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The hydrology, biochemistry and management of drained coastal acid sulphate soil backswamps in the lower Clarence River floodplain

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The hydrology, biogeochemistry and management of drained coastal acid sulfate soil backswamps in the lower Clarence River floodplain

A thesis submitted as requirement in full for the degree of

Doctor of Philosophy

by

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# Table of contents

Table of contents…………………………………………………… ii
Declaration of originality………………………………………… viii
Abstract…………………………………………………………….. ix
List of Tables………………………………………………………. xi
List of Figures……………………………………………………… xiv
Publications associated with this thesis……………………………. xxxi
Acknowledgements…………………………………………………. xxxiii

Chapter 1. Introduction
1.1. Format of thesis......................................................... 1-1
1.2. The formation of coastal acid sulfate soils in eastern Australia........ 1-2
   1.2.1. Clarence River coastal floodplain.............................. 1-4
1.3. Important chemical and physical properties of acid sulfate soils...... 1-8
1.4. Drainage of coastal floodplains and modification of hydrology....... 1-12
1.5. Some effects of drainage and modified hydrology...................... 1-13
   1.5.1. Floodplain hydrology and water balance...................... 1-13
   1.5.2. Generation and export of sulfide oxidation products.......... 1-14
   1.5.3. Vegetation changes............................................. 1-15
1.6. Problem definition and focus of thesis................................ 1-16
   1.6.1. Areas of uncertainty............................................. 1-17
   1.6.2. Statement of theses............................................. 1-19
   1.6.3. Part I: The quantification and assessment of existing hydrological and biogeochemical processes in drained acid sulfate soil backswamps............................................. 1-20
   1.6.4. Part II: Examining the effects of changes to the management of drainage systems............................................. 1-22

Chapter 2. Artificial drainage of floodwaters from sulfidic backswamps: effects on deoxygenation in an Australian estuary
2.1. Abstract............................................................... 2-2
2.2. Introduction........................................................... 2-3
2.3. Materials and methods................................................ 2-5
   2.3.1. Study areas....................................................... 2-5
   2.3.2. Meteorological monitoring.................................... 2-8
   2.3.3. Backswamp vegetation........................................ 2-8
   2.3.4. River, drain and groundwater quality....................... 2-9
2.3.5. Sample collection, treatment and analysis .......................... 2-10
2.3.6. Drain discharge estimates ............................................. 2-11
2.3.7. Drain flux estimates ..................................................... 2-12
2.3.8. Estimates of river flow and deoxygenation potential of ASS backswamp drainage .................................................. 2-12
2.3.9. Surface sediment ......................................................... 2-13
2.4. Results ............................................................................ 2-14
2.4.1. Flooding ................................................................. 2-14
2.4.2. Effects of flooding on vegetation ........................................ 2-15
2.4.3. River water quality ......................................................... 2-16
2.4.4. Drain water chemistry ..................................................... 2-17
2.4.5. Surface sediment chemistry .............................................. 2-25
2.4.6. Drain discharge and flux estimates ...................................... 2-26
2.5. Discussion ..................................................................... 2-29
2.6. Conclusions ................................................................... 2-32
2.7. Acknowledgments ............................................................ 2-33

Chapter 3. Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to Melaleuca quinquenervia encroachment

3.1. Abstract ........................................................................... 3-2
3.2. Introduction ...................................................................... 3-3
3.3. Materials and methods ....................................................... 3-5
  3.3.1. Study site ...................................................................... 3-5
  3.3.2. Historic vegetation boundary mapping ............................. 3-7
  3.3.3. Shallow groundwater survey .......................................... 3-7
  3.3.4. EM38 survey ................................................................. 3-9
  3.3.5. Soil survey .................................................................... 3-10
  3.3.6. Leaf analysis ................................................................. 3-11
  3.3.7. Evapotranspiration of groundwater ................................. 3-11
3.4. Results ............................................................................ 3-12
  3.4.1. Vegetation boundary analysis .......................................... 3-12
  3.4.2. Individual trees ............................................................. 3-12
  3.4.3. Encroaching tree lines ................................................... 3-19
  3.4.4. Evapotranspiration of groundwater ................................. 3-26
  3.4.5. Leaf sample analysis ...................................................... 3-26
3.5. Discussion ....................................................................... 3-27
  3.5.1. M. quinquenervia encroachment ...................................... 3-27
  3.5.2. Alteration of groundwater and sediment geochemistry .... 3-28
  3.5.3. Enhanced water use and ion exclusion ............................ 3-30
  3.5.4. Enhanced sulfide oxidation ............................................. 3-31
  3.5.5. Metal mobility and mineral precipitation / dissolution ....... 3-33
Addendum to Chapter 3. Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to *Melaleuca quinquenervia* encroachment: the influence of micro-topography

