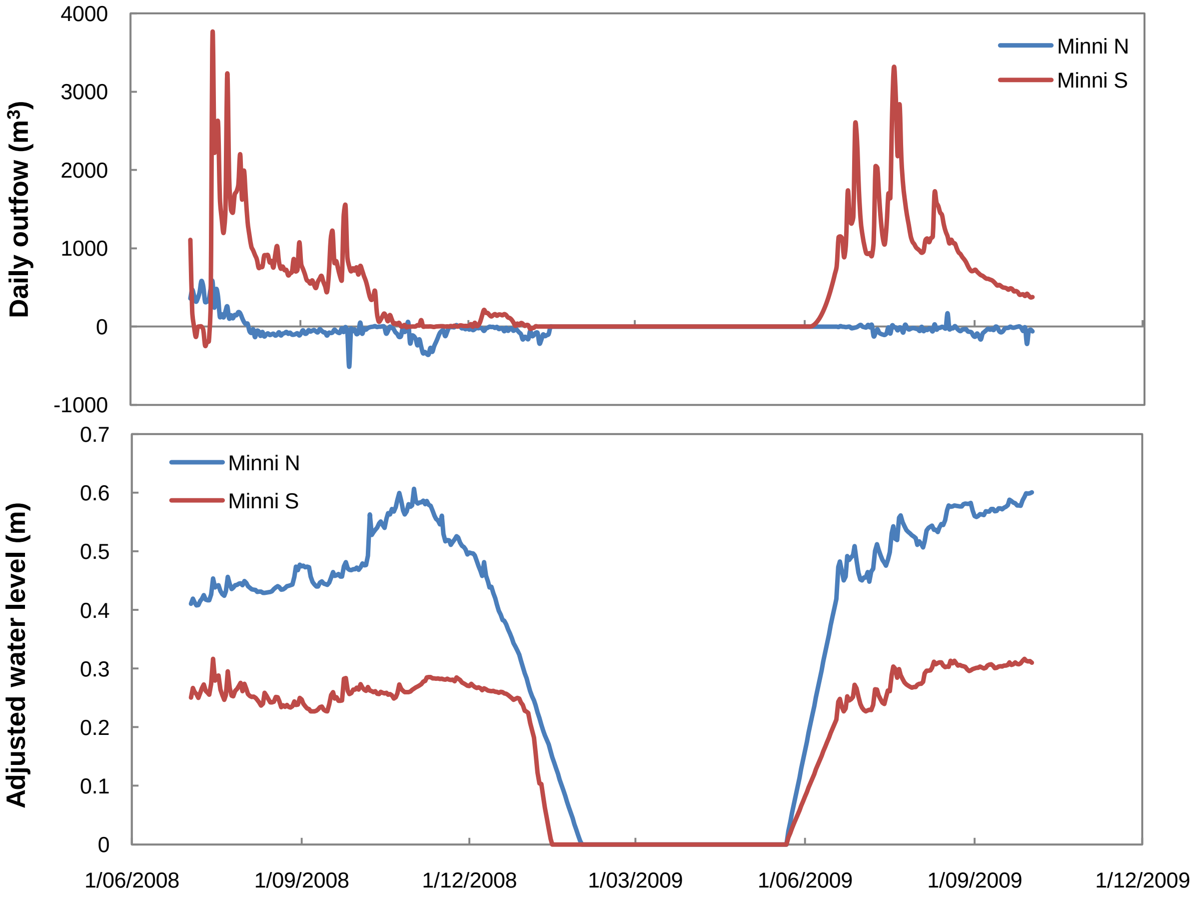


Figure 27. Drain flow and water level as time series

The drain did not appear to be functional, and instead water collected in the northern half of ML as if it were a basin. In contrast, the drain was flowing at the southern end of the site for most of the wet season. A number of smaller drains appeared to be connected to the main drain toward the southern end of the wetland, adding to the flow volumes. The drain flow at Minni S is highest in winter for both years studied, although water levels at Minni N peak later in the year. Peaks in the flow time series occur during or following large rainfall events, and elevated water levels in the wetland occur concurrently.

5.1.3 Surface water

Surface water ponding occurred on site in the wetland basin and other low-lying areas throughout the wet season. The wetland was inundated as groundwater levels rose to the ground surface and rainfall collected in topographical depressions. In summer, the surface water was removed by evaporation and depression of the water table. Figure 28 highlights the variability of seasonal wetland hydrology by comparing two photos taken of the same view of the ML wetland in summer and winter. Wetland vegetation was mostly dead in winter, when acidic surface water or elevated metal concentrations may have been phytotoxic to the plants.

Figure 28. View of ML from near Minni N: dry in March 2009 (top), and inundated in August 2009 (bottom)

5.1.4 Water balance

The water balance result, ΔV, is plotted as a time series in Figure 29. The measured change in water level in the wetland, ΔH_2 as defined in section 4.2, is plotted below ΔV for comparison. During the dry period, estimate of H_2 required the use of groundwater level data from Bore 1, which was collected monthly and interpolated to give daily values. Figure 30 shows the variation of wetland water level H_2 over time. Interpolation was used to smooth out differences between the level data from the gauging station and Bore 1 datasets. The error associated with the estimation of wetland water level is visible in the plot for ΔH_2 (Figure 29). Many of the large fluctuations in water level, after rainfall events, are shown as spikes in the data in both the ΔV and ΔH_2 time series. In particular, correlation between the two time series is good for the early winter period of both 2008 and 2009. Due to the error in calculating H_2 in summer, the comparison in the dry period yields the worst results. The water balance model predicts a positive change in volume associated with summer rains, but in reality, rainfall is unlikely to cause surface water ponding. Instead, it is expected that evapotranspiration or infiltration would cause rainwater to disappear within a few hours. Regardless, these events cannot be captured by the H_2 data, because groundwater level measurements were only taken once per month in this period, and daily data was estimated using interpolation. Results for spring show that large events do not correlate between time series. The negative trend during November and December 2008 is shown by both time series. This represents falling water levels associated with increasingly dominant evaporation.

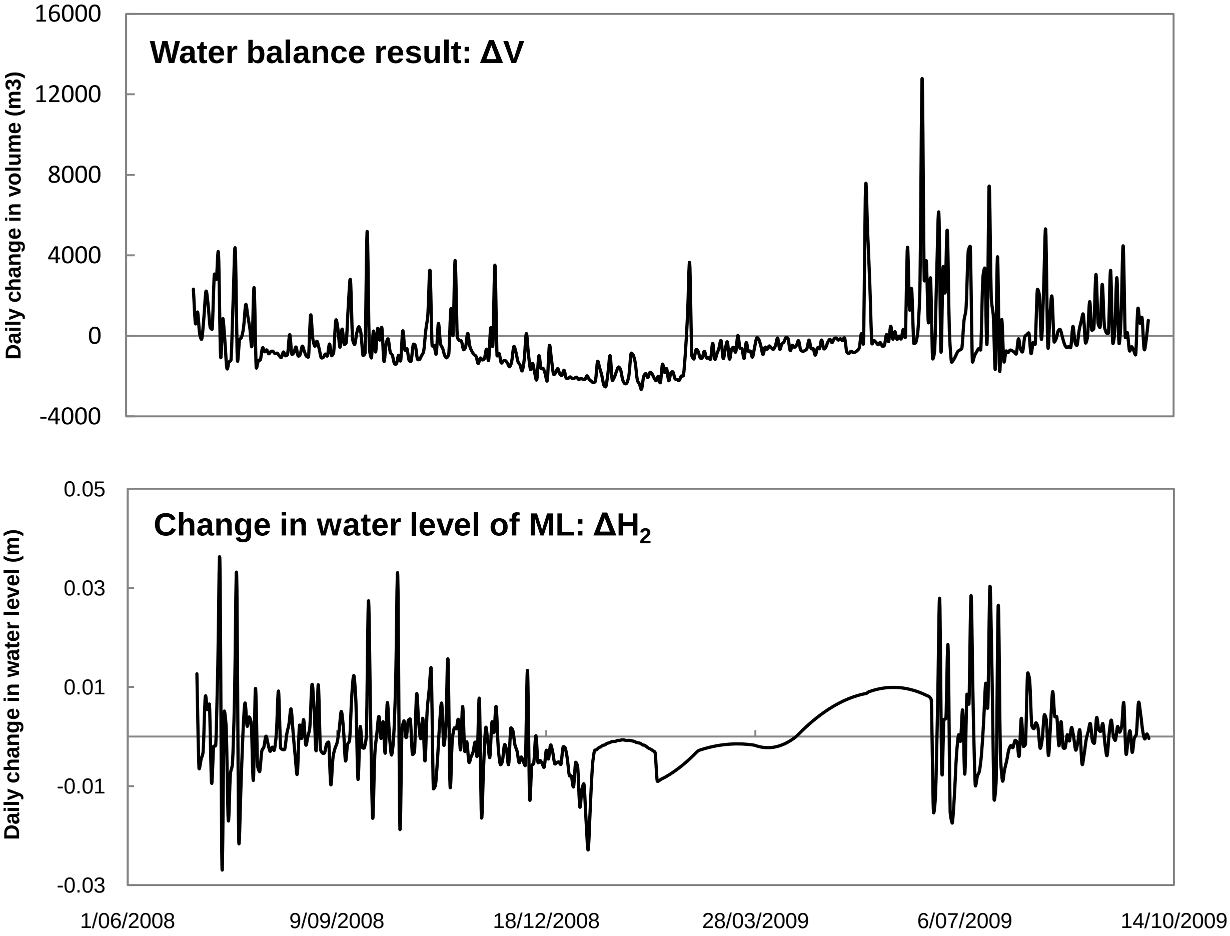


Figure 29. Water balance result ΔV (m^3) and estimated change in water level ΔH_2 (m) as daily time series

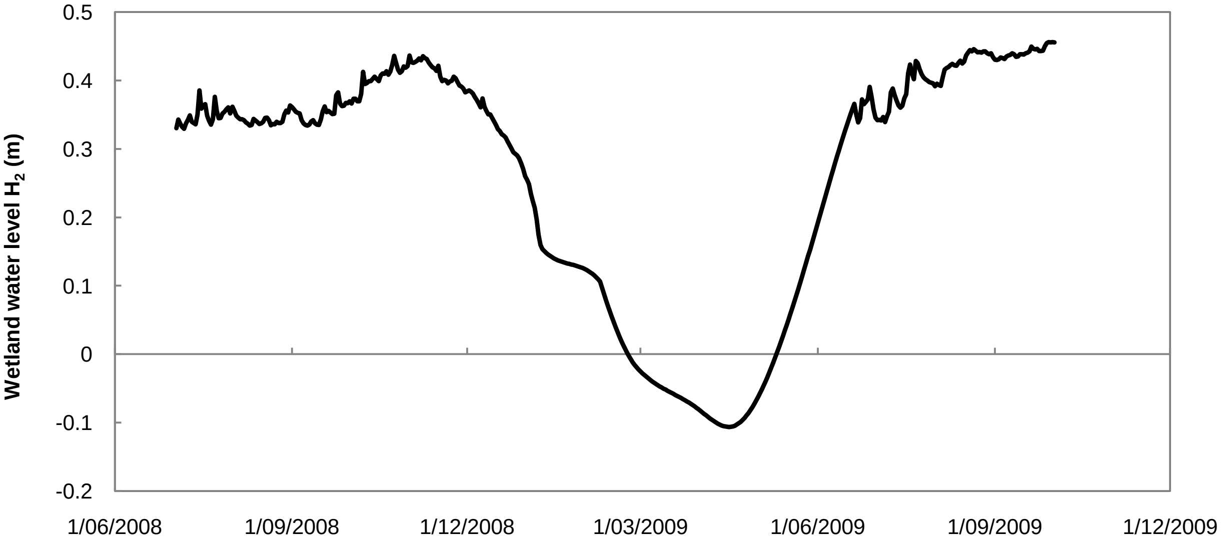


Figure 30. Estimated wetland water level H_2 (m) over time

The water balance components are plotted in Figure 31 to allow seasonal trends to be visualised. Data plotted have units of volume and represent masses of water entering or leaving the wetland per day. As such, the magnitudes (scale) of parameters are directly comparable. The rainfall plot shows that most of the annual rainfall falls in winter or early spring, and 2009 had more rain than 2008. Summer and autumn were dry except for a couple of large events (probably thunderstorms). The maximum rainfall input volume in one day was 13,316 m^3 on June 16, 2009. The maximum daily volume for any other parameter was 4,306 m^3 of drain outflow on July 15, 2008. The maximum daily rainfall volume over the period was more than three times greater than the maximum of any other water balance component. This illustrates the dominance of rainfall as a water balance input component. Groundwater discharge is a smooth time series because data was collected once every 3 – 4 weeks and interpolation applied to get daily levels. Discharge of groundwater to ML ceases in dry periods because the water level goes below ground and there is no longer a seepage face. Peak groundwater discharge occurred in spring in 2008 and in late winter in 2009. Evaporation data was collected as daily time series. It is of greater resolution than groundwater discharge, as alterations in conditions on timescales of one day are captured. Evaporation was greatest in early summer when ponded water is still present and shallow lake evaporation data is being used. For the dry period, bare soil evaporation data was used, and the shift between the two evaporation data sets can be seen at the end of summer 2008 (Figure 31). Drain outflow had maximum values at the same time as the winter rains. This suggests that the wetland does not exhibit a considerable “wetting up” phase and instead begins to flow with the rains early in the wet season. Interestingly, the flow out of ML is larger in 2008, even though more rain fell in 2009. This is discussed in detail in section 6.1.1.

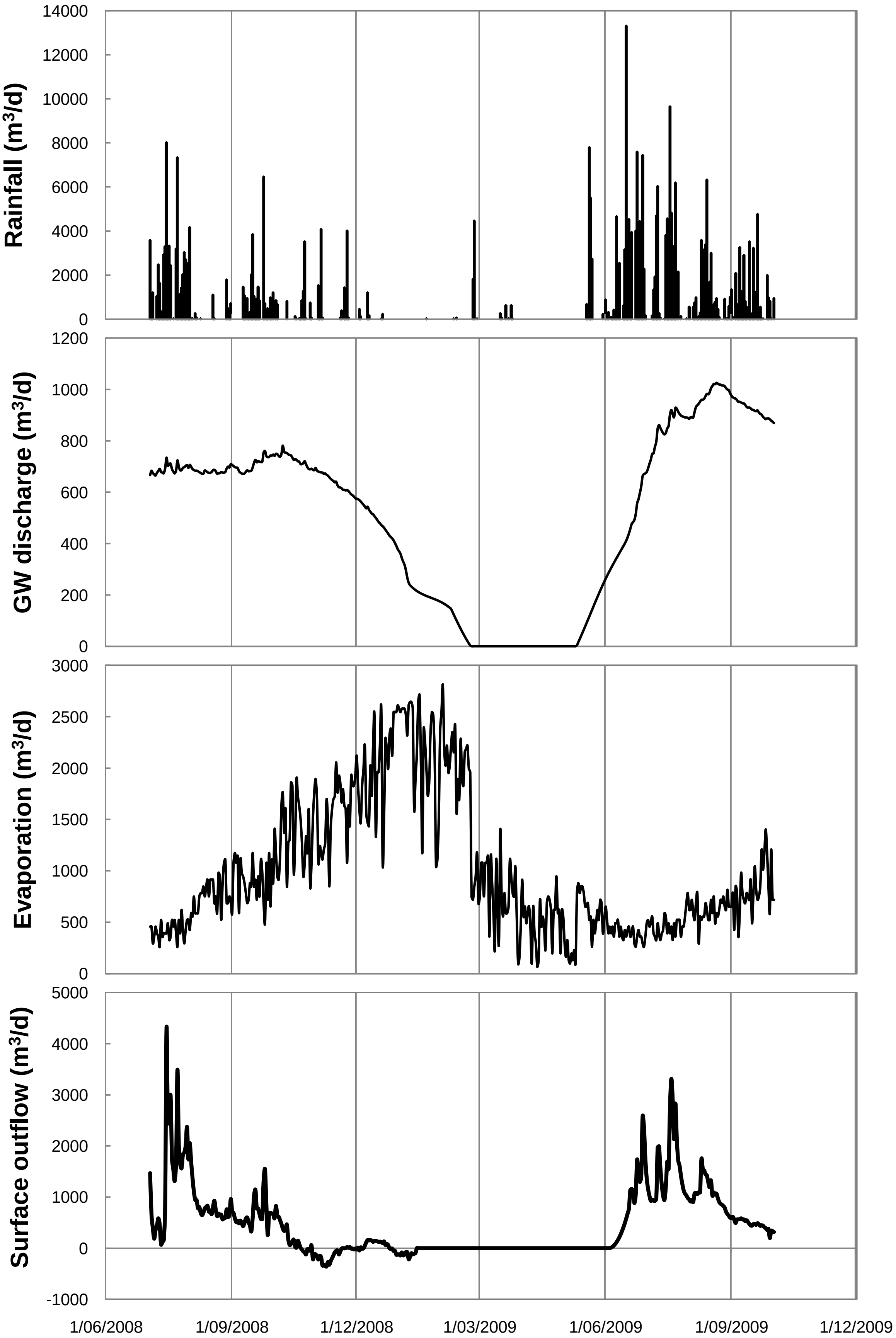


Figure 31. Water balance parameters as input or output volumes over time

The water balance components are displayed in Table 6 as seasonal volumes. Daily volumes of water for each component were summed over seasons. Input components were summed and the relative magnitudes of rainfall and groundwater discharge were calculated as percentages of total seasonal input. The process was repeated for the output components. This allowed the seasonally dominant water balance components to be established. In both 2008 and 2009 winter seasons, rainfall dominated the inputs, and drain outflow dominated the outputs. The percentage contributions of each component were comparable between the two winter seasons. In spring, the relative contributions of rainfall and groundwater discharge are comparable. In spring 2008, groundwater slightly dominated, while in 2009 rainfall was higher. It should be noted that while 2008 and 2009 winter and spring seasons are compared here, the water balance dataset runs from July 3, 2008 to October 2, 2009, and thus the data for winter 2008 and spring 2009 are slightly incomplete.

Table 6. Seasonal results of water balance

Note: * indicates data does not cover the entire season, blue cells indicate increased water storage in ML, and red cells indicate a decrease in storage over the season.

		winter*	**spring**	**summer**	**autumn**	**winter**	**spring***
Season beginning		1/06/2008	1/09/2008	1/12/2008	1/03/2009	1/06/2009	1/09/2009
Inputs	**P**	67,072	48,076	8,682	18,832	153,368	33,781
	GW_{in}	41,176	62,860	24,494	2,691	69,378	29,485
	I	108,248	110,936	33,176	21,523	222,746	63,265
	%P	62	43	26	87	69	53
	$\%GW_{in}$	38	57	74	13	31	47
Outputs	**Q_{out}**	69,216	22,427	118.361	0	102,386	15,000
	E	35,772	115,475	181,992	54,310	45,824	26,274
	O	104,988	137,901	182,110	54,310	148,210	41,274
	$\%Q_{out}$	66	16	0	0	69	36
	%E	34	84	100	100	31	64
Change in storage	**ΔV**	3,260	-26,965	-148,934	-32,787	74,535	21,991
	ΔH_2	0.033	0.019	-0.405	0.204	0.252	0.021

General observations to be made from the seasonal results of the ML water balance (Table 6) are as follows:

- in winter, rainfall is the major input and drain flow is the major output
- in spring, rainfall and groundwater discharge both contribute to input water, while evaporation is the dominant output
- in summer, groundwater is the major input and evaporation the dominant output, as the water level falls below the surface, and
- in autumn, inputs are low but dominated by rainfall, whilst evaporation is the only output.