3.8. Abstract .................................................................................. 3-38
3.9. Introduction ............................................................................. 3-39
3.10. Materials and methods .............................................................. 3-40
  3.10.1. Study site .......................................................................... 3-40
  3.10.2. Elevation survey and EM38 sampling .................................. 3-40
  3.10.3. Surface salt mineralogy and chemical analysis ...................... 3-41
3.11. Results and discussion ............................................................... 3-42
  3.11.1 Micro-topography and solute accumulation ......................... 3-42
  3.11.2. Salt efflorescence on surface roots ..................................... 3-45
3.12. Conclusions ........................................................................... 3-47

Chapter 4. Changes in surface water quality after inundation of acid sulfate soils with different vegetation cover

4.1. Abstract .................................................................................. 4-2
4.2. Introduction ............................................................................. 4-3
4.3. Materials and methods .............................................................. 4-6
  4.3.1. Soil collection and treatment .............................................. 4-6
  4.3.2. Surface vegetation cover sampling and analysis .................... 4-8
  4.3.3. Soil sampling and analysis ............................................... 4-8
  4.3.4. Water sampling and analysis ............................................ 4-9
4.4. Results ................................................................................... 4-10
  4.4.1. Surface vegetation cover .................................................. 4-10
  4.4.2. Reduction and acidity in surface soils ................................. 4-13
  4.4.3. Geochemistry of surface waters ...................................... 4-14
  4.4.4. Field surface waters ....................................................... 4-22
4.5. Discussion ............................................................................... 4-22
4.6. Conclusions ........................................................................... 4-26
4.7. Acknowledgments .................................................................. 4-26

Chapter 5. The acid flux dynamics of two artificial drains in acid sulfate soil backswamps on the Clarence River floodplain, Australia

5.1. Abstract .................................................................................. 5-2
5.2. Introduction ........................................................................................................ 5-3
5.3. Materials and methods ..................................................................................... 5-4
  5.3.1. Study areas .................................................................................................. 5-4
  5.3.2. Drain water quality ...................................................................................... 5-7
  5.3.3. Water levels ................................................................................................ 5-7
  5.3.4. Sample collection, treatment and analysis .................................................. 5-8
  5.3.5. Discharge estimates ..................................................................................... 5-9
  5.3.6. Flux estimates ............................................................................................. 5-9
  5.3.7. Soils ............................................................................................................. 5-11
  5.3.8. Hydraulic conductivity ............................................................................... 5-11
5.4. Results and discussion ..................................................................................... 5-13
  5.4.1. Site characteristics ..................................................................................... 5-13
  5.4.2. Hydraulic conductivity ............................................................................... 5-14
  5.4.3. Tidal influence on drain water levels and groundwater gradients ............... 5-16
  5.4.4. Flux rates .................................................................................................... 5-18
  5.4.5. Flux pathways, temporal dynamics and drain water chemistry .................. 5-19
  5.4.6. Hourly acid flux, tidal modulation and local hydrology ......................... 5-25
  5.4.7. Acid flux comparison ................................................................................. 5-30
  5.4.8. Groundwater responsiveness to drain water levels ................................ 5-31
5.5. Conclusions ....................................................................................................... 5-33
5.6. Acknowledgments ............................................................................................. 5-34

Chapter 6. Reducing acid flux from a coastal acid sulfate soil backswamp by drain water retention
  6.1. Abstract ........................................................................................................... 6-2
  6.2. Introduction .................................................................................................... 6-3
  6.3. Materials and methods ................................................................................ 6-6
    6.3.1. Study site .................................................................................................. 6-6
    6.3.2. Meteorological monitoring ..................................................................... 6-7
    6.3.3. Soils and hydraulic conductivity ............................................................... 6-8
    6.3.4. Groundwater and drain water levels ....................................................... 6-9
    6.3.5. Drain water quality ................................................................................. 6-10
    6.3.6. Sample collection and analysis ............................................................... 6-11
    6.3.7. Drain flow and flux calculations .............................................................. 6-12
    6.3.8. Drain water retention .............................................................................. 6-13
    6.3.9. Surface soil collection and analysis ......................................................... 6-14
    6.3.10. Water table, groundwater gradient and acid flux modelling ................ 6-14
  6.4. Results and discussion .................................................................................. 6-16
8.3.5. Soils and hydraulic conductivity…………………………… 8-11
8.3.6. EM38 surveying………………………………………… 8-12
84. Results and discussion………………………………………… 8-12
  8.4.1. Romiaka tidal drain 1…………………………………… 8-12
  8.4.2. Romiaka transition drain……………………………… 8-16
  8.4.3. Shark Creek…………………………………………… 8-22
8.5. General discussion and conclusions………………………… 8-28
  8.5.1. Practical implications for opening floodgates……… 8-29
8.6. Acknowledgments………………………………………… 8-32

Chapter 9. Conclusions
  9.1. Summary……………………………………………………… 9-1
      9.1.1. Interactions between hydrology, vegetation, soils
      and water quality…………………………………………… 9-1
      9.1.2. Acid flux dynamics…………………………………… 9-4
      9.1.3. Changes to drainage system management…………… 9-9
  9.2. Further research…………………………………………… 9-11

References………………………………………………………… 10-1
Declaration of originality

I, Scott Gregory Johnston, declare that this thesis, submitted as fulfilment of the requirements for the Degree of Doctor of Philosophy, is my own work. It has not been submitted for award of any other qualifications in any institute. Information from the published or unpublished work of others has been acknowledged in the text and a list of references is provided.

Signature…………………………………   Date…………………

viii
Abstract

This study examined the water quality and hydrological characteristics of several artificially drained acid sulfate soil (ASS) backswamps on the lower Clarence River coastal floodplain. Drainage fluxes of acidity and deoxygenating compounds were quantified and biogeochemical processes affecting the chemical characteristics of surface waters investigated. Alteration of groundwater and soil geochemistry due to encroachment of *Melaleuca quinquenervia* was examined. The effects of a weir and tidal exchange on acid export, drain water quality and groundwater behaviour were also assessed.

After a major flood artificial drainage transferred anoxic surface waters from ASS backswamps to the estuary beyond what would have occurred naturally. This drainage made a substantial contribution to the magnitude of a deoxygenation event in the Clarence River estuary. Anaerobic decomposition of flood intolerant pasture species coupled with Fe and S redox transformations was a dominant process affecting the chemistry of backswamp floodwaters. Deoxygenation processes, redox transformations and acidification in ASS backswamp surface waters are controlled by complex interactions between hydrology, soils and vegetation. The pool of labile vegetative carbon and the concentration of acidic solutes in surface soils have major effects on redox conditions and surface water acidity in ASS backswamps. Therefore, drainage induced changes to backswamp vegetation communities has substantial implications for surface water quality. Encroachment of *Melaleuca quinquenervia* in an ASS backswamp was found to have caused large increases in soil and groundwater acidity. This is likely to enhance acid flux loads by increasing the acidity of surface waters and
groundwater seepage.