The change of water storage in ML, ΔV, was calculated as inputs subtracted by outputs for each season, and the daily changes in wetland water level, ΔH_2, were summed over each season. Whilst ΔV is derived from the water balance, ΔH_2 is calculated from measured water levels. Table 6 allows the two estimates of change in water storage to be compared. Cells of the table are coloured red when storage is decreasing over the season (to highlight a negative change in volume) and are coloured blue when storage is increasing. The two estimates agree that in winter 2008 and 2009, and spring 2009, storage is increasing. This is due to the dominance of rainfall in these seasons. In summer, storage is decreasing for both estimates. Evaporation dominates the water balance and water levels in the wetland fall, as does the surrounding groundwater table. In spring 2008 and autumn 2009 however, the two estimates for wetland water storage disagree. It is during these periods between the “wet” and “dry” seasons that hydrological regimes become more difficult to model. Inter-annual variation in conditions is likely to impact on these seasons the most. While summer and winter storage changes are easy to predict because one input and one output consistently dominate, the autumn and spring hydrology is affected by a combination of components. For example, in spring rainfall and groundwater discharge both add water to the system; in autumn, a small number of storm events cause rainfall to dominate. In spring 2008, the water balance model predicts a decrease in storage, while H_2 suggests an increase. In reality, water levels at ML peak in late winter or spring, and then decline as evaporation begins to increase. It is likely that the evaporation estimate made by the water balance model over-predicts evaporated volumes toward the end of the wet season, as surface water ponds dry up. The Morton shallow lake estimate (section 4.2) is used until the end of the wet period, marked by H_2 dropping below zero. In fact, as water levels in ML decline in spring and summer, surface water stores diminish and due to the basin-like topography, the water surface area for evaporation decreases quickly. A variable wetland surface area was not included in this water balance, and instead a constant was used which represented the total extent of seasonally inundated or waterlogged land. Therefore, at the beginning and end of the wet season, when only parts of the wetland are inundated, the evaporation estimate made by the water balance is likely to be excessive. In autumn, the ΔH_2 estimate suggests an increase in water storage, because H_2 is calculated using Bore 1 data, and the groundwater table was rising over this period. This groundwater level rise does not intersect the ground level until late in the season, and so estimates of groundwater discharge are low. The calculation of groundwater discharge requires surface water to be present to provide a seepage face through which groundwater flows into the wetland (section 4.2). Therefore, the discrepancy between water storage estimates in autumn is due to the difference in definitions of water storage. While ΔH_2 assesses a rise in water level, whether above or below ground, as an increase in storage, ΔV considers only above ground wetland storages.

5.2 Wetland geochemistry

5.2.1 Water

Water quality results are presented below in condensed form. Interesting results and trends are presented in this section; tables of complete results are presented in Appendix C.

The results of continual pH monitoring of drain water at gauging stations Minni N and Minni S during the wet periods of 2008 and 2009 are shown in Figure 32. In 2008, the pH readings became unreliable as the drain started to dry out. In 2009, readings from Minni N became erratic after mid-August.

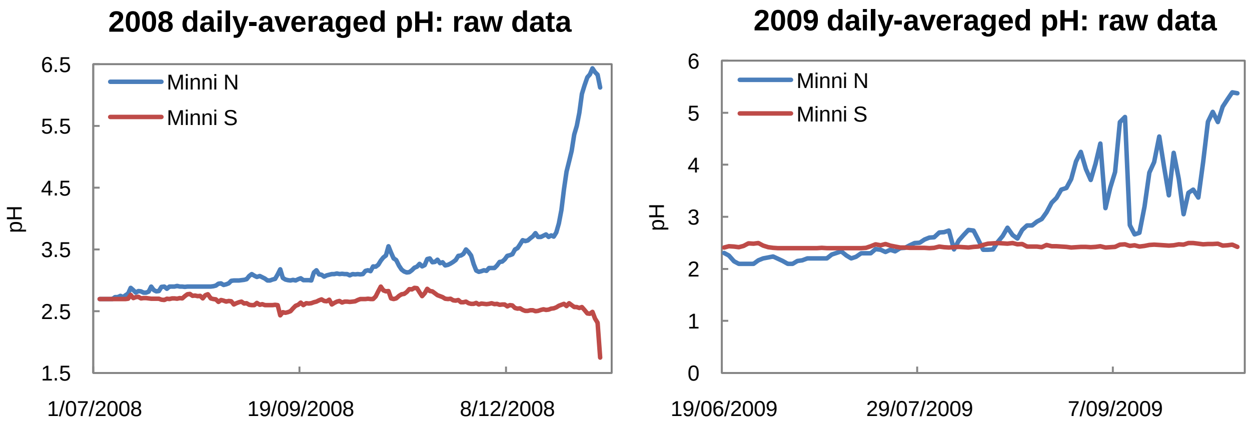


Figure 32. Raw, daily-averaged drain water pH time series for 2008 and 2009

A refined (truncated) dataset for 2008 is presented with field measurements of drain pH for 2009 in Figure 33. The scale of the y-axis is the same in both plots to allow for direct comparison of pH, but note that the x-axes are different because the monitoring of drain water took place over different periods each year. Inspection of these plots yields the following general observations:

- pH of water at Minni N is more variable than Minni S
- at Minni N, pH is low and relatively constant in early winter, but increases and becomes more variable later in the wet season
- small scale pH variations seen at one station are not matched by the other station, and
- pH of drain water was similar in 2008 and 2009 and individual gauging stations showed similar patterns between years.

These results suggest that if water flows north to south through the wetland, it is likely to become more acidic. The concept of the wetland as a source of acidity is discussed further in section 6.2.1.

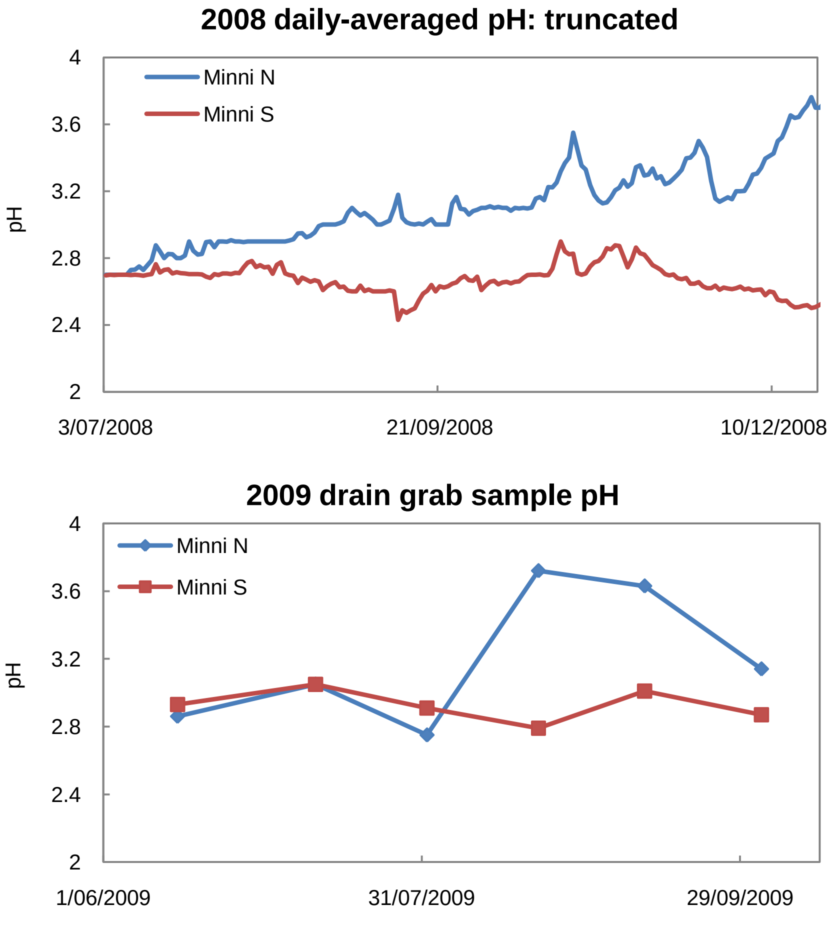


Figure 33. Refined drain water pH time series for 2008 and 2009

Chemical composition of drain water is also spatially and temporally variable. Figure 34 shows the concentration of several metal species in drain water at Minni N and Minni S as time series. The concentration axes of plots have the same range for each species to allow direct comparison of drain water quality at the two gauging stations. The time series run from September 11, 2008 to September 11, 2009.

In 2008, the concentrations of Al, Fe, Mn and Zn were generally higher at Minni S than at Minni N. Concentrations of Fe, Al, Mn and Zn at Minni S follow a similar trend: concentrations decline from September until December and then increase in January. At Minni N, concentrations were low and generally steady, although Mn and Zn exhibit a similar falling and rising trend to Minni S concentrations.

In contrast, 2009 concentrations of Al, As, Fe, Mn and Zn were generally higher at Minni N than at Minni S. At Minni N, Al and Zn concentrations exhibited a falling trend over the winter season. Concentrations of As and Mn were variable and peaked in July. Concentrations of Fe rose over the winter at Minni N, but fell at Minni S. Other metal concentrations also fell at Minni S over the winter, including As, Al and Zn.

Falling trends in metal concentrations over the winter can be related to continual flushing of sediments. As rainwater and groundwater combine to waterlog sediments, they become weathered, acid sulfate soil products dissolve, and the water becomes acidified. As it drains away, the water removes bound metal cations from sediment grains as hydrogen ions compete for surface adsorption sites. As this process takes place over the winter, with greater flushing during large rainfall events, the amount of easily desorbed trace metals declines and drained water metal concentrations fall. This explanation is particularly fitting for Minni S, which receives water from well-drained land in the southern half of ML. In the northern half, surface water collects over the season and it is probable that reducing conditions develop in the waterlogged sediments. This may be causing release of metals by redox-controlled mechanisms. In summer, as the groundwater table falls, evaporation increases and contaminants become concentrated in surface water. This may account for the increase in some metal concentrations at Minni N and Minni S in January 2009. The same pattern is not visible in the 2009 data, because the time series does not continue until the summer.

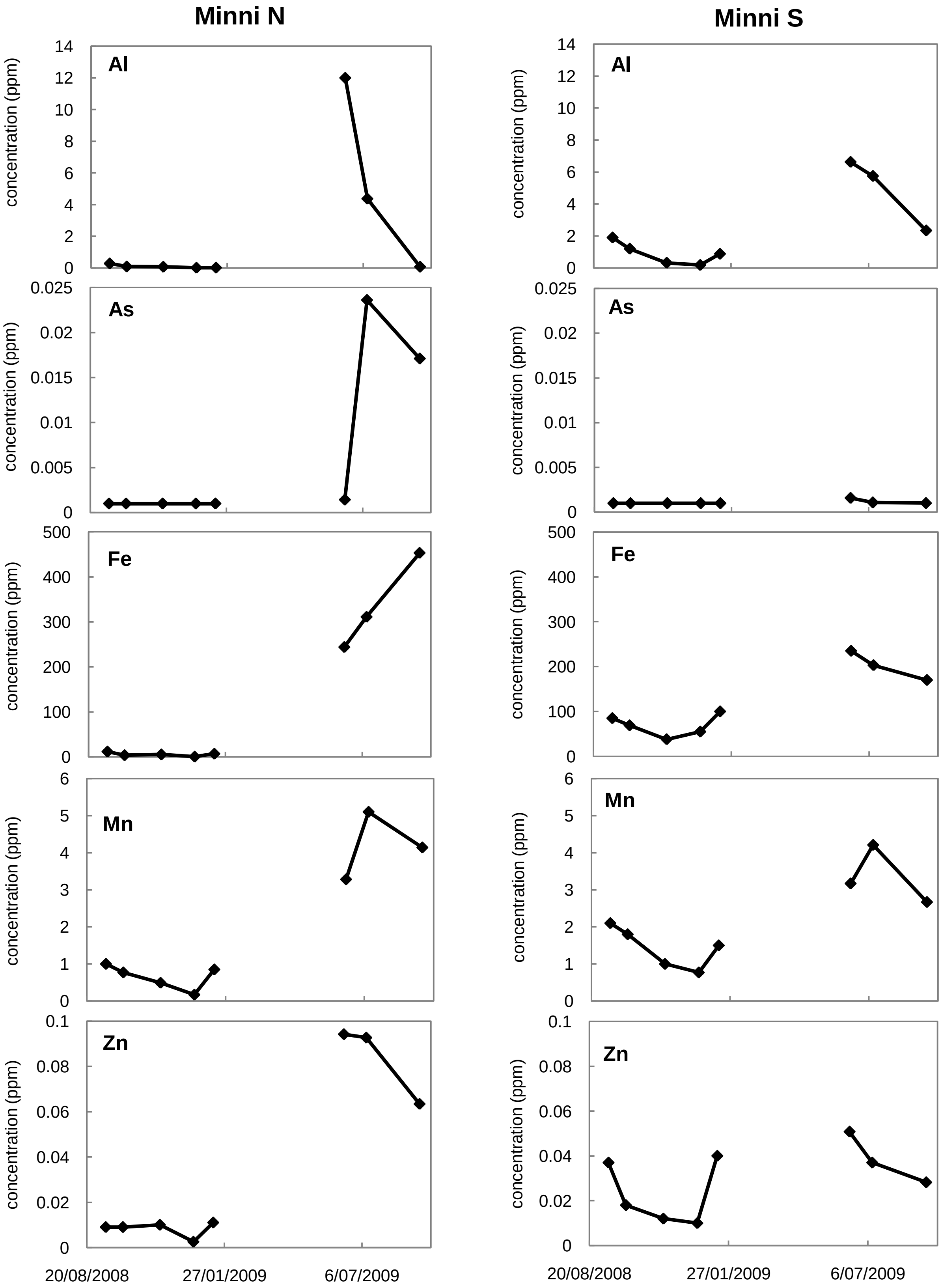


Figure 34. Comparison of metal concentrations in drain water at Minni N and Minni S over time

Note: concentrations below detection are plotted at half the detection limit.

Groundwater quality is spatially and temporally variable at ML. Time series of ORP and pH are presented in Figure 35 for the September 2008 to September 2009 period. Due to a change of instrument, ORP readings taken in the field before November 11, 2008 are not comparable with those made after (Boland 2009). Data is missing from the Bore 8 series because the bore was dry over the summer and winter.

Redox potential of groundwater sampled at bores 1, 3 and 4 exhibited seasonal variability, with periods of oxic and anoxic conditions. Water from bores 5 and 6 were usually anoxic but ORP exhibited a rising trend toward the end of the sampling period. Water from bores 7 and 8 was permanently oxic, although as stated previously, data from Bore 8 was unavailable for the dry season.

The groundwater sampled at bores 1, 2, 4, 6 and 8 was permanently neutral and showed little variability (pH 6.43 – 7.70) over the study period. Water from Bore 5 showed greater pH variation than these bores, with pH ranging from 5.86 to 7.77. While groundwater from Bore 7 was consistently acidic (pH 3.02 – 4.07), groundwater from Bore 3 exhibited a strongly seasonal trend of acidification and neutralisation (pH 3.93 – 6.68).

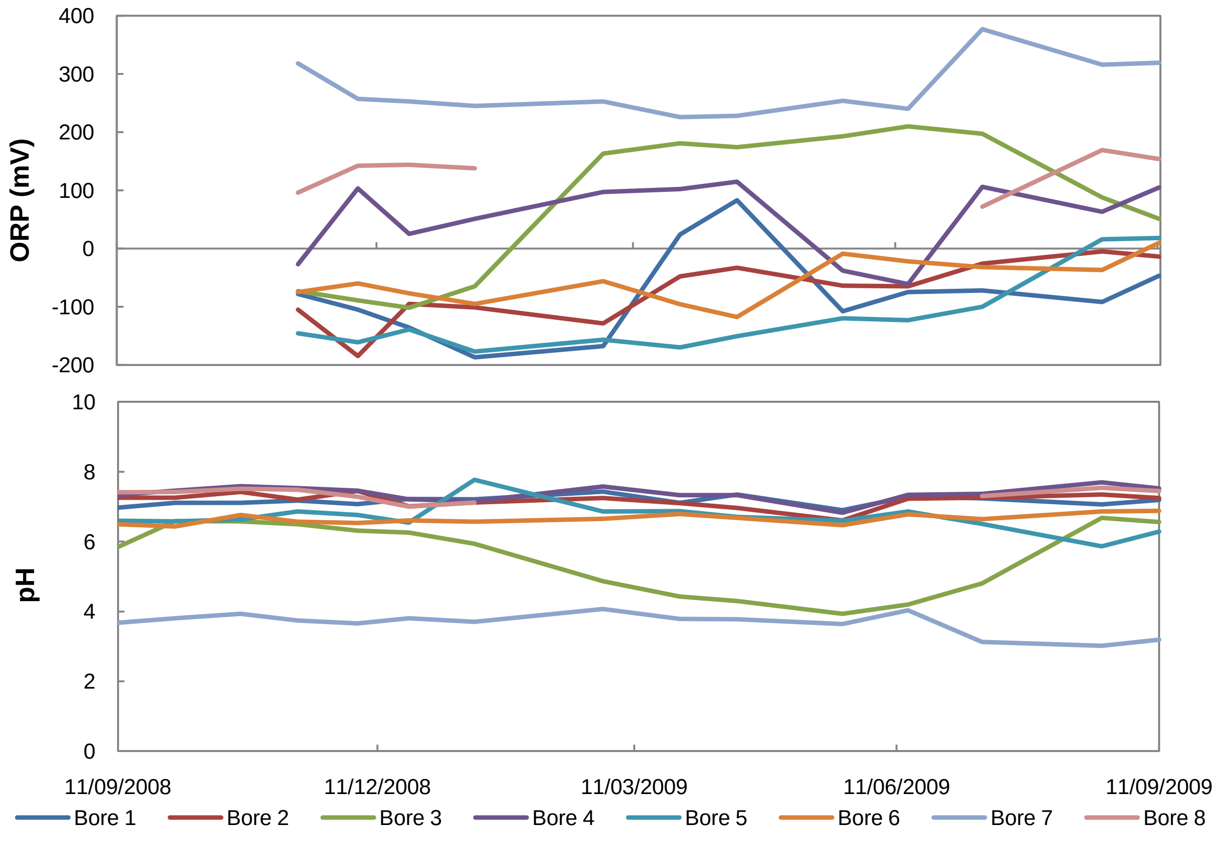


Figure 35. Redox potential and pH of groundwater as time series

Chemical composition of groundwater was also variable. The bores exhibited a large range of metal concentrations. Figure 34 shows the results of Al analysis of groundwater from all bores over the study period. The logarithmic scale used for the concentration axis demonstrates the enormous variability in water quality over the study site. Water from bores 3 and 7 had the highest aluminium concentrations, and for most of the other metals tested as well. Notably, the water from these bores also exhibited the lowest pH. The maximum Al concentration recorded was 120 ppm in Bore 7 water in October 2008. Water from bores 1, 2, 4, 5, and 8 all had concentrations below detection limit on at least one occasion. The detection limit for Al was 0.0005 ppm.