The acid flux of drained ASS backswamps is highly dynamic on an hourly, daily and seasonal basis. Acid flux rates can vary greatly between backswamps and are strongly influenced by sulfuric horizon hydraulic properties and effluent groundwater gradients. Some ASS backswamps have acid soil horizons with very high saturated hydraulic conductivity ($K_{\text{sat}}$) associated with macropores. Such sites can have very high rates of acid flux via groundwater seepage to the drainage system. Tidal variations in drain water levels are important as they regulate the magnitude of the effluent groundwater gradients which drive this seepage. An ‘acid export window’ concept was developed to explain observed acid export behaviour. The position of backswamp water levels relative to backswamp surface elevations and local tidal minima in bisecting drains exerts a dominant control on acid export.

Acid groundwater seepage was reduced by about 65 - 70% by using a weir to prevent tidal draw down of drain water levels and reduce effluent hydraulic gradients. Floodgate opening and tidal exchange improved drain water pH and dissolved oxygen concentrations. However, there are limitations and complexities associated with short duration floodgate openings which limit its efficacy as a stand alone acid management strategy. ASS backswamps with very high $K_{\text{sat}}$ also have substantial risk of experiencing saline intrusion into shallow groundwater if floodgates are opened.
List of Tables

Table 2.1. Chemical analyses of backswamp surface waters at Blanches and Maloneys study sites following the February flood…………………………………………………………. 2-21

Table 2.2. Chemical analyses of shallow ASS groundwater at Blanches and Maloneys study sites……………………………………………………………………………….. 2-23

Table 2.3. Iron and sulfur fractions in backswamp surface sediments at Blanches and Maloneys study sites…………………………………………………………………… 2-25

Table 2.4. Total discharge and total flux estimates for the Blanches and Maloneys study site drains for 30 days following the February flood…………………………………… 2-26

Table 3.1. Linear regression analysis ($r^2$) between mean soil EC$_a$ and the chemical composition of groundwater from the sulfuric horizons adjacent M. quinquenervia no. 1 and 2……………………………………………………………………………..………… 3-16

Table 3.2. The chemical composition of groundwater from the sulfuric horizons in open swamp areas and encroached M. quinquenervia forest at Shark Creek ASS backswamp. 3-21

Table 3.3. Concentration of selected ions in green living leaves, senescent leaves and forest floor litter from encroached M. quinquenervia………………………………….. 3-27

Table 3.4. Mean surface elevations and soil EC$_a$ for open swamp areas and encroached M. quinquenervia forest areas at Shark Creek backswamp……………………………… 3-43

Table 3.5. The chemical composition of a water extract (1:50) of the salt efflorescence
Table 4.1. Mean chemical composition of surface soils (0 - 2 cm) from the soil blocks associated with the different vegetation types before, and after (26 days) of inundation.

Table 4.2. The chemical composition of field surface waters collected from areas of different vegetation types in the Shark Creek backswamp.

Table 5.1. Comparing variation between the methods used to calculate flux at Maloney's; \( F_d \) daily interpolation and \( F_h \) hourly logger inferred.

Table 5.2. Comparing key characteristics of the study site backswamps.

Table 5.3. Saturated hydraulic conductivity (m/day) of the sulfuric horizons at Blanches and Maloney's.

Table 5.4. Total flux estimates of acidity and other sulfide oxidation products for Blanches and Maloney's drains during 2001.

Table 5.5. Comparing the chemical composition (µmol L\(^{-1}\)) of drainage outflow water at Blanches and Maloney's during 2001.

Table 5.6. Comparing physico-chemical characteristics of drainage outflow water at Blanches and Maloney's during 2001.

Table 5.7. Change in drain water ionic ratios relative to groundwater during acid export events.
Table 6.1. Sensitivity analysis of the groundwater table model [Eq. (6.5) and Eq. (6.6)] to different values of specific yield ($S_y$) and a crop factor ($C_f$)………………………….. 6-15

Table 6.2. Saturated hydraulic conductivity ($K_{sat}$) of the sulfuric horizons at the study site backswamp…………………………………………………………………………... 6-17

Table 6.3. Mean daily flow weighted concentrations and ±standard error of titratable acidity, $SO_4^{2-}$, dissolved Fe and dissolved Al in drainage outflow water at station A before and after the weir was installed……………………………………………………... 6-24