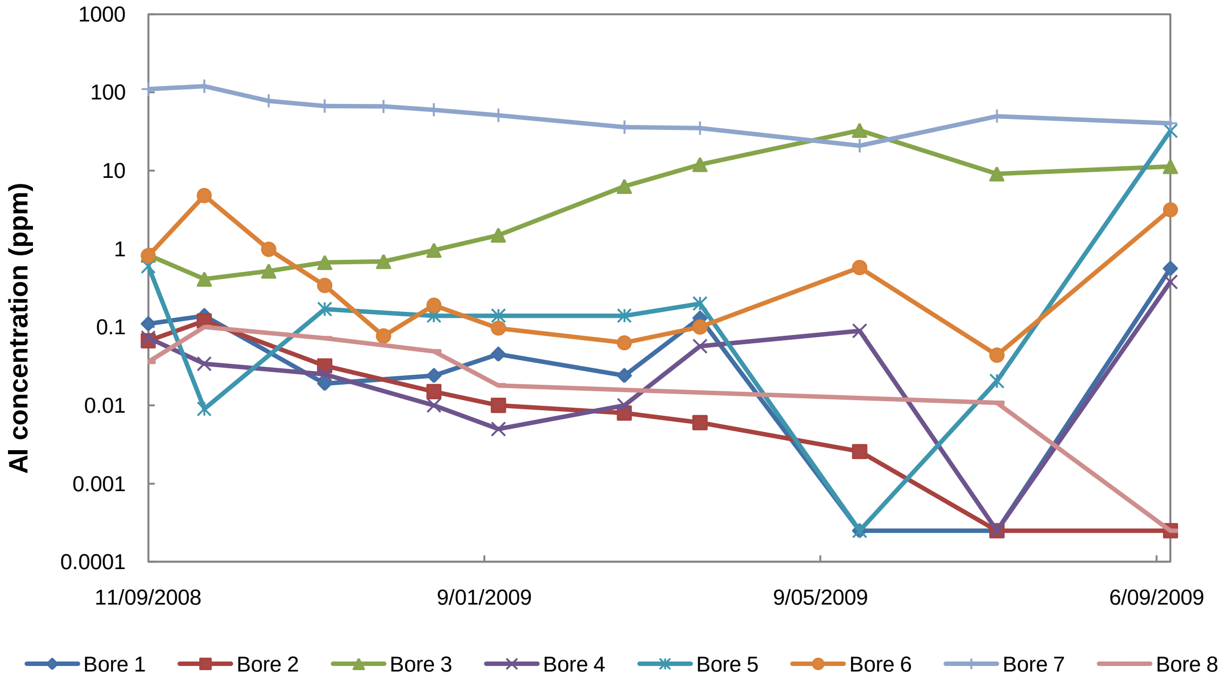


Figure 36. Time series of concentration of aluminium in groundwater from monitoring bores

Note: y-axis uses a logarithmic scale, concentrations below detection are plotted at half the detection limit

By examining temporal fluctuations in physical and chemical properties of groundwater at each bore, theoretical mechanisms for metal mobilisation may be considered. Selected chemical results from groundwater monitoring bores 1, 2, 3, 5 and 7 are presented in the following pages. The complete results from all bores are tabulated in Appendix C.

Bore 1 is situated in the centre of ML and thus the parameters measured at Bore 1 may be indicative of the wetland subsurface in general. Selected physical and results are displayed in Figure 37. The water table height shows seasonal dependence, falling over the dry months and being recharged in winter. The maximum height of the water table in 2008 was 0.520 m below ground, while in 2009 the water table rose to 0.454 m below ground. This can be attributed to the higher winter rainfall in 2009, which acts to both increase surface water store in the wetland and recharge the local groundwater. The rise of the water table past the previous year's maximum height affected chemical concentrations in the groundwater. Figure 37 shows that Al, As, Cl, Fe, Pb and Zn were all found at maximum concentration in the sample from September 11, 2009. On this date, the water table had risen to 0.464 m below ground, higher than the maximum level from 2008. Because the concentration of Cl increased in phase with the metals on this date, the dominant process for contaminant mobilisation in groundwater at Bore 1 appears to be dissolution of accumulated salts and precipitates near the sediment surface. Variations in groundwater ORP appear to be responsible for changes in concentration of As and Pb. These metals are released around the same period as ORP shifts from anaerobic (-168 mV) to oxic (24 mV) between February 28 and March 27, 2009. The concentration of Mn falls over the study period before increasing again as water levels become high. The reason for the decline in Mn concentration is unclear, although one possibility is that as the ORP was becoming reducing, reductive dissolution of Mn-oxyhydroxides may have been occurring during this time. Free Mn cations may have been sorbed to sediment particles upon release due to the favourably neutral pH conditions.

Groundwater from Bore 2 was neutral over the study period, and metal concentrations were comparatively lower than water from Bore 1. For example, Al, Fe and Zn concentrations were of the order of ten times less in Bore 2 water than Bore 1. The lowest water level in Bore 2 was recorded in April 2009. As the water table began to rise with the onset of winter rainfall, there was a release of SO_4 and the pH fell to 6.61. This is thought to be due to dissolution of acid products following the oxidation of metal sulfides during the dry period. There was also increased Fe concentration at this time, suggesting iron sulfides may have been oxidised and the free ions released following dissolution. The sulfate dissolution and pH decline occurred in phase with an increase in Mn and Zn concentrations. The concentration of Ca also increased, possibly due to dissolution of $CaCO_3$, which buffered the acidity and caused subsequent pH levels to increase. There was a large peak in Al concentration in October 2008, but the mechanisms for this release are unclear. Concentrations of Fe increased steadily from September 2008 until February 2009, so the Al release in October could be associated with reductive dissolution of Fe-oxyhydroxides. This could have been initiated under earlier reducing conditions, but no reliable ORP data is available before November 2009 to support this theory. The decline of Al concentration after October 2008 can be attributed to its instability at neutral pH. The rising trend in Ca, Mn and SO_4 concentrations in spring 2009 may be due to dissolution of accumulated salts in sediments that do not experience annual flushing, as described for Bore 1.

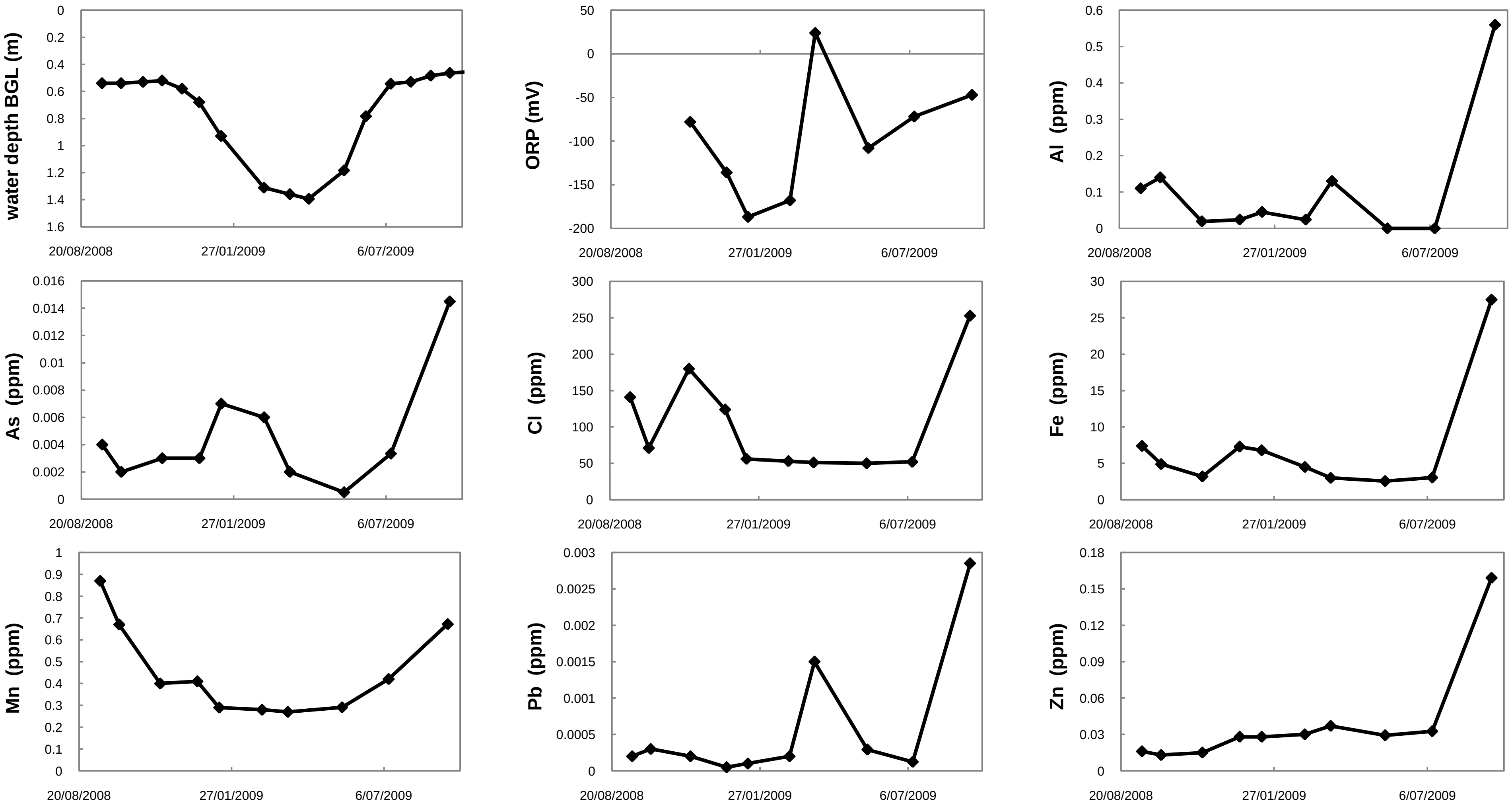


Figure 37. Bore 1 groundwater: selected physical parameters and chemical concentrations over the study period

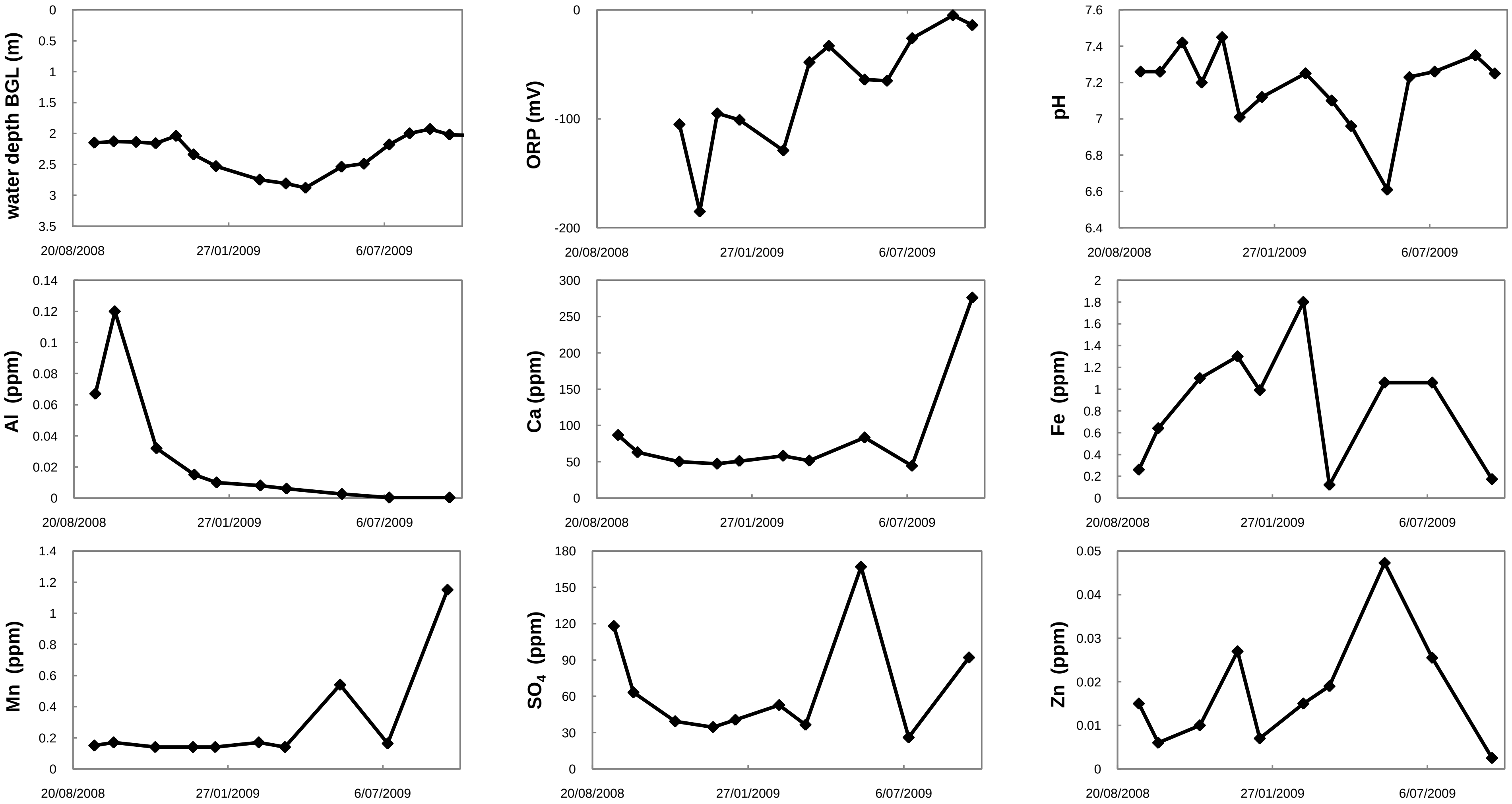


Figure 38. Bore 2 groundwater: selected physical parameters and chemical concentrations over the study period

Groundwater from Bore 3 exhibited seasonal pH variability and high trace element concentrations. The minimum pH recorded for Bore 3 water was 3.93 on May 23, 2009. The water table was lowest on the preceding field trip. This pattern of sediment oxidation followed by groundwater recharge and acidification is common in acid sulfate soils. The increased concentrations of Fe and SO_4 associated with the decreased pH support the hypothesis that acidity in groundwater at Bore 3 is driven by acid sulfate soil reactions. The fall in pH to below 4 occurs concurrently with a marked increase in Al and Ni concentrations, and a small increase in V. As the water table rose over winter, the soil became waterlogged and ORP declined. When the ORP reached a level close to zero, the pH increased, possibly due to the consumption of protons by reduction reactions. Concentrations of Al, Ni, SO_4 and Fe all declined after the pH became neutral. Levels of As and Fe seem to be related to variations in ORP. Under reducing conditions, As and Fe levels increased, but when oxidation occurred the levels declined. There is a lag time between ORP shift and concentration response, which is thought to be related to kinetics of adsorption-desorption reactions. The concentration of V increased dramatically at the end of the study, which may be due to dissolution of surface salts as described previously for other bores, as the water level increased at the end of the 2009 wet season to a higher level than the previous year.

Water from Bore 5 was consistently neutral, and conditions were reducing for most of the study period. The mobilisation of contaminants occurring in groundwater at Bore 5 appears to be related to either flushing of accumulated surface salts under high water table conditions, or release of metals due to oxidation of previously reduced sediments. When reduced sediments become oxidised, sulfides oxidise and an increase in SO_4 and metal concentrations is expected, along with a decrease in pH. At Bore 5, the minimum pH of groundwater was 6.29, and most metals would be expected to remain adsorbed. Instead, the large peaks in Al, As, Fe and Pb are thought to be associated with the dissolution of salts that had accumulated above the high water table “mark”, as discussed for Bore 1. In September 2009, the water table had risen to 0.59 m below ground, while in October 2008 the water table peaked at 0.74 m below ground.

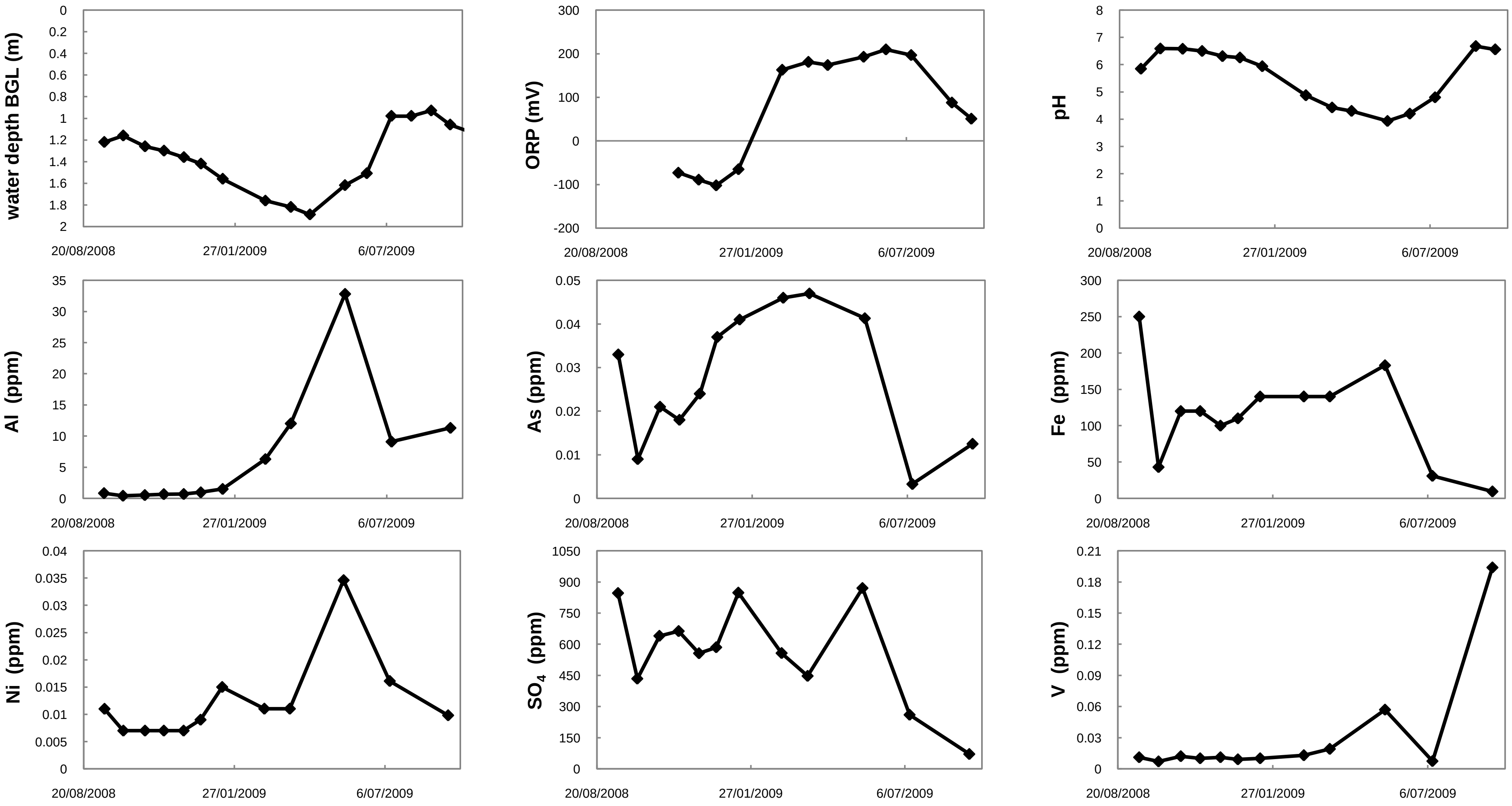


Figure 39. Bore 3 groundwater: selected physical parameters and chemical concentrations over the study period

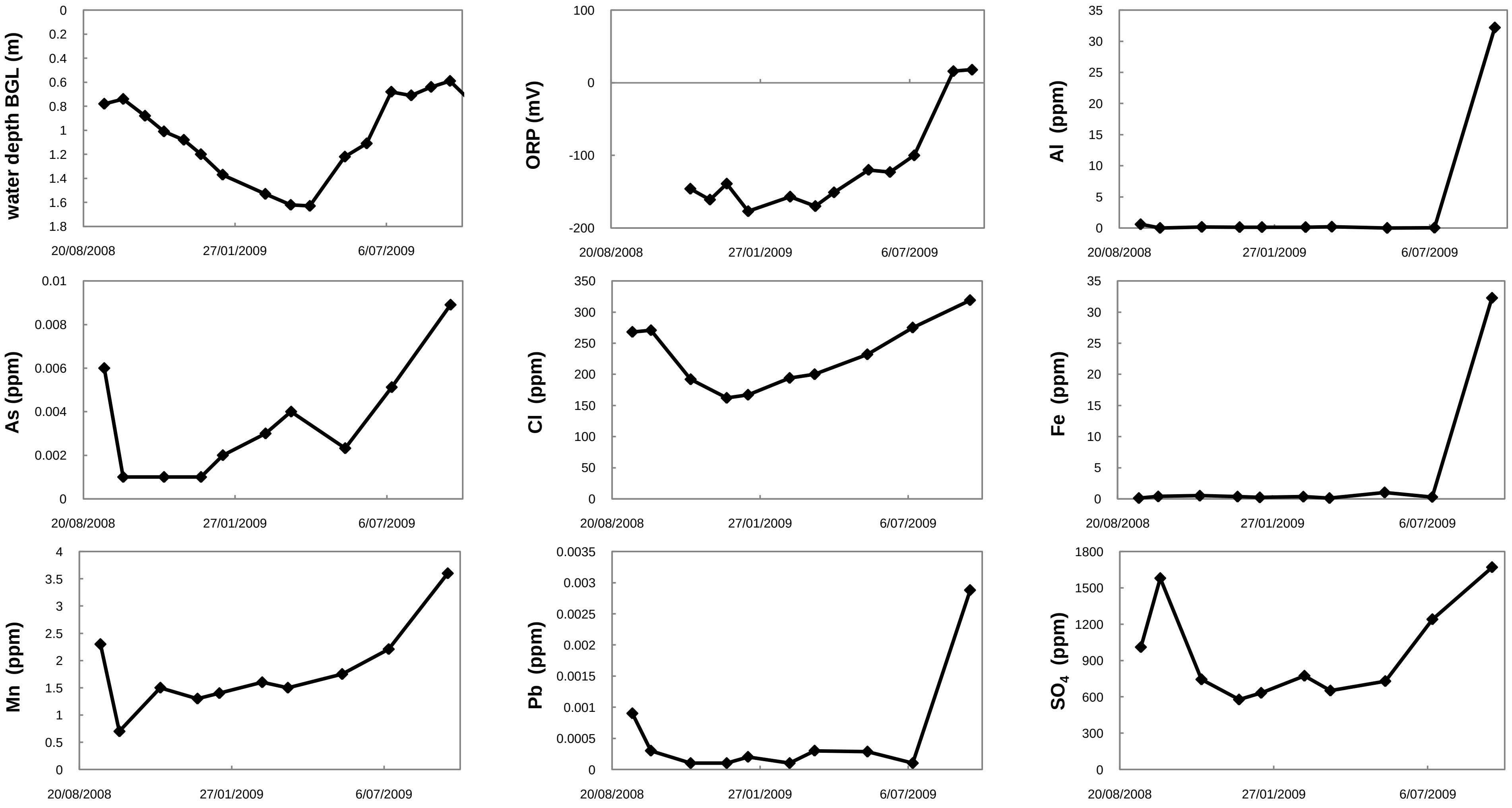


Figure 40. Bore 5 groundwater: selected physical parameters and chemical concentrations over the study period

Water from Bore 7 was consistently acidic and oxic. The pH remained steady and mechanisms for fluctuations in metal release are therefore difficult to identify. The concentrations of metals in the groundwater from Bore 7 were the highest of all the bores tested. Concentrations of Al and Fe were frequently of order 100 ppm. The concentrations of SO_4 were also very high, ranging from 757 to 2130 ppm. Variability in SO_4 concentrations seem to be linked to changes in ORP and pH. For example, in July 2009, elevated SO_4 occurred concurrently with a peak in ORP and a drop in pH. This suggests that oxidation of sulfides caused the production of SO_4 ions and hydrogen ions. The concentration of Al and V also increased at this time, suggesting mobilisation of these metals occurred due to increased acidity. The high levels of As in the groundwater of Bore 7 could suggest that arsenopyrite was present and As release is due to oxidation. The large peak in As concentration at the start of winter 2009 is associated with the rise of the water table after summer. This supports the proposition that sulfides are oxidised during dry times and acidity products and metals associated with the sulfide minerals are dissolved. Bore 7 groundwater had the highest levels of Cd detected at ML. At all other bores, Cd concentration was frequently below detection. Although the concentration in Bore 7 groundwater appears to experience a peak in November 2008, which is associated with a slight decrease in pH, the concentration was consistently of the order of 0.1 ppb.

The results of field monitoring of surface water pH are given in Table 7. Full results are presented in the field notes (Appendix A). The pH of most areas with ponded water was very low (2.92 – 3.24), with only one pH neutral sample, coming from a waterlogged area with grass. Sulfidic smelling waters were presumably anaerobic and undergoing sulfate reduction, indicating that insoluble metal sulfides could have been forming.

Table 7. Results of surface water pH monitoring

sample	pH	notes
S1	6.85	waterlogged area with grass, sulfidic smell
S2	2.97	pond with orange water and algae/ooze, lighter colour than S1
S3	2.69	northern ML - vegetation dead, orange water, sediment cracked red/orange
S4	3.22	ponded area north side of road, sulfidic smell and mosquito larvae
S5	3.24	opposite side of road from S4, vegetated area with ponded water, no smell or larvae
S6	3.11	between Minni S and Bore 5, ponded water

S7	3.09	between Bore 5 and 6, ponded water
S8	2.92	drain water sample from halfway along southern half of drain
S9	3.16	waterlogged area just W (into vegetation) near Bore 7

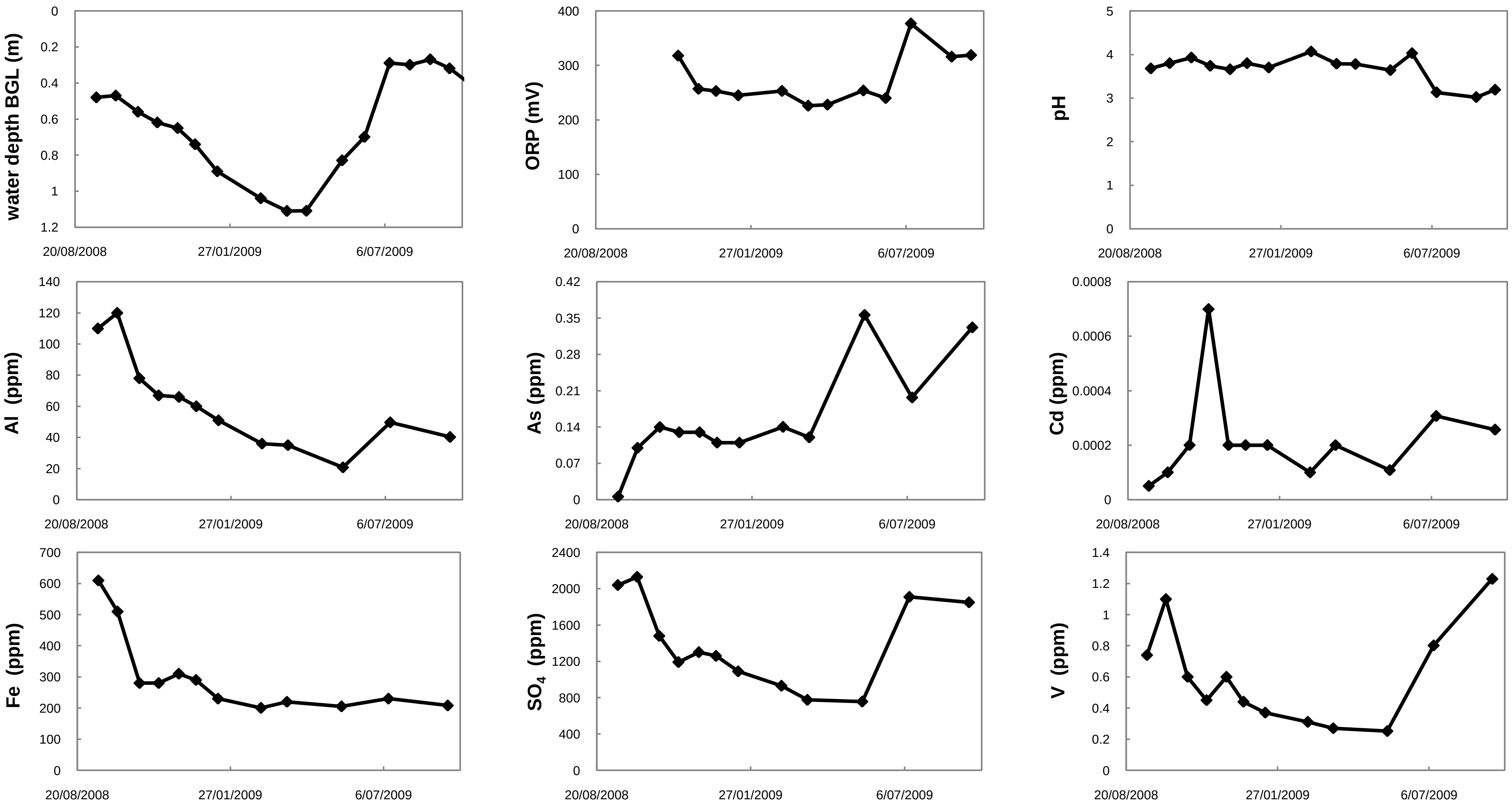


Figure 41. Bore 7 groundwater: selected physical parameters and chemical concentrations over the study period

5.2.2 Soil

The results of soil testing are shown in Table 8. Sediments from close to the wetland, such as 1, 7, S and 5, were moisture and OM-rich. Soil pH was generally neutral, particularly for surface sediments. The pH of sediments decreased with depth for profile samples. Conductivity was highest in sediments close to the wetland, particularly 1A and S, surface sediments that become flooded in the wet season and dried out in summer, causing evapo-concentration of salts.

Table 8. Results of soil testing for moisture content, organic matter, pH and EC

Note: * indicates that only one measurement was taken

Sample ID	Moisture content (%)	Organic matter (%)	pH	EC (µS/cm)
Surface				
2	16.1 ± 0.84	6.27 ± 1.5	8.51 ± 0.16	74 ± 9
3	16.0 ± 0.80	9.33 ± 0.53	6.09 ± 0.22	71 ± 16
4	11.2 ± 1.0	7.87 ± 0.32	8.17 ± 0.31	133 ± 25
5	42.2 ± 0.55	14.8 ± 2.9	8.34 ± 0.12	175 ± 13
6	21.5 ± 0.57	3.67 ± 0.23	8.75 ± 0.07	91 ± 32
8	13.4 ± 0.15	3.09 ± 0.67	8.66 ± 0.12	96 ± 9
Profile				
1A	46.7 ± 4.5	10.9 ± 4.8	7.60 ± 0.34	565 ± 51
1B	35.1 ± 1.5	6.98 ± 4.3	7.85 ± 0.09	346 ± 13
1C	79.5 ± 1.3	13.2 ± 1.1	5.84 ± 0.11	332 ± 26
1D	84.8 ± 0.36	5.99 ± 3.4	5.58 ± 0.03	337 ± 19
7A	27.1 ± 1.1	13.2 ± 0.92	5.99 ± 0.06	190 ± 25
7B	8.65 ± 0.49	2.20 ± 0.84	4.77 ± 0.09	184 ± 9
7C	12.7 ±0.14	0.66*	4.30 ± 0.06	103 ± 16
S	47.1 ± 4.1	14.3 ± 1.6	5.32 ± 0.24	798 ± 17

Results of XRF analysis for majors are presented in Table 9. Soil samples from the wetland (i.e. 1, N and S) were all Fe and OM-rich. Levels of Fe generally increased with depth. Deep sediment from Profile 1 was over 75% organic (from LOI), probably due to accumulation and sedimentation of detritus in the wetland over time. Samples taken on the coastal side of the wetland (2, 4 and 8) had high Ca, indicating that limestone may be one of the source materials for the sands there. Samples 3, 5 and 6 were sands or organic-rich sands. Profile 7 had high Fe and OM in surface sediments, with a similar composition to the wetland sediments, but soils from depth were predominantly sands; this stratigraphy is likely the result of deposition of OM such as wetland plant detritus, which may have historically occurred around the wetland perimeter during flood. The soils at depth in Profile 7 had the lowest Ca of all analysed sediments. Calcium concentrations may be indicative of carbonate and alkalinity levels, and so low Ca in deep sediments near Bore 7 may explain the extreme acidity of groundwater: the low carbonate level indicates that the soil has little buffering capacity.

The full results of XRF trace element analysis are provided in Appendix D. Table 10 shows condensed results: the mean and standard deviation of selected trace element concentrations in ML sediments are compared with levels for a typical sandstone (Drever 1982). The mean was calculated by incorporating results below detection as values of half the detection limit. The table shows that the trace element concentrations at ML exhibited high spatial variability, with standard deviation often of the same order of magnitude as the mean. The typical sandstone concentrations were comparable to ML mean trace element concentrations when considering the large standard deviation. Concentrations of Co, Mn and Sr were higher in ML sediments than typical sandstone.

Table 9. XRF results: majors

SAMPLE	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	LOI (%)	SUM (%)	Assessment
1A	31.7	1.15	0.87	2.58	0.05	1.70	22.6	0.26	0.36	0.22	0.21	37.4	99.0	Carbonates
1B	38.0	0.82	0.94	1.58	0.03	1.99	25.1	0.24	0.44	0.16	0.23	29.8	99.3	Carbonates
1C	12.6	0.31	0.32	5.25	0.02	0.21	2.05	0.14	0.11	0.33	0.25	78.1	99.7	Silicates General
1D	3.04	0.49	0.29	16.9	0.05	0.38	1.19	0.04	0.09	0.06	0.20	76.0	98.7	Silicates General
2	44.2	1.73	1.18	1.60	0.06	1.35	22.5	0.22	0.51	0.22	0.05	25.0	98.5	Carbonates
3	83.4	0.54	2.62	0.71	0.02	0.11	0.44	0.38	1.72	0.06	0.02	9.69	99.8	Silicates General
4	53.5	3.69	1.65	3.30	0.13	0.91	14.5	0.25	0.69	0.24	0.05	20.4	99.3	Carbonates
5	53.8	0.36	1.72	1.12	0.08	1.06	6.66	0.26	1.12	0.42	0.50	32.5	99.6	Silicates General
6	65.8	0.32	1.77	0.61	0.04	0.33	13.2	0.30	1.10	0.15	0.25	16.0	99.9	Silicates General
7A	64.5	0.62	3.80	5.32	0.03	0.22	1.04	0.31	1.08	0.16	0.01	22.3	99.3	Silicates General
7B	88.0	0.70	3.02	1.94	0.02	0.12	0.17	0.39	1.62	0.02	bd	3.08	99.1	Silicates General
7C	92.0	0.61	2.78	0.82	0.01	0.12	0.11	0.41	1.82	0.01	bd	0.93	99.6	Silicates General
8	57.3	1.44	1.66	1.39	0.05	0.99	17.1	0.26	0.83	0.16	0.05	18.8	100.1	Carbonates
S	29.2	1.56	0.94	38.0	0.26	0.14	0.79	0.23	0.49	3.68	bd	23.0	98.3	Silicates General
NA	10.3	0.64	0.56	10.2	0.04	0.18	0.52	0.13	0.16	0.77	0.02	75.4	98.8	Silicates General
NB	28.0	4.59	1.26	20.9	0.18	0.30	0.72	0.18	0.59	1.39	0.01	40.3	98.4	Silicates General

Table 10. XRF trace element concentrations compared with those in typical sandstone

ELEMENT (ppm)	ML sediments mean	ML sediments standard deviation	Typical concentration in sandstone (Drever 1982)
As	6	4	1
Co	14	19	0.3
Cr	36	28	35
Cu	4	5	2
Ga	3	2	12
Mn	381	500	50
Ni	2	2	2
Pb	10	8	7
Rb	30	15	60
Sc	7	3	1
Sr	328	340	20
Th	7	5	5.5
Ti	4517	3465	Major
U	2	1	2
V	31	35	20
Y	14	9	10
Zn	11	10	16
Zr	462	491	220

5.2.3 Soil incubation experiment

The results of XRF major analyses were examined closely for the soils used in the incubation experiment. It was thought that differences in conditions (e.g. pH, ORP) that develop during the experiment and the resultant quality of water samples might be related to the soil composition of each sample. Figure 42 shows the XRF major results plotted for the soils used in the experiment. Soils from 1A and 1B were combined in the experiment to form ExptC, while NA and S were ExptN and ExptS respectively.

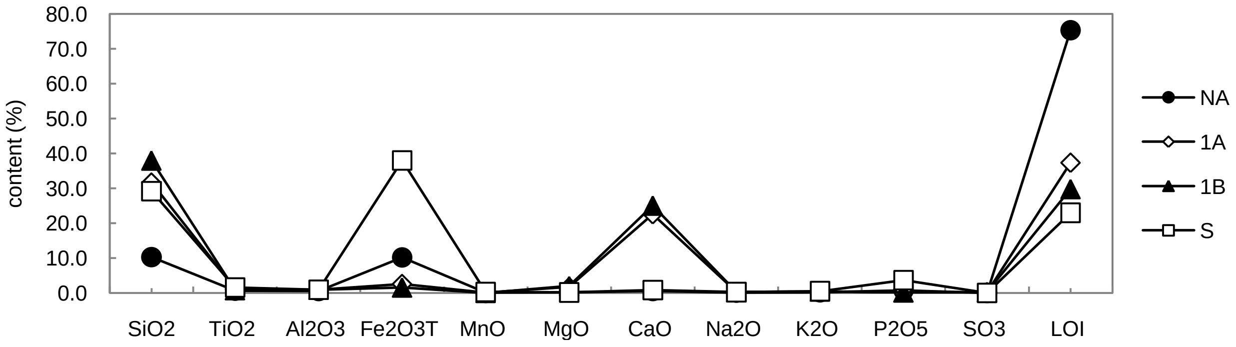


Figure 42. Composition of sediments used in the incubation experiment (from XRF majors results)

ExptC sediments were sandy with high Ca and OM concentrations. ExptN had the highest amount of OM, and contained Fe. ExptS had the highest Fe concentrations, and the least amount of OM.

The results of pH and ORP monitoring of samples over the experiment incubation period are displayed in Figure 43. Water in sample N was acidic and oxic throughout the experiment, while water in samples C and S was neutral but becoming anoxic. Water in sample C became anaerobic at the end of the experiment. The high Ca concentrations in the sediments of sample C may have been associated with carbonates and therefore explain the alkalinity of sample water. All samples contained OM based on LOI results, but the relative percentages of labile and refractory OM may have controlled the establishment of bacteria populations responsible for reduction. Thus, the ORP conditions varied between samples. The difference in pH and ORP conditions in samples was associated with variable chemical results of water analysis (Table 11).

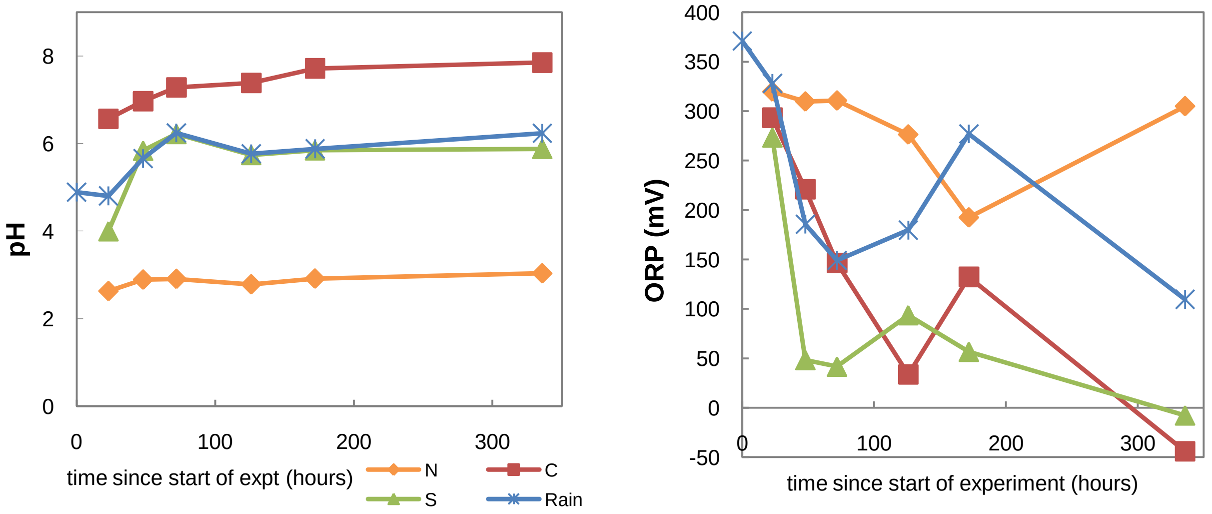


Figure 43. pH and ORP variability between samples during incubation with rainwater

Table 11. Results of water sample analysis from soil incubation experiment

Analyte	Units	ExptN	ExptC	ExptS	ExptR
Al	ppb	≤0.5	10900	≤0.5	35.4
As	ppb	5.56	8.72	2.67	≤1
Ca	ppm	123	140	82.4	1.66
Cd	ppb	0.064	0.389	0.146	0.512
Fe	ppm	2.32	251	45.8	0.876
K	ppm	5.94	26.3	0.471	2.09
Mg	ppb	15500	50800	12000	1630
Mn	ppb	448	6980	7510	8.18
Na	ppm	52.2	74.9	36.4	18.6
Ni	ppb	5.94	35.9	7.71	0.997
Pb	ppb	0.18	3.54	0.233	0.411
V	ppb	1.52	30.6	≤0.1	0.166
Zn	ppb	68.2	398	86.4	158
Acidity	ppm	592	<1	N/A	N/A
Total Alkalinity	ppm CaCO3	<1	246	2	2
SO_4	ppm	1230	158	383	7
Cl	ppm	119	70	55	22

Chemical results of water sample analyses show that ExptC had the highest trace element concentrations for almost all measured parameters. Concentrations of Al, Fe, Ni, Pb, V and Zn were at least one order of magnitude higher in ExptC water than other water samples. The dominant process for the mobilisation of these contaminants appears to be Fe-oxyhydroxide reductive dissolution. Under reducing conditions, Fe is used as an oxidant and Fe-oxyhydroxides become dissolved, releasing sorbed metals. The conditions were reducing in ExptC, and Fe levels were high in the water sample. Conditions became anoxic in ExptS, and chemical results show that Mn levels became elevated, possibly due to Mn reduction.

5.3 Acidic discharge from ML

Discharge volumes calculated in the water balance can be combined with water quality data to estimate the quantities of contaminants discharged from ML at Minni S. Discharge volumes were summed and pH readings averaged to estimate monthly discharge of sulfuric acid, using a published method (Sammut, White & Melville 1996). The mean pH of discharge waters through Minni S in 2009 over the June to September period was 2.44, which equates to a sulfuric acid concentration of 1.8 mol m^{-3}. Table 12 summarises the results, and allows comparison of 2008 and 2009 acid discharge volumes. The pH of drain water at Minni S was slightly more acidic in 2009 than 2008, but the large flow volumes in 2009 resulted in larger quantities of sulfuric acid being discharged. For example, the estimated mass of sulfuric acid discharged in July and August 2009 was more than double the 2008 estimate. Given that the majority of discharge occurs between June and September, the monthly discharge quantities calculated for 2009 and presented in Table 12 may be summed to produce a conservative estimate of annual sulfuric acid export from ML of 21.9 tonnes.

Table 12. Monthly estimates of acid discharged from ML, wet seasons 2008 and 2009

Note: nd indicates no data was available

H_2SO_4 discharged (t)	2008	2009
June	nd	3.9
July	3.3	9.3
August	2.8	6.0
September	2.7	2.7
October	0.7	nd

Water quality data for Minni S grab samples from June, July and September 2009 were used to calculate the masses of Al and Fe discharged (Table 13). Previous work at this site, presented by Boland (2009), involved the use of a water balance and water quality data to determine the relative importance of water balance components as sources of acid and aluminium. These calculations have not been extended by the current study, because it is believed that complex reactions occur in the wetland sediments through which groundwater discharges, meaning that simple “concentration multiplied by volume” estimates may not be valid. Instead, the quantities of Al and Fe discharged at Minni S over three months in the wet season have been calculated.

The results in this subsection provide order of magnitude estimates of the severity of environmental impact on downstream ecosystems. These estimates may be used by future researchers to gain funding for rehabilitation at the ML site.

Table 13. Estimates of quantities of Al and Fe discharged from ML, wet season 2009

2009	Al (kg)	Fe (kg)
June	146	5188
July	280	9892
September	37	2691

6 Discussion

6.1 Wetland hydrology

6.1.1 Water balance limitations

Daily rainfall, water levels at gauging stations, and calculated wetland water level (H_2) time series are shown for comparison in Figure 46. Table 14 shows a comparison between the winter rainfall of 2008 and 2009. Data from between June 1 and August 31 each year were used to calculate the values in this table. Although the total winter rainfall is significantly greater in 2009, the wetland water levels and outflow at gauging stations do not appear to differ significantly between years (Figure 46). As noted in the methodology section 4.2, the velocity probes were installed at the gauging stations on June 19, 2009. The largest rainfall event in the 2009 winter occurred on June 16, but due to interpolation of velocity and level data between May 22 and June 19, the time series do not capture the flood event, and this is one limitation of the water balance.

Table 14. Comparison of 2008 and 2009 winter rainfall

	Total winter rainfall (mm)	**Maximum daily rainfall (mm)**
2008	304.9	31.4
2009	466.8	40.8

The water balance results are not fully supported by field observations, which suggest that 2009 was a very wet year for ML. Indeed, water at the southern end of the site flooded the access road. This was never known to occur in 2008 (D. Boland, pers. comm.). A blockage of the culvert under the road near Minni S is thought to be responsible for this anomaly. Results indicate that the maximum daily surface outflow rate from the drain occurred in winter 2008. The velocity and level probes for the Minni S gauging station are set up in the culvert on the south side of the road. Water that passes through the culvert usually flows south, and the drain continues for approximately 3 km further south before discharging water to the ocean. The level recorded at Minni S is not affected by flooding of the land upstream, on the northern side of the access road, and thus does not give an accurate representation of ML water level during flood. Field observations of surface water ponding on the northern side of the access road at Minni S indicate a steady increase in wetland water level but this is not supported by Minni S level data (Figure 46). Figure 44 is a photo taken from approximately 100 m east of Minni S, looking west along the access road. The ISCO autosampler is visible as a grey dome at the end of the road. Flooding of the road and the wetland is clearly visible.

Figure 44. Surface water ponding at southern end of ML with flooded access road (22/08/09)

Figure 45. Surface water ponding at southern end of ML, adjacent to road between bores 5 and 6 (01/08/09)

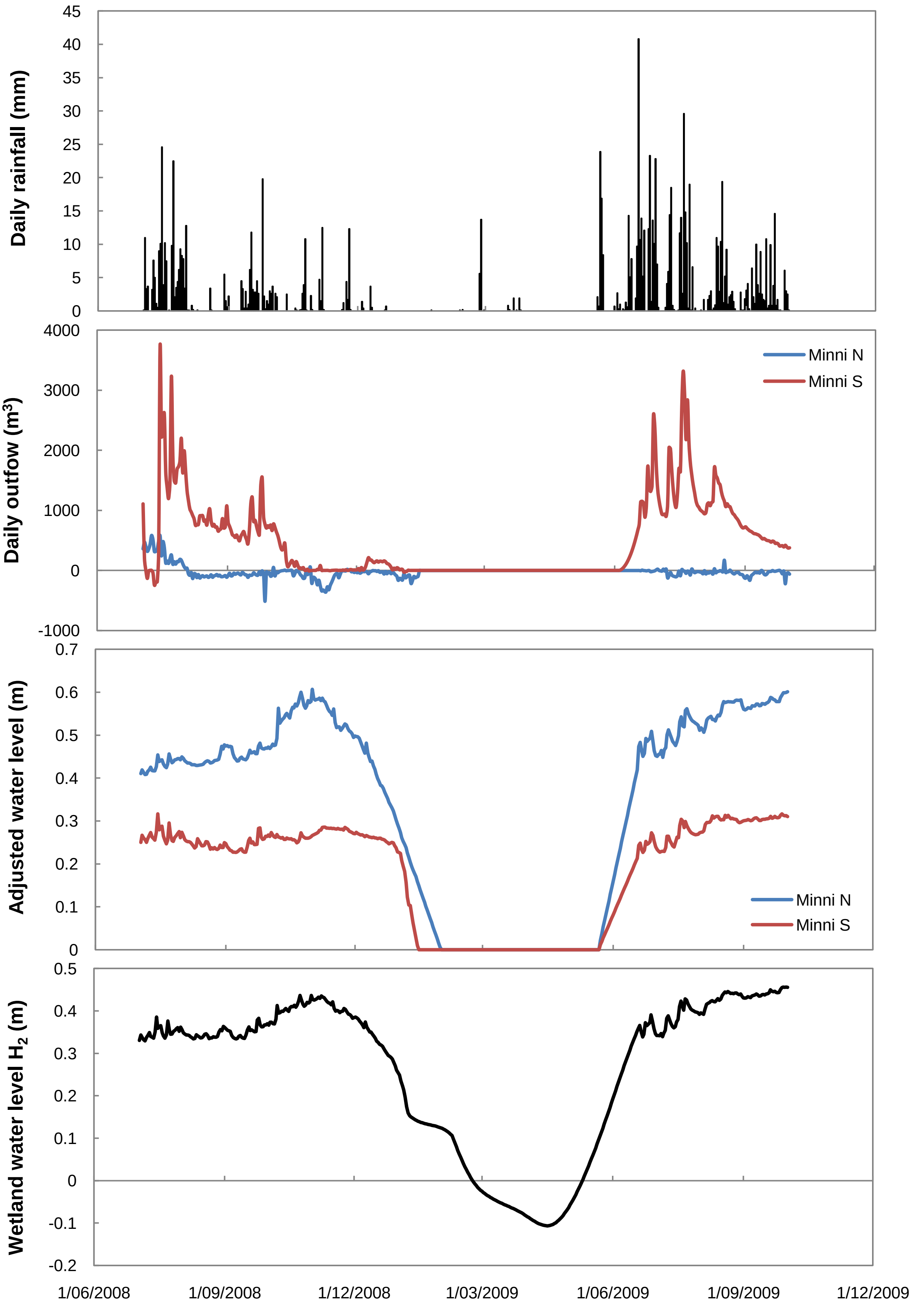


Figure 46. Rainfall, outflow and water level at gauging stations and wetland water level as daily time series

Minni N water levels do not appear to be significantly higher in 2009 either (Figure 46). This is thought to be because the site topography causes surface water to flow in a general southerly direction. This leads to either flow offsite via the drain at Minni S, or flooding of the land at the southern end of ML. The topography causes low-lying areas to collect water during wet periods. This was observed in the field, and Figure 45 shows an example of surface water ponding in ML, north of the access road between bores 5 and 6.

The water balance estimations are limited by the difficulty in estimating ML topography. The size of the basin that fills up during wet periods is a key parameter for the estimation of rainfall, groundwater discharge, and evaporation. The water balance uses crude estimates of ML surface area to determine volumetric values for rainfall and evaporation. In reality, the surface area changes seasonally as individual pockets of land fill with and empty of water. The estimate for groundwater discharge in the water balance assumes that ML is a long basin that receives water by horizontal flow through a seepage face, which is defined as the width of the shore between the wetland bed and surface water level. In reality, the site consists of many low-lying areas that may become small ponds. Ponding occurs when the groundwater level intersects the surface, or when rainfall collects in the basins and fails to infiltrate due to waterlogged sediments or low hydraulic conductivity.

6.1.2 Conceptual hydrologic model for Muddy Lake

Rainfall has been described as the lifeblood of wetlands (Semeniuk 2007). It recharges groundwater in the surrounding sands, which causes the water table to rise and intersect the ground surface in low-lying pockets of land (Semeniuk 2007). The current study has shown the hydrologic dominance of rainfall and evaporation by calculation of a wetland water balance.

Field observations and water balance data have allowed a conceptual hydrologic model to be established. The dominance of components of the water cycle varies over the seasons, which cause changes in the various water stores. As temperatures and evaporation begin to decline in autumn and early winter, rainfall infiltrates the sandy soils of the land around ML. Water that falls directly on the wetland probably ponds on the surface, as infiltration is limited by the low conductivity of the peaty sediment. As the wet season continues, rainfall recharges the groundwater store and the water table rises. Water collects in the wetland basin by a combination of rainfall and groundwater discharge, which occurs once the water table has risen above ground. The wetland remains inundated and water storage increases over the wet season, although some water is lost via drain discharge offsite. In spring and summer, rainfall eases as air temperature and solar radiation increase. The wetland water level falls as wetland plants grow and evapotranspiration losses become significant. Over the dry season, evaporation dominates and the water table falls below ground, causing groundwater discharge to halt due the loss of the seepage face.

The results of this study show that inter-annual rainfall variability has implications for the position of the water table and the extent and duration of surface water ponding. The wet season of 2009 was far wetter than 2008, and the water table responded accordingly. The extent of surface water ponding increased over the study site. These inter-annual rainfall variations also have implications for dry season hydrology. The period of wetland inundation may be extended in wet years, and the water table may not fall to the same depth as in preceding years. The following winter, groundwater stores may recharge more quickly and surface water ponding may occur earlier in the season.

6.2 Wetland geochemistry

6.2.1 Acid production

Surface water was drained from ML via drain discharge at Minni S. The flow through Minni N was negligible, and surface water flow between the study site and surrounding lowlands is prevented by road embankments along the northern and southern property boundaries. The pH of water at Minni N was frequently higher than at the discharge point at Minni S. This suggests that the ML wetland may act as a source of acidity, and water that collects in the basin over the wet season is acidified by sediment-water interactions.

Previous research at ML, including chemical testing of bore logs, has indicated the presence of potential and actual acid sulfate soils at the study site (Boland 2009). In particular, sediments from deep in the Bore 1 log show large potential for acidification. This suggests that the deep wetland sediments may be anaerobic enough to cause metal sulfide production and the sequestration of metals from discharging groundwater. Monitoring of groundwater has shown that acid may be produced seasonally, such as in the groundwater from Bore 3. In contrast, water from Bore 7 was permanently acidic. Groundwater has been found to discharge into the wetland during winter, particularly from the inland side, where bores 3 and 7 are located. Surface water in ML was consistently acidic. Rain recharges groundwater and causes acidic water to discharge to the wetland. Rain falling directly on the wetland dissolves acidity products stored in surface sediments over the dry season. In summer, the wetland sediments are dry and coated with orange and yellow crusts of iron and aluminium oxides, common in CLASS landscapes and listed as visual indicators of lake acidification in the recent Western Australian draft treatment and management guidelines (Contaminated Sites Branch: Environmental Regulation Division 2009). These precipitates are deposited when surface water evaporates and salts are concentrated on surface sediments. Although groundwater may not discharge to the wetland in summer through a seepage face, evaporation of surface soil moisture (bare soil evaporation) may cause upward flux of acid groundwater through capillary action, and acidity products are then deposited on the surface as upward travelling water evaporates.

Bushfire is thought to have caused vegetation and detritus loss from the wetland near Minni N (A. Lillicrap pers. comm.), which has exposed the soil to seasonal oxidation and acidification. Fire is one of a range of factors which have been identified as contributing to vegetation loss leading to acid sulfate soil scalding in New South Wales (Rosicky et al. 2004). After initial vegetation loss occurs, acid sulfate soils become oxidised and acidity products accumulate in the surface sediments in the dry season. The acidity and elevated trace metal concentrations are phytotoxic and vegetation cannot return to the area (Rosicky et al. 2004). Scalded surface soils were present in many areas of the ML study site, and were found to be particularly prone to surface water ponding in the wet season, and water was usually acidic. The bare soil may be easily eroded and so scalded areas become depressions in the landscape, which in turn leads to surface water ponding in the wet season.

6.2.2 Mobilisation of metals and trace elements

Contaminants were mobilised in groundwater with low pH, reducing conditions, or when water table rise caused dissolution of accumulated salts.

Acidic groundwater is common in CLASS landscapes and elevated trace element concentrations are known to occur in acidic conditions (Contaminated Sites Branch: Environmental Regulation Division 2009). In the current study, the groundwater from acidic groundwater bores had the highest concentrations of trace elements. The seasonal release of acid in Bore 3 was associated with mobilisation of Al and Ni.

The sediments below the wetland were Fe and OM-rich, and incubation experiments revealed storage of trace elements. The Fe-oxyhydroxides and OM in these sediments may bind metals and improve water quality of groundwater before it is discharged into the wetland. However, under reducing conditions, Fe-oxyhydroxides dissolved and metals were released. It is possible that the experiment duration was not sufficient to cause formation of insoluble metal sulfides.

Close to the surface, wetland plants affect contaminant cycling. Plants transport oxygen from the air to the root zone and this causes sediment oxidation and the formation of Fe hydroxides. Iron plaque was observed on wetland plant roots in ML, which have recently been reported to be a significant sink for arsenic in wetlands (Keon 2002).

Similar to the "first flush" phenomenon reported in the CLASS floodplains of eastern Australia (e.g. Green et al. 2006), dissolution of accumulated salts in surface sediments was found to cause elevated trace element concentrations in groundwater at ML. When the water table rose to a level higher than was reached in the preceding wet season, significant mobilisation of contaminants occurred.

Extremely wet seasons may mobilise contaminants stored in sediments near the surface, while drought may cause oxidation of sediments that are usually waterlogged. Inter-annual variability of the wetland water balance may be a significant factor in trace element mobilisation.

6.3 Environmental impacts of degraded wetlands

Estimations of acid and metal discharge from ML were calculated in this study. Using the conservative estimate of annual sulfuric acid production and the area of ML, a rate per area of annual production may be calculated. The area of ML is approximately 30 ha, and with a conservative estimate of annual sulfuric acid discharge of 21.9 t, the rate of production is 700 kg H_2SO_4/ha/yr. This is high compared to estimates of CLASS floodplain acid production in NSW: 100-200 kg H_2SO_4/ha/yr for the Tweed River floodplain; and 200-300 kg H_2SO_4/ha/yr for the Richmond River (White et al. 1997).

Freshwater guidelines may be used to assess the potential for discharge waters to be toxic to downstream ecosystems. The trigger value for Al in freshwater environments with pH < 6.5 is 0.8 µg L^{-1} (ANZECC 2000). The water discharged from ML had Al concentrations greater than 6 mg L^{-1}, of the order of 1,000 times greater than the trigger value. The guidelines state that Al in acidic environments is toxic to fish, invertebrates and amphibians.

The presence of highly acidic stagnant water is conducive to mosquito breeding. Mosquito larvae are acid tolerant and were abundant in surface water at ML. Furthermore, mosquitoes were present in swarms on the site in spring. The abundance of mosquito larvae in lakes has been identified as a visual indicator of acidification (Contaminated Sites Branch: Environmental Regulation Division 2009), and has implications for the spread of mosquito-borne diseases such as Ross River virus.

The current study has quantified the export of acid and toxic Al offsite. At the current level of contamination, the site can be classified as severely degraded and a risk to the environmental health of downstream ecosystems. The incidence of CLASS and disturbed wetlands on the SCP indicates that the potential for coastal environmental impacts is extreme. The topics of management and remediation of acid sulfate soils have received significant attention in recent years, with the publication of a number of government guidelines (e.g. Contaminated Sites Branch: Environmental Regulation Division 2009; National Working Party on Acid Sulfate Soils 2000).

6.4 Management and remediation options

Although the management and remediation of CLASS landscapes was not the focus of this study, a brief discussion of current best management practices and their appropriateness to the landscape studied is warranted. This study focussed on the impacts of hydrology and geochemistry of a CLASS-affected wetland on discharge water quality. Improved understanding of the mechanisms for acid production and contaminant release in this environmental setting will enable management and remediation strategies to be applied appropriately.

The draft WA guidelines for the treatment and management of soil and water in acid sulfate soil landscapes were released in January of this year. The guidelines include a section on the treatment of acidic drains and lakes.

- Where drains have been installed to depths below sulfidic layers, redesigning the drainage system is recommended. If drainage of the land is still necessary, drains can be widened and made shallower so that sulfidic layers remain covered, but the hydraulic capacity is not compromised.
- Aerobic wetlands may be used to treat acidic discharges that have high iron content. These are commonly used in AMD settings. The concept is the removal of dissolved metal species by the production of oxides. The water depth in the wetland is maintained at less than one meter deep, and reeds are planted to slow water flow through the wetland and oxidise sediments. The oxygenated water causes precipitation of iron oxyhydroxides.

- Compost wetlands are an alternative option, where a rich organic substrate is used to encourage the development of reducing conditions. As sulfate is reduced to sulfide, acidity is removed. Metals are precipitated as sulfide minerals, and Al precipitates on the surface as its hydroxide. The wetland must be cleaned out periodically, and sediments must be handled carefully to avoid oxidation of the sulfides.
- Limestone drains may be used to increase alkalinity of waters. Crushed limestone is cheap and may be a viable option in many CLASS landscapes if limestone is readily available nearby. Iron oxyhydroxides may precipitate and coat the limestone, reducing its effectiveness, and so anoxic conditions are often preferred. The limestone drain may be buried beneath a layer of soil so that water flows through the limestone underground, in anoxic conditions, and alkalinity is increased effectively.
- A combination of compost wetland and limestone drain may be used, known as a "reducing and alkalinity producing system". Water infiltrates through a compost layer, reducing iron, and then passes through a subsurface limestone layer before being discharged downstream.

The methods outlined above focus on two favourable outcomes: neutralised water, and the production of metal sulfides. In CLASS landscapes, to return of the land and water to these conditions is to return the landscape to its undisturbed state.

The laboratory experiment presented here on ML sediments showed that reducing conditions caused release of metals and trace elements, possibly through the reduction of Fe-oxyhydroxides. This suggests that many of the remediation methods above that use anoxia to treat discharges may be inappropriate for ML. However, it is suggested that the current conditions at ML may not be conducive to sulfide production because of the seasonal variations in hydrology and ORP. White et al. (1997) state that four conditions are necessary for sulfide formation in CLASS landscapes: a supply of sulfate; easily decomposed OM; Fe-rich sediments; and reducing conditions with reducing microbes. The ML wetland meets the criteria in winter, but conditions are oxic in summer. One of the recognised reaction mechanisms for the production of sulfides is known to occur slowly (White et al. 1997), and sulfides may not have time to form over the winter period at ML. Furthermore, any that are produced are oxidised in the following summer. Seasonal oxidation and reduction of sediments due to cyclic wetland hydrology has been identified as preventing metal sulfide formation elsewhere (Olivie-Lauquet et al. 2001). One appropriate remediation strategy for ML may be to alter the hydrology to ensure that reducing conditions are permanently maintained in the wetland. Addition of lime and compost to the wetland sediments before re-flooding may help to ameliorate acid and metal production. Altering the site hydrology, for example by backfilling drains, and returning the wetland to a more natural hydrologic regime would both increase the likelihood of insoluble sulfide formation, and prevent the export of acid and contaminants offsite.

7 Conclusions and Recommendations

This study combined field and laboratory investigations with a water balance to elucidate the seasonal dominance of the hydrologic components and their affect on wetland geochemistry. The study site is severely degraded, with acidic surface scalds, vegetation exclusion and seasonally acidic and contaminated surface water, which is a breeding ground for mosquitoes but does not appear to support a healthy ecosystem. Concentrations of some elements are considered toxic and the discharge of water offsite may be affecting the downstream environment.

The seasonal wetland water balance gave results that correlated with field observations:

- in winter, rainfall is the major input and drain flow is the major output
- in spring, rainfall and groundwater discharge both contribute to input water, while evaporation is the dominant output
- in summer, groundwater is the major input and evaporation the dominant output, as the water level falls below the surface, and
- in autumn, inputs are low but dominated by rainfall, whilst evaporation is the only output.

Water balance calculations also allowed for estimation of the annual export of acidity, which was higher than for extensively studied CLASS floodplains of NSW.

Trace element mobilisation was found to occur under acidic, reducing, or flood conditions. The mechanisms for release are different and cause spatial and temporal variability of water quality over the study site. Groundwater was identified as the original source of acidity, produced through iron sulfide oxidation. Groundwater discharge to the wetland and low-lying areas of the site caused transport of acid and trace elements. Wetland sediments were identified as potential stores for contaminants, but the currently seasonal oxidation and reduction cycles are preventing sequestration of trace elements in surface soils by the formation of metal sulfides. Instead, metals are probably being bound temporarily to Fe-oxyhydroxides and being precipitated as oxides on surface sediments in dry periods. Thus, they are re-mobilised in the following wet season. Inter-annual variability of hydrology was related to differences in water quality between the two wet seasons studied.

The elucidation of acidity generation mechanisms and a review of recent draft WA guidelines have allowed for a discussion of appropriate remediation strategies. At this stage, it is recommended that backfilling of drainage and application of compost to scalded wetland sediments may allow for the maintenance of permanently anaerobic conditions, which would encourage metal sulfide minerals to form. Sulfide minerals are a relatively permanent store of trace elements, and their production may reduce the toxicity of wetland surface water.

However, additional research is required that would ensure the efficacy of future remediation efforts. The role of refractory and labile OM in trace metal mobilisation and mineral cycling in sediments has been identified as an important factor, and warrants detailed research. The affect of inter-annual hydrologic variability has also been identified as a control of redox conditions in the wetland sediments. This site should be studied long-term to assess for example the impact of periods of extreme weather conditions such as drought or flood. Even in the case that the site is remediated, the study of the wetland hydrology should be continued, both to assess the effect of remediation, and to increase scientific knowledge of the acid and metal dynamics of SCP wetlands. To model the rise of the water table and assess the interaction of ponded surface water with groundwater discharge, it is suggested that the installation of monitoring bores in seasonally inundated locations may be appropriate. For example, two more bores could be added to the monitoring program: one in the north of ML between Bore 7 and Minni N, and one in the south in an area known to accumulate water in winter, such as the area between Minni S and Bore 5. These could be monitored until the surface water ponding occurred, to determine if the surface and groundwater is ever disconnected. This is possible due to the low hydraulic conductivity of peaty wetland sediments. The disconnection of ground and surface water has implications for the redox conditions in surface sediments and the flux of contaminants to surface water early in the wet season.

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Appendix A: Field notes

27/03/09 site visit for groundwater monitoring and surveying

7.30-10.30am

Laura Ellis, Daniel Boland

Bore	Depth (m)	pH	ORP (mV)	EC (uS/cm)	Temp (C)
ML01	1.36	7.11	24	563	20.4
ML02	2.81	7.1	-48	660	19.9
ML03	1.82	4.43	181	1210	23.6
ML04	2.45	7.33	102	1127	19.9
ML05	1.62	6.87	-170	2228	19.8
ML06	1.46	6.79	-96	815	22.5
ML07	1.11	3.79	226	2160	23.4
ML08	2.57	-	-	-	-

below ground

Notes:

Bore 8 completely dry

Bore 4: orange flocs in water

Bore 5: very silty

10.30 am - 2pm

Laura, Daniel, Adam Lilicrap, Carolyn Oldham, Azra Mat Daud, Bibhash Nath, Vera (dept of ag) and Suzie (Curtin)

SITE TOUR

sediment in wetland (dry) behind Mini N is oxidised.

- evidence of bushfire, may have caused removal of organics, rapid oxidation of sulfidic sediments - scalds
- surface soil stained shades of red/orange due to iron mineral precipitation
- hole dug to ~1m and soil taken from near surface and at depth

vegetation near Mini S /drain was discussed:

- couch grass in channels, handles acidity/salinity
- kikuyu grass grows higher up banks, doesn't like acidity
- peppermint trees like calcite (look for them near dunes)
- maleleuca (paperbark) trees like waterlogged soils
- eucalypts don't like acidity

visited 5 mile brook, north of site, until locked gate (water corp)

surface water sample was tested

EC	1217	uS/cm
pH	7.15	
ORP	75	mV
temp	25	deg C

2pm-5pm
Laura, Daniel, Azra
SURVEYING BORES/GAUGING STATIONS
all surveyed using dumpy/staff
direction: bore 5, Mini S, 4, 2, 8, Mini N, 1
surveying finished following day

results:

bore	height of casing above ground	relative ground level
1	0.496	-0.5
2	0.72	1.16
3	0.481	0.54
4	0.483	0
5	0.49	0
6	0.471	0.43
7	0.561	-0.21
8	0.482	0.92

28/03/09 site visit to finish surveying, bore testing
7.30-10.30am
Laura, Daniel, Azra
SURVEYING
1, 3,6,5 then 3 to 7

BORE TESTS
logger/capacitance probe used
1L water added to bore with capacitance probe inside at depth of WL
logger recorded head drop over ~5 minutes
bores 2,3 were tested with water bailed from bore, all others with DI or tap water
bore 8 not done - dry
Daniel to calculate K's based on these tests.

16/04/09 site visit for groundwater monitoring

Laura, Daniel
weather: fine, sunny

bore	depth (TOC, m)	Height of casing	Depth BGL	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)
ML01	1.89	0.496	1.394	7.35	83	523	23.7
ML02	*3.4*	*0.72*	*2.68*	6.96	-33	643	24
ML03	2.37	0.481	1.889	4.3	174	1248	23.7
ML04	3.01	0.483	2.527	7.33	115	1101	22
ML05	2.12	0.49	1.63	6.71	-151	1996	20.6
ML06	1.93	0.471	1.459	6.68	-118	628	23.3
ML07	1.67	0.561	1.109	3.78	228	1916	22
ML08	3.08	0.482	2.598	-	-	-	-

bore 8 level uncertain due to very low water level
bore 4 very orange with flocs
bore 6 hard to filter, taken back to lab for non-acidified sampling

note	probably forgot to add 0.2 for plopper when measuring heights, adjusted in computer plots

23/05/09 site visit for groundwater monitoring, soil sampling

Laura, Siddarth, Bibhash
weather: cold, cloudy, previous couple of days wet

bore	depth (TOC, m)	Height of casing	Depth BGL	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)
ML01	1.68	0.496	1.184	6.9	-108	529	19.3
ML02	3.26	0.72	2.54	6.61	-64	942	20.6
ML03	2.1	0.481	1.619	3.93	193	1526	19.7
ML04	3.3	0.483	2.817	6.83	-38	1278	18.3
ML05	1.71	0.49	1.22	6.6	-120	2240	18.1
ML06	1.73	0.471	1.259	6.47	-9	409	19.1
ML07	1.39	0.561	0.829	3.64	254	1927	19.2
ML08	3.14	0.482	2.658	-	-	-	-

bore 8 nearly dry
water in drain and just starting to flow

hole dug near bore 7 (5m40cm NE of bore)

A	20 cm	black organic rich sand	sampled
B	34 cm	coarse sand mottled grey with orange brown	sampled
C	46 cm	dark grey coarse sand, organic rich	sampled

15/06/09 site visit to start autosamplers, groundwater monitoring, soil sampling

Laura, Siddarth
weather: fine

bore	depth (TOC, m)	Height of casing	Depth BGL	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)
ML01	1.28	0.496	0.784	7.28	-75	646	19.2
ML02	3.21	0.72	2.49	7.23	-65	582	21.7
ML03	1.99	0.481	1.509	4.2	210	2500	17.9
ML04	2.99	0.483	2.507	7.34	-61	1157	19.1
ML05	1.6	0.49	1.11	6.86	-123	2163	17.1
ML06	1.64	0.471	1.169	6.78	-22	490	18.3
ML07	1.26	0.561	0.699	4.03	240	2096	18
ML08	2.97	0.482	2.488	-	-	-	-

not enough water in bore 8 to get sample
started autosamplers and took grab samples

	level (height board, m)	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.261	2.86	369	3890	13.9	water not flowing - appears stagnant
Minni S	0.17	2.93	501	3560	15.9	water flowing south

profile hole dug near bore 1 (5 m NE of bore, off road, just inside wetland)

O	15 cm	grass/root zone	
A	8 cm	black organic rich sand	sampled
B	6 cm	brown sand	sampled
C	10 cm	semi-saturated dark grey, organic rich	sampled
D	67 cm	saturated black organic rich	sampled

24/06/09 site visit for soil sampling

Laura, Siddarth
weather: raining, cold, overcast, storms for previous few days

Profile hole dug near the drain and Minni S (approx 20 m north of Minni S, within 5 m of drain)
very hard to dig due to hard lumps, gravel or hard peat
water level almost at surface, hole kept filling with water
dug to ~0.4 m and took sample under root zone
soil was dark brown mud with hard lumps

water level in drain 0.25m at minni S

Profile hole dug near bore 7 (~3 m to SE of bore)

A	10-15 cm	dark organic rich sandy loam, roots	sampled
B	13 cm	dark coarse sand, roots	sampled
C	65 cm	grey coase sand, orange mottles, water level 20 cm from bottom of hole	sampled

surface soil (top 10 cm) samples taken from near each bore (within 3 m) not already sampled

bore	where sample taken
2	just east
3	just west
4	just south
5	just east
6	just west
8	just west

11/07/09 site visit for ground/drain water monitoring

Laura, Daniel
weather: fine, cold

bore	depth (TOC, m)	Height of casing	Depth BGL	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)
ML01	1.04	0.496	0.544	7.24	-72	576	18.4
ML02	2.9	0.72	2.18	7.26	-26	580	20.2
ML03	1.46	0.481	0.979	4.8	197	726	17.3
ML04	2.66	0.483	2.177	7.37	106	1115	18.5
ML05	1.17	0.49	0.68	6.51	-100	3040	17.5
ML06	1.06	0.471	0.589	6.64	-32	637	18
ML07	0.85	0.561	0.289	3.13	377	3720	16.5
ML08	2.7	0.482	2.218	7.3	72	1633	19.1

GRAB SAMPLES	level (height board, m)	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.505	3.05	480	3640	13.2	water not flowing - appears stagnant
Minni S	0.27	3.05	425	3850	14.5	water flowing south

ON SCREEN	level (m)	pH	velocity (mps)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.469	2.3	-0.02	3836	12.7	
Minni S	0.16	2.4	0.36	4113	?	temp not noted

notes: drove along drain, doesnt flow until halfway along southern half
ML may be more of a lake - the drain doesnt appear to stop water ponding

	height board - ISCO height
Minni N	0.036
Minni S	0.11

01/08/09 site visit for drain/suface water sampling

Laura, Bibhash
weather: fine, sunny, warm

bore	depth (TOC, m)	Height of casing	Depth BGL
ML01	1.026	0.496	0.53
ML02	2.72	0.72	2
ML03	1.46	0.481	0.979
ML04	2.4	0.483	1.917
ML05	1.2	0.49	0.71
ML06	1.02	0.471	0.549
ML07	0.86	0.561	0.299
ML08	2.362	0.482	1.88

did not bail bores due to time restrictions

GRAB SAMPLES	level (height board, m)	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.53	2.75	485	2970	13.2	taken directly from drain
Minni S	0.275	2.91	477	3290	17	taken directly from drain

ON SCREEN	level (m)	pH	velocity (mps)	EC (uS/cm)	temperature (deg C)	notes
Minni N		2.6	0	3508	11.1	level on screen not noted; water appears stagnant and connected to lake
Minni S	0.172	2.4	0.18	3634	14.6	

	height board - ISCO height
Minni N	?
Minni S	0.103

Surface water sampled around site - physical measurements (map shown in Figure 13, page 34)

SURFACE SAMPLES	where	EC (uS/cm)	temperature (deg C)	pH	ORP (mV)	notes
S1	waterlogged area with some surface water ponding, sulfidic smell	10200	13.8	6.85	-70	measured in field; smells sulfidic
S2	small pond (approx 10x4 m) 10-20 m north of S1, orange colour, orange algae/ooze	2730	15.2	2.97	387	measured in field; no sulfidic smell, lighter colour than S1
S3	in north half of ML - vegetation dead or dying, water appears orange/red, sediment is orange with cracks which show darker red sediment at depth, very muddy, sticky like quicksand	3190	22.4	2.69	493	measured in field; high temp - been in sun
S4	exposed ponded area north side of road, 20 m east of bore 1	4880	9.9	3.22	nm	measured in lab; smells sulfidic, mosquito larvae
S5	opposite side of road from S4, vegetated area with ponded water	3780	9.9	3.24	nm	measured in lab; no smell, no larvae
S6	between minni S and bore 5, ponded water	3760	10.2	3.11	nm	measured in lab
S7	between bore 5 and 6, ponded water	3010	10.6	3.09	nm	measured in lab
S8	drain water sample from halway along southern half of drain	2890	10.8	2.92	nm	measured in lab
S9	waterlogged area just W (into vegetation) near bore 7	4490	11.4	3.16	nm	measured in lab

nm: not measured in lab because it was thought that samples would have been exposed to O2

field notes:

walked to edge of property near minni N - road running along fenceline in neighbouring property, blocking drain/surface flows

water is flowing (trickling) N to S through the culvert under the central access road splitting ML in two

22/08/09 site visit for ground/drain water monitoring

Laura, Azra
weather: cold, showers, cloudy

bore	depth (TOC, m)	Height of casing	Depth BGL	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)
ML01	0.98	0.496	0.484	7.06	-92	2490	17.1
ML02	2.65	0.72	1.93	7.35	-5	771	17.9
ML03	1.41	0.481	0.929	6.68	88	412	15.9
ML04	2.3	0.483	1.817	7.7	63	1217	16.8
ML05	1.13	0.49	0.64	5.86	16	4140	15.8
ML06	0.92	0.471	0.449	6.86	-37	712	16
ML07	0.83	0.561	0.269	3.02	316	3020	14.9
ML08	2.35	0.482	1.868	7.54	169	1331	17.1

GRAB SAMPLES	level (height board, m)	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.575	3.72	231	3740	14.9	
Minni S	0.3	2.79	458	3000	16	

ON SCREEN	level (m)	pH	velocity (mps)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.539	2.9		3791	13.5	
Minni S	0.212	2.5	0.13	3399	15.2	error occurred during sampling, half the ISCO bottles look like they only have 1 sample

	height board - ISCO height
Minni N	0.036
Minni S	0.088

Azra sampled small orange lake (S2 from previous trip), another site inside ML near minni N, and S6 from last trip

11/09/09 site visit for ground/drain water monitoring

Laura, Azra, Bibhash
weather: overcast

bore	depth (TOC, m)	Height of casing	Depth BGL	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)
ML01	0.96	0.496	0.464	7.19	-47	2690	17.6
ML02	2.74	0.72	2.02	7.25	-14	836	19
ML03	1.54	0.481	1.059	6.56	51	603	16.3
ML04	2.31	0.483	1.827	7.52	105	1187	17.1
ML05	1.08	0.49	0.59	6.29	18	3470	15.7
ML06	0.96	0.471	0.489	6.88	10	744	17.2
ML07	0.88	0.561	0.319	3.19	319	329	16.7
ML08	1.12	0.482	0.638	7.45	154	1441	17.7

hand pump broke on first bore, samples filtered in lab. All samples for metals acidified onsite

GRAB SAMPLES	level (height board, m)	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.59	3.63	256	3190	15.8	
Minni S	0.31	3.01	461	2800	15.5	

ON SCREEN	level (m)	pH	velocity (mps)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.545	2.6	-0.04	3201	14.5	examined veg in drain for iron rust, took photos
Minni S	0.206	2.5	0.08	3008	14.6	

	height board - ISCO height
Minni N	0.045
Minni S	0.104

Field notes:

Water ponded on road at Minni S, possibly water from ML being transported offsite via overland flow.

3/10/09 site visit for ground/drain water monitoring

Laura, Azra
weather: fine, ~20 deg C

bore	depth (TOC, m)	Height of casing	Depth BGL
ML01	0.95	0.496	0.454
ML02	2.75	0.72	2.03
ML03	1.61	0.481	1.129
ML04	2.32	0.483	1.837
ML05	1.25	0.49	0.76
ML06	1.1	0.471	0.629
ML07	0.97	0.561	0.409
ML08	2.32	0.482	1.838

GRAB SAMPLES	level (height board, m)	pH	ORP (mV)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.59	3.14	457	1633	17.9	took grab sample 1 hour after screen reading to validate high pH
Minni S	0.32	2.87	502	2660	19.3	temp discrepancy prob because grab samples removed from water body, placed in sun on car while readings taken

ON SCREEN	level (m)	pH	velocity (mps)	EC (uS/cm)	temperature (deg C)	notes
Minni N	0.561	5.4	-0.06	4125	15.7	pH, EC may have drifted, autosampler samples discarded
Minni S	0.21	2.4	0.05	2844	15.4	autosampler samples discarded; looked for the culvert under road from north side, appears to be blocked. Lots of algae and sediment buildup, can’t find culvert, water very high (~0.75 m - measured with broomstick) compared to south side (~0.5 m - may have eroded past base of height board due to water flow?)

	height board - ISCO height	average difference
Minni N	0.029	0.0365
Minni S	0.11	0.103

notes from field:
lots of water in drain at minni N and S and near bore 1 (high level)
possibly less water in ponding sites along road joining minni S and bore 6
very noticeable veg growth all over site, long grass everywhere

Appendix B: Notes on chemical analyses by AAC

Analyses were carried out without dilution except for sample 260809 ExptC, 260809 ExptN, 260809 ExptS and 110909 MiniN which were diluted 10 fold.

Ca, Fe, K and Na were analysed by a Varian Liberty Series II Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), a series of multi-element standard solutions were used to calibrate ICP-AES and the wavelength used were: Ca 422.673 nm, Fe 259.940 nm, K 769.896 nm, Na 589.940 nm.

Al, As, Cd, Mg, Mn, Ni, Pb, V and Zn were measured by a Varian 820-MS Inductively Coupled Plasma Mass Spectrometer (ICP-MS). A series of multi-element standard solutions were used to calibrate the instrument, Ga and In were used as the internal standard to correct for matrix effects and the instrument drift, the isotope monitored were Al27, As75, Cd111, Mg25, Ni60, Pb208, V51 and Zn66.

Appendix C: Results of laboratory water analyses

Physicals and major ions

Client ID	Sampled On	Acidity (mg/L)	Alkalinity (mg/L)	CO3 (mg/L)	EC (mS/m)	DOC (mg/L)	Hardness (mg/L)	TOC (mg/L)	TDS calc (mg/L)	Cl (mg/L)	N_NO3 (mg/L)	SO4_S (mg/L)	HCO3 (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)
Minni N	11/09/2009									211		1840		103	22.9	23.6	101
Minni N	11/07/2009									280		1730		82.9	23.2	19.6	79.2
Minni N	15/06/2009									154		1980		56.8	20.8	15.9	65.4
Minni N	14/01/2009	8	1	<1	201	8.3	560	8.8	1100	80	0.01	797	1	41.4	14.7	12.3	54.7
Minni N	22/12/2008	9	1	<1	76.2	2.8	150	2.8	420	61	0.01	208	1	179	10.5	26.6	84.2
Minni N	13/11/2008	11	1	<1	122	3.3	210	3.5	670	89	0.01	309	1	279	80.3	34.9	91.5
Minni N	1/10/2008	15	1	<1	148	3.3	290	3.7	810	119	0.01	430	1	296	33.4	45.4	180
Minni N	11/09/2008	15	1	<1	171		350		940	143	0.01	500	1	304	34.3	45.5	137
Minni S	11/09/2009									249		1190		135	18.8	37.9	137
Minni S	11/07/2009									325		1620		114	18.9	32.4	116
Minni S	15/06/2009									145		1590		59.4	19	19.4	78
Minni S	14/01/2009	97	1	<1	323	10	360	10	1800	213	0.02	1070	1	52.3	22.3	20.5	97.4
Minni S	22/12/2008	24	1	<1	191	10	210	10	1100	151	0.01	545	1	92.2	39.7	31.6	137
Minni S	13/11/2008	9	1	<1	162	5.6	230	5.9	890	108	0.01	423	1	204	42.4	34.9	112
Minni S	1/10/2008	30	1	<1	238	6.8	420	7.2	1300	181	0.01	809	1	230	38.9	44.6	203
Minni S	11/09/2008	73	1	<1	265		490		1500	200	0.01	879	1	174	25.9	27.1	161
BORE 01	11/09/2009									253		481		77.7	30.2	24.3	52.7
BORE 01	11/07/2009									52		27		31.7	21.7	18.7	50.7

BORE 01	23/05/2009									50		13		72.9	33.4	35.5	107
BORE 01	27/03/2009	2	195	<1	50.5		150		280	51	0.09	13.4	238	103	26.7	22.6	90.7
BORE 01	28/02/2009	5	250	<1	60.7	12	150	13	330	53	0.03	10.4	305	49.3	24.1	13.8	43.9
BORE 01	14/01/2009	5	225	<1	73.8	4.9	180	5	410	56	0.24	14.1	275	40.3	23.6	12.8	40.4
BORE 01	22/12/2008	5	250	<1	110	12	350	12	610	124	0.04	140	305	41.7	23.4	11.3	38.7
BORE 01	13/11/2008	15	225	<1	144	18	330	18	790	180	0.01	198	275	27.9	24.3	9.26	32.9
BORE 01	1/10/2008	5	175	<1	69.6	<10	160	10	380	71	1.4	61.1	214	47.8	30.8	9.48	46.1
BORE 01	11/09/2008	20	220	<1	87.7		290		480	141	0.04	74.9	268	285	30.4	29.6	157
BORE 02	11/09/2009									79		92		86.6	16.9	18.4	53.2
BORE 02	11/07/2009									56		26		63	18	14.5	52.8
BORE 02	23/05/2009									80		167		50.1	17.8	11.7	48.2
BORE 02	27/03/2009	110	190	<1	58.4		180		320	59	0.06	36.4	232	47.2	17	11.4	47.5
BORE 02	28/02/2009	7	225	<1	65.1	32	200	32	360	61	0.02	52.7	275	50.9	17.4	12.1	47.9
BORE 02	14/01/2009	5	200	<1	60.1	1.8	180	2	330	59	0.03	40.5	244	58.2	18.2	13.7	50.2
BORE 02	22/12/2008	5	200	<1	58.1	<10	160	<10	320	59	0.04	34.5	244	51.4	16.4	11.8	46.9
BORE 02	13/11/2008	5	200	<1	57.8	<10	170	<10	320	60	0.03	39.3	244	83.2	15	17.1	50.5
BORE 02	1/10/2008	5	175	<1	66.1	<10	220	<10	360	64	0.31	63.2	214	44.6	19.1	8.13	45.6
BORE 02	11/09/2008	13	225	<1	88.1		290		480	77	0.02	118	275	276	14.6	14.9	58.3
BORE 03	11/09/2009									44		71		184	8.4	13.4	47.7
BORE 03	11/07/2009									44		260		173	6	14.7	40.8
BORE 03	23/05/2009									67		870		181	7.7	15	35.2
BORE 03	27/03/2009	50	1	<1	109		230		600	71	0.04	447	1	199	11.8	16.1	35
BORE 03	28/02/2009	82	1	<1	129	25	300	25	710	66	0.01	557	1	190	10.7	14.8	28.9

BORE 03	14/01/2009	6	1	<1	182	28	700	28	1000	67	0.01	848	1	186	14.1	13.2	31.8
BORE 03	22/12/2008	8	25	<1	123	11	520	13	680	62	0.03	585	31	250	16.6	17.5	34.9
BORE 03	4/12/2008	5	50	<1	124	12	470	14	680	65	0.07	556	61	104	13.5	9.1	35.7
BORE 03	13/11/2008	9	25	<1	133	11	560	19	730	65	0.02	663	31	77.5	11.2	8.9	34.9
BORE 03	24/10/2008	5	50	<1	NSS	14	510	14		59	0.05	640	61	73.1	12.7	3.83	29
BORE 03	1/10/2008	16	125	<1	103	27	490	29	560	48	0.05	434	153	63.7	3.51	5.33	38.6
BORE 03	11/09/2008	90	1	<1	178		510		980	72	0.01	846	1	73.4	4.78	3.88	28.8
BORE 04	11/09/2009									95		225		154	19.3	27.5	47.9
BORE 04	11/07/2009									105		198		144	17.6	25.7	46
BORE 04	23/05/2009									88		334		92.7	15.2	23.8	45
BORE 04	27/03/2009	30	135	<1	102		330		560	87	0.19	183	165	123	15.1	26.1	43.9
BORE 04	28/02/2009	10	200	<1	111	14	520	13	610	87	0.07	243	244	97.2	14.3	24.4	45.8
BORE 04	14/01/2009	5	125	<1	92.4	10	340	11	510	84	0.01	240	153	165	14.5	25.3	45.2
BORE 04	22/12/2008	7	175	<1	114	<10	410	<10	630	84	0.25	266	214	97.2	13.6	21.1	39.7
BORE 04	13/11/2008	7	150	<1	90.6	3.3	330	3.4	500	91	0.64	191	183	184	15.7	24.9	39.3
BORE 04	1/10/2008	21	250	<1	105	11	470	<10	580	88	1.6	176	305	142	16.2	17.9	67.2
BORE 04	11/09/2008	10	263	<1	114		500		630	96	1.2	208	320	181	14.7	16.3	57
BORE 05	11/09/2009									319		1670		251	67.3	78	193
BORE 05	11/07/2009									275		1240		614	70.6	104	196
BORE 05	23/05/2009									232		729		191	48.6	60.7	137
BORE 05	27/03/2009	60	140	<1	184		720		1000	200	0.14	651	171	165	43.4	49.3	119
BORE 05	28/02/2009	5	100	<1	205	26	770	27	1100	194	0.02	773	122	176	44.4	52.3	123
BORE 05	14/01/2009	5	150	<1	NSS	<10	650	<10		167	0.05	632	183	213	46.6	58.7	143

BORE 05	22/12/2008	7	125	<1	NSS	1.1	610	1.1		162	0.06	577	153	204	43.1	52.2	129
BORE 05	13/11/2008	8	100	<1	200	<10	730	<10	1100	192	0.02	744	122	229	51.6	43.3	143
BORE 05	1/10/2008	16	250	<1	369	14	2000	14	2000	271	58	1580	305	298	80.7	49.3	201
BORE 05	11/09/2008	57	235	<1	286		950		1600	268	0.01	1010	287	310	79.2	52.6	210
BORE 06	11/09/2009									60		156		87.9	27	9.7	42
BORE 06	11/07/2009									57		115		87	19.6	11.2	43
BORE 06	23/05/2009									36		62		212	20.5	12.4	40.7
BORE 06	27/03/2009	40	230	<1	88.5		340		490	54	0.02	176	281	78.8	17.1	12	44.2
BORE 06	28/02/2009	5	125	<1	74	9	210	9	410	55	0.32	177	153	67.8	16.3	9.9	46.8
BORE 06	14/01/2009	33	100	<1	82.7	15	290	14	450	58	0.27	253	122	75	19	8.8	43.9
BORE 06	22/12/2008	5	125	<1	71.7	18	220	19	390	56	0.42	155	153	89.6	19.6	15.2	45
BORE 06	4/12/2008	5	150	<1	66.4	11	210	11	370	56	0.1	161	183	68.1	19.9	9.8	43.4
BORE 06	13/11/2008	5	150	<1	75.6	7.6	250	7.8	420	57	0.03	191	183	121	19.9	8.9	44.5
BORE 06	24/10/2008	5	250	<1	118	8.7	580	8.9	650	59	0.05	442	305	38	13.2	2.96	26.8
BORE 06	1/10/2008	16	150	<1	79.1	16	260	17	440	59	0.63	169	183	73.2	21.5	5.27	46.6
BORE 06	11/09/2008	15	215	<1	87.4		260		480	58	0.03	155	262	206	23.4	6.8	46.8
BORE 07	11/09/2009									181		1850		108	46.2	49	141
BORE 07	11/07/2009									239		1910		111	51.5	52.3	150
BORE 07	23/05/2009									198		757		97	47.3	42.5	141
BORE 07	27/03/2009	220	1	<1	195		280		1100	180	0.12	776	1	59.3	39.3	25.5	121
BORE 07	28/02/2009	5	1	<1	265	3.4	300	3.5	1500	159	0.03	931	1	66.9	43.1	29.9	117
BORE 07	14/01/2009	350	1	<1	295	47	310	46	1600	153	0.05	1090	1	79.6	46.3	34.4	119
BORE 07	22/12/2008	490	1	<1	300	15	340	15	1700	171	0.05	1260	1	72.2	48.9	32.6	114

BORE 07	4/12/2008	12	1	<1	303	12	290	12	1700	160	0.26	1300	1	70.9	44.4	30.8	116
BORE 07	13/11/2008	460	1	<1	267	14	250	14	1500	148	0.41	1190	1	66.2	41.2	28.5	106
BORE 07	24/10/2008	13	1	<1	334	18	420	18	1800	177	0.07	1480	1	54.2	51	11.3	122
BORE 07	1/10/2008	1100	1	<1	417	18	490	18	2300	189	3	2130	1	168	52.5	24	230
BORE 07	11/09/2008	230	1	<1	362		470		2000	187	0.01	2040	1	189	27.5	13.3	129
BORE 08	11/09/2009									261		156		94.7	13.8	32.5	121
BORE 08	11/07/2009									256		263		50.7	13.9	31.2	102
BORE 08	14/01/2009	5	125	<1	104	<10	300	<10	570	128	0.25	204	153	53.7	16.1	33.5	91.8
BORE 08	22/12/2008	35	225	<1	120	<10	440	15	660	139	0.08	202	275	112	18.1	39.1	99.1
BORE 08	13/11/2008	5	175	<1	116	<10	270	<10	640	157	0.17	156	214	61.7	21.2	35.9	79.5
BORE 08	1/10/2008	5	150	<1	107	2.7	250	2.7	590	176	1.8	128	183	153	25.6	33.8	167
BORE 08	11/09/2008	22	223	<1	121		370		660	189	2.6	124	271	105	13.2	24.3	148

Metals and metalloids

Client ID	**Sampled On**	**Al (mg/L)**	**As (mg/L)**	**B (mg/L)**	**Ba (mg/L)**	**Cd (mg/L)**	**Co (mg/L)**	**Cr (mg/L)**	**Cu (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Mo (mg/L)**	**Ni (mg/L)**	**Pb (mg/L)**	**V (mg/L)**	**Zn (mg/L)**
Minni N	11/09/2009	0.28	0.001			<0.0001				12	1		<0.001	<.0001	<0.005	0.009
Minni N	11/07/2009	0.088	0.001			<0.0001				4	0.77		<0.001	<0.0001	<0.005	0.009
Minni N	15/06/2009	0.07	0.001			0.0004				5.6	0.49		0.002	0.0003	<0.005	0.01
Minni N	14/01/2009	0.009	0.001	0.05	0.095	<0.0001	<0.005	<0.001	<0.002	0.78	0.17	<0.001	<0.001	<0.0001	<0.005	0.0025
Minni N	22/12/2008	0.017	0.001	<0.02	0.061	0.0001	<0.005	<0.001	<0.002	7.2	0.85	<0.001	0.002	0.0003	<0.005	0.011
Minni N	13/11/2008	12	0.00143	0.02	0.071	0.000332	<0.005	<0.001	<0.002	244	3.28	<0.001	0.0124	0.000709	0.000163	0.0942
Minni N	1/10/2008	4.37	0.0236	0.03	0.083	0.0001	<0.005	<0.001	<0.002	311	5.1	<0.001	0.0258	0.000798	0.000651	0.0927

Minni N	11/09/2008	0.0741	0.0171	0.05	0.072	<0.00005	<0.005	<0.001	<0.002	453	4.14	<0.001	0.00779	0.00101	<0.0001	0.0634
Minni S	11/09/2009	1.9	0.001			<0.0001				85	2.1		0.018	0.0002	<0.005	0.037
Minni S	11/07/2009	1.2	0.001			0.0003				69	1.8		0.002	0.0002	<0.005	0.018
Minni S	15/06/2009	0.32	0.001			<0.0001				38	1		0.001	<0.0001	<0.005	0.012
Minni S	14/01/2009	0.18	0.001	0.06	0.065	<0.0001	<0.005	<0.001	<0.002	55	0.77	<0.001	<0.001	<0.0001	<0.005	0.01
Minni S	22/12/2008	0.88	0.001	0.02	0.03	<0.0001	<0.005	<0.001	<0.002	100	1.5	<0.001	0.001	0.0004	<0.005	0.04
Minni S	13/11/2008	6.63	0.00158	0.04	0.037	0.000293	<0.005	0.002	<0.002	235	3.17	<0.001	0.00517	0.00174	0.00157	0.0508
Minni S	1/10/2008	5.75	0.00108	0.09	0.017	7.15E-05	<0.005	0.002	<0.002	203	4.21	<0.001	0.00684	0.000501	0.0107	0.037
Minni S	11/09/2008	2.34	0.00101	0.11	0.016	<0.00005	<0.005	<0.001	<0.002	170	2.67	<0.001	0.00593	0.000444	0.00241	0.0282
BORE 01	11/09/2009	0.11	0.004			<0.0001				7.4	0.87		<0.001	0.0002	<0.005	0.016
BORE 01	11/07/2009	0.14	0.002			<0.0001				4.9	0.67		0.001	0.0003	<0.005	0.013
BORE 01	23/05/2009	0.019	0.003			<0.0001				3.2	0.4		0.003	0.0002	<0.005	0.015
BORE 01	27/03/2009	0.024	0.003	0.03	0.31	<0.0001	<0.005	0.003	0.005	7.3	0.41	<0.001	0.001	<0.00005	<0.005	0.028
BORE 01	28/02/2009	0.045	0.007	<0.02	0.36	<0.0001	<0.005	<0.001	<0.002	6.8	0.29	<0.001	<0.001	0.0001	<0.005	0.028
BORE 01	14/01/2009	0.024	0.006	<0.02	0.3	<0.0001	<0.005	<0.001	<0.002	4.5	0.28	<0.001	0.001	0.0002	<0.005	0.03
BORE 01	22/12/2008	0.13	0.002	<0.02	0.45	<0.0001	<0.005	<0.001	<0.002	3	0.27	<0.001	0.002	0.0015	<0.005	0.037
BORE 01	13/11/2008	<0.0005	<0.001	0.02	0.32	<0.00005	<0.005	<0.001	<0.002	2.56	0.291	<0.001	0.00143	0.00029	0.000476	0.0292
BORE 01	1/10/2008	<0.0005	0.00334	<0.02	0.53	<0.00005	<0.005	<0.001	<0.002	3.05	0.42	<0.001	0.00108	0.000123	0.000601	0.0325
BORE 01	11/09/2008	0.56	0.0145	0.02	0.67	0.000299	<0.005	<0.001	<0.002	27.5	0.672	<0.001	0.00983	0.00285	0.0184	0.159
BORE 02	11/09/2009	0.067	0.002			<0.0001				0.26	0.15		<0.001	0.0004	<0.005	0.015
BORE 02	11/07/2009	0.12	0.001			<0.0001				0.64	0.17		0.001	0.0002	<0.005	0.006
BORE 02	23/05/2009	0.032	0.001			0.0001				1.1	0.14		0.001	0.0002	<0.005	0.01
BORE 02	27/03/2009	0.015	0.001	0.03	0.19	<0.0001	<0.005	<0.002	<0.002	1.3	0.14	<0.001	<0.001	0.0001	<0.005	0.027

BORE 02	28/02/2009	0.01	0.001	<0.02	0.25	<0.0001	<0.005	<0.001	<0.002	0.99	0.14	<0.001	<0.001	<0.0001	<0.005	0.007
BORE 02	14/01/2009	0.008	0.001	<0.02	0.2	<0.0001	<0.005	<0.001	<0.002	1.8	0.17	<0.001	<0.001	<0.0001	<0.005	0.015
BORE 02	22/12/2008	0.006	0.001	<0.02	0.18	<0.0001	<0.005	<0.001	<0.002	0.12	0.14	<0.001	<0.001	0.0006	<0.005	0.019
BORE 02	13/11/2008	0.00257	0.00515	<0.02	0.2	6.44E-05	<0.005	0.001	<0.002	1.06	0.541	<0.001	0.00229	0.000382	0.000822	0.0473
BORE 02	1/10/2008	<0.0005	0.00167	0.03	0.22	<0.00005	<0.005	<0.001	0.003	1.06	0.163	<0.001	0.00132	0.000104	0.00141	0.0255
BORE 02	11/09/2008	<0.0005	0.00189	0.05	0.2	<0.00005	<0.005	<0.001	<0.002	0.172	1.15	0.001	0.00767	<0.00005	0.00104	<0.005
BORE 03	11/09/2009	0.83	0.033			0.0001				250	0.21		0.011	0.0003	0.011	0.063
BORE 03	11/07/2009	0.41	0.009			0.0002				43	0.16		0.007	0.0004	0.007	0.046
BORE 03	23/05/2009	0.52	0.021			<0.0001				120	0.17		0.007	0.0003	0.012	0.057
BORE 03	27/03/2009	0.67	0.018	0.04	0.084	0.0004	<0.005	0.005	0.005	120	0.19	<0.001	0.007	0.0002	0.01	0.047
BORE 03	28/02/2009	0.69	0.024	0.03	0.088	0.0001	<0.005	0.002	<0.002	100	0.19	<0.001	0.007	0.0003	0.011	0.054
BORE 03	14/01/2009	0.96	0.037	0.04	0.1	0.0002	<0.005	0.002	<0.002	110	0.14	<0.001	0.009	0.0002	0.009	0.045
BORE 03	22/12/2008	1.5	0.041	0.03	0.073	0.0001	<0.005	0.002	<0.002	140	0.16	<0.001	0.015	0.0006	0.01	0.076
BORE 03	4/12/2008	6.3	0.046	0.02	0.064	0.0001	<0.005	0.002	<0.002	140	0.08	<0.001	0.011	0.0012	0.013	0.068
BORE 03	13/11/2008	12	0.047	0.03	0.074	<0.0001	<0.005	0.002	<0.002	140	0.068	<0.001	0.011	0.0017	0.019	0.13
BORE 03	24/10/2008	32.8	0.0413	<0.02	0.064	0.000104	<0.005	0.003	<0.002	183	0.0667	<0.001	0.0346	0.00209	0.0569	0.145
BORE 03	1/10/2008	9.09	0.00327	0.03	0.055	0.000239	<0.005	0.003	0.007	30.9	0.0289	0.001	0.0161	0.000225	0.00732	0.0658
BORE 03	11/09/2008	11.3	0.0125	0.04	0.082	0.000121	<0.005	<0.001	<0.002	9.51	0.0464	<0.001	0.00981	0.00329	0.194	0.072
BORE 04	11/09/2009	0.073	0.002			0.0001				0.13	0.28		0.002	0.0003	<0.005	0.026
BORE 04	11/07/2009	0.034	0.001			<0.0001				0.39	0.21		0.002	0.0001	<0.005	<0.005
BORE 04	23/05/2009	0.025	0.002			<0.0001				0.51	0.19		0.002	0.0003	<0.005	0.013
BORE 04	27/03/2009	0.01	0.002	0.07	0.1	<0.0001	<0.005	0.003	0.003	0.37	0.31	0.002	0.002	<0.0001	<0.005	0.009
BORE 04	28/02/2009	0.005	0.002	0.06	0.11	0.0005	<0.005	<0.001	<0.002	0.24	0.47	0.002	0.001	0.0001	<0.005	0.13

BORE 04	14/01/2009	0.01	0.003	0.06	0.097	<0.0001	<0.005	<0.001	<0.002	0.35	0.35	0.002	0.001	<0.0001	<0.005	0.009
BORE 04	22/12/2008	0.057	0.003	0.06	0.11	<0.0001	<0.005	<0.001	<0.002	0.13	0.4	0.002	0.001	0.0003	<0.005	0.019
BORE 04	13/11/2008	0.0895	0.0052	0.05	0.11	0.000056	<0.005	<0.001	<0.002	1.02	0.432	0.003	0.00387	0.000364	0.000297	0.0314
BORE 04	1/10/2008	<0.0005	0.00428	0.06	0.11	5.52E-05	<0.005	<0.001	<0.002	0.292	0.722	0.002	0.00396	0.000127	0.000331	0.0295
BORE 04	11/09/2008	0.377	0.029	0.07	0.16	0.000108	<0.005	<0.001	<0.002	32.3	0.925	0.003	0.00773	0.00409	0.0164	0.121
BORE 05	11/09/2009	0.6	0.006			<0.0001				110	2.3		0.002	0.0009	0.011	0.032
BORE 05	11/07/2009	0.009	0.001			<0.0001				0.043	0.7		0.003	0.0003	<0.005	0.024
BORE 05	23/05/2009	0.17	0.001			<0.0001				94	1.5		0.002	0.0001	<0.005	0.033
BORE 05	27/03/2009	0.14	0.001	0.06	0.08	<0.0001	<0.005	0.006	0.006	71	1.3	<0.001	<0.001	0.0001	<0.005	0.024
BORE 05	28/02/2009	0.14	0.002	0.04	0.084	0.0002	<0.005	<0.001	<0.002	70	1.4	<0.001	0.001	0.0002	<0.005	0.038
BORE 05	14/01/2009	0.14	0.003	0.03	0.078	<0.0001	<0.005	<0.001	<0.002	79	1.6	<0.001	0.001	0.0001	<0.005	0.027
BORE 05	22/12/2008	0.2	0.004	0.04	0.06	<0.0001	<0.005	<0.001	<0.002	71	1.5	<0.001	<0.001	0.0003	<0.005	0.036
BORE 05	13/11/2008	<0.0005	0.00232	0.04	0.056	<0.00005	<0.005	<0.001	<0.002	92.8	1.75	<0.001	0.00331	0.000286	0.000331	0.0503
BORE 05	1/10/2008	0.0204	0.00512	0.06	0.054	0.000101	<0.005	0.003	0.007	281	2.21	0.001	0.0045	0.000101	0.000684	0.046
BORE 05	11/09/2008	32.2	0.00891	0.06	0.057	0.000264	<0.005	<0.001	<0.002	332	3.6	<0.001	0.00664	0.00288	0.0856	0.0675
BORE 06	11/09/2009	0.82	0.066			<0.0005				10	0.098		0.002	0.0017	0.01	0.016
BORE 06	11/07/2009	4.8	0.027			<0.0001				21	0.11		0.002	0.0027	0.017	0.37
BORE 06	23/05/2009	0.99	0.09			<0.0001				17	0.09		0.001	0.001	0.009	0.055
BORE 06	27/03/2009	0.34	0.03	0.03	0.083	0.0004	<0.005	0.017	0.017	21	0.079	0.002	0.009	0.0005	0.007	0.053
BORE 06	28/02/2009	0.077	0.036	0.02	0.076	<0.0001	<0.005	<0.001	<0.002	15	0.075	<0.001	<0.001	0.0001	0.005	0.022
BORE 06	14/01/2009	0.19	0.033	<0.02	0.079	0.0001	<0.005	<0.001	<0.002	6	0.067	<0.001	<0.001	0.0001	<0.005	0.022
BORE 06	22/12/2008	0.097	0.031	<0.02	0.063	0.0002	<0.005	<0.001	<0.002	26	0.14	<0.001	0.01	0.0003	<0.005	0.024
BORE 06	4/12/2008	0.063	0.052	<0.02	0.054	<0.0001	<0.005	<0.001	<0.002	17	0.071	<0.001	<0.001	0.0004	<0.005	0.048

BORE 06	13/11/2008	0.1	0.034	0.02	0.06	<0.0001	<0.005	0.002	<0.002	5.9	0.054	<0.001	0.003	0.0005	<0.005	0.073
BORE 06	24/10/2008	0.576	0.031	<0.02	0.055	5.42E-05	<0.005	0.003	0.002	4.69	0.0465	<0.001	0.00185	0.00194	0.0108	0.0599
BORE 06	1/10/2008	0.0439	0.0438	0.02	0.078	0.000126	<0.005	0.011	<0.002	11.6	0.0866	<0.001	0.0022	0.000219	0.00542	0.067
BORE 06	11/09/2008	3.16	0.129	0.03	0.085	0.000438	<0.005	<0.001	0.006	31.7	0.184	<0.001	0.012	0.0158	0.24	0.095
BORE 07	11/09/2009	110	0.006			<0.00005				610	0.35		0.028	0.035	0.74	0.097
BORE 07	11/07/2009	120	0.1			0.0001				510	0.37		0.008	0.02	1.1	0.12
BORE 07	23/05/2009	78	0.14			0.0002				280	0.38		0.006	0.0072	0.6	0.27
BORE 07	27/03/2009	67	0.13	0.07	0.051	0.0007	<0.005	0.007	0.007	280	0.24	<0.001	0.005	0.0042	0.45	0.13
BORE 07	28/02/2009	66	0.13	0.12	0.072	0.0002	<0.005	0.009	<0.002	310	0.2	<0.001	0.003	0.0071	0.6	0.097
BORE 07	14/01/2009	60	0.11	0.04	0.03	0.0002	<0.005	0.011	<0.002	290	0.16	<0.001	0.003	0.0043	0.44	0.093
BORE 07	22/12/2008	51	0.11	0.06	0.034	0.0002	<0.005	0.012	<0.002	230	0.12	<0.001	0.004	0.0052	0.37	0.31
BORE 07	4/12/2008	36	0.14	0.04	0.039	0.0001	<0.005	0.014	<0.002	200	0.11	<0.001	0.003	0.0081	0.31	0.29
BORE 07	13/11/2008	35	0.12	0.05	0.037	0.0002	<0.005	0.034	0.005	220	0.11	<0.001	0.004	0.0075	0.27	0.21
BORE 07	24/10/2008	20.8	0.356	0.06	0.038	0.000108	<0.005	0.017	<0.002	205	0.102	<0.001	0.00369	0.00372	0.251	0.0909
BORE 07	1/10/2008	49.7	0.197	0.09	0.03	0.000307	<0.005	0.027	<0.002	230	0.482	<0.001	0.0175	0.0295	0.802	0.167
BORE 07	11/09/2008	40.3	0.332	0.1	0.03	0.000257	<0.005	0.01	<0.002	208	0.625	<0.005	0.0264	0.0858	1.23	0.122
BORE 08	11/09/2009	0.036	0.002			<0.0001				0.005	0.044		0.008	0.0004	0.005	0.012
BORE 08	11/07/2009	0.1	0.002			<0.0001				0.99	0.024		0.002	0.0002	0.01	0.01
BORE 08	14/01/2009	0.072	0.002	0.05	0.062	<0.0001	<0.005	<0.001	<0.002	0.12	0.032	<0.001	0.006	0.0002	<0.005	0.02
BORE 08	22/12/2008	0.049	0.005	0.05	0.058	<0.0001	<0.005	<0.001	<0.002	0.096	0.06	<0.001	0.003	0.0001	<0.005	0.021
BORE 08	13/11/2008	0.018	0.006	0.06	0.057	0.0001	<0.005	<0.001	<0.002	0.063	0.08	<0.001	0.003	<0.0001	<0.005	0.016
BORE 08	1/10/2008	0.0108	0.00805	0.06	0.058	<0.00005	<0.005	<0.001	0.006	0.716	0.0872	0.001	0.016	0.000226	0.00364	0.0384
BORE 08	11/09/2008	<0.0005	0.00413	0.08	0.06	<0.00005	<0.005	<0.001	<0.002	0.502	0.0468	0.001	0.00991	0.000101	0.00174	0.0267

Appendix D: XRF trace element results

Analyte (ppm)	**As**	**Ba**	**Co**	**Cr**	**Cu**	**Ga**	**Mn**	**Nb**	**Ni**	**Pb**	**Rb**	**Sc**	**Sr**	**Th**	**Ti**	**U**	**V**	**Y**	**Zn**	**Zr**
Detectable range (ppm)	10 - 330	10 - 4000	2 - 210	3 - 4000	3 - 2360	3 - 40	4 - 2500	2 - 268	3 - 2360	10 - 133	2 - 1300	3 - 55	2 - 700	3 - 1003	5 - 22600	3 - 650	4 - 526	2 - 720	3 - 290	3 - 490
Overlap	Pb	Ce,Ti	Fe,Sr	V,La	Sr,Th		Cr	Y,La U,Th	Y		U	Ca		Bi, Rb	Ba	Rb, Sr	Ba,Ti	Rb,Pb		Sr,Ba Th
1A	bd	184	26	30	bd	2	351	13	2	9	16	10	795	5	3830	bd	16	11	bd	276
1B	bd	226	12	40	bd	2	218	17	2	14	18	10	872	4	5131	2	19	12	bd	272
1C	4	1828	25	bd	bd	3	104	9	bd	bd	12	6	126	3	721	2	7	3	4	118
1D	6	434	bd	5	bd	3	120	14	bd	bd	12	7	48	4	729	2	9	8	7	243
2	2	163	2	61	16	2	245	15	2	12	19	11	895	4	5276	1	22	12	26	384
3	8	590	bd	46	9	4	127	14	bd	bd	52	bd	58	4	2962	bd	15	7	26	287
4	4	270	3	71	bd	3	443	37	5	12	27	9	670	12	12579	2	33	21	26	943
5	2	653	10	7	18	3	671	9	bd	bd	42	3	257	4	1280	1	9	4	19	131
6	2	356	bd	28	bd	2	359	8	bd	6	38	8	243	3	1047	1	12	5	15	202
7A	15	386	43	63	6	6	133	18	bd	bd	39	9	81	15	3059	2	150	25	bd	305
7B	6	644	21	74	bd	5	85	20	bd	4	53	3	44	11	4939	1	71	18	bd	335
7C	16	652	70	73	bd	3	69	18	1	2	56	bd	45	6	4831	bd	31	13	bd	238
8	2	245	1	62	bd	1	210	19	2	14	28	9	784	5	6080	1	25	16	17	533
S	bd	2963	7	bd	bd	9	2131	33	6	32	24	8	151	3	5144	1	23	18	bd	672

NA	9	5503	3	bd	bd	4	236	13	bd	bd	12	7	122	6	2920	bd	20	7	10	326
NB	5	698	3	18	bd	2	601	82	6	22	24	9	62	21	11744	3	38	39	23	2126