Table 6.4. Mean chemistry of paired spot water samples at station A (downstream from weir) and station B (upstream from weir) after weir installation………………….. 6-25

Table 7.1. The mean difference between paired spot monitoring and SDL measurements of drain water quality made at station A at Blanches and Maloney's drains during 2001, 2002, 2003……………………………………………………………………………….. 7-10

Table 7.2. Approximate backswamp surface elevation ranges at Blanches and Maloney's in relation to the maximum recorded spring tides in the adjacent estuary during 2001 - 2003………………………………………………………………………. 7-31

Table 8.1. Piezometer well identification, horizontal spacing and slotting screen intervals………………………………………………………………………………….. 8-9

Table 8.2. Mean saturated hydraulic conductivity values at the study sites………………... 8-14

Table 8.3. Comparing the saturated hydraulic conductivity of the sulfuric horizons in some ASS backswamps located in coastal floodplain environments in eastern Australia.. 8-30
List of Figures

Figure 1.1. A schematic representation of the stages of infilling (A - D) of a barrier estuary in NSW. Source: Roy 1984……………………………………………………………………………. 1-4

Figure 1.2. A schematic illustration of the sequential infilling of the Clarence River estuarine basin during the Holocene. Source: Hashimoto and Hudson 2000…………………………………. 1-5

Figure 1.3. The distribution of ASS within <1 m of the ground surface in the lower Clarence River floodplain and the location of Everlasting Swamp, Shark Creek and Coldstream ASS backswamps. High risk ASS boundaries from Milford (1997) and Morand (1997)……………………………… 1-7

Figure 1.4. A schematic representation of some of the main processes and topics examined in chapter 2 and chapter 4. Numbers in parenthesis relate to the relevant chapter……………………. 1-20

Figure 1.5. A schematic representation of some of the main processes and topics examined in chapter 3 and chapter 4. Numbers in parenthesis relate to the relevant chapter……………… 1-21

Figure 1.6. A schematic representation of some of the main processes and topics examined in chapter 5 and chapter 6. Numbers in parenthesis relate to the relevant chapter……………….. 1-22

Figure 1.7. A schematic representation of some of the main processes and topics examined in chapter 7 and chapter 8. Numbers in parenthesis relate to the relevant chapter……………….. 1-23

Figure 2.1. a) Clarence River catchment and b) lower floodplain, study site locations and associated ASS backswamps. ASS backswamp boundaries after Milford (1997)……………….. 2-6

Figure 2.2. Blanches and Maloneys study sites, showing the location of submersible data loggers / flow / water level monitoring stations (A - B), drains, floodgates and acid sulfate soil backswamp margin……………………………………………………………………………. 2-7
Figure 2.3. a) Clarence River\(^\wedge\) and Blanches Drain hydrographs (note different scales), b) time series pH and DO at the floodgate SDL (monitoring station A) and c) hourly rainfall. Water level in m AHD (Australian Height Datum, 0 AHD = mean sea level). \(^\wedge\) = Outside Blanches drain floodgates…………………………………………………………………………………………………… 2-16

Figure 2.4. a) Shark Creek \(^\wedge\) and Maloney's Drain hydrographs (note different scales), b) time series pH and DO at the floodgate SDL and c) time series EC at the floodgate SDL (monitoring station A). \(^\wedge\) = Outside Maloney's drain floodgates…………………………………………………………………………………………………. 2-18

Figure 2.5. Post-flood changes in Blanches and Maloney's drainage water a) discharge volumes, b) Eh, c) dissolved organic carbon, d) chemical oxygen demand, e) total Fe and f) dissolved Fe. All concentration data is based on samples taken at the floodgates (monitoring station A)………………. 2-20

Figure 2.6. Post-flood changes in Blanches and Maloney's drainage water a) mean daily temperature at the floodgate SDL, b) titratable acidity (to pH 5.5), c) Cl\(^-\):SO\(_4^{2-}\) ratios (molar) and d) total Al. All concentration data is based on samples taken at the floodgates (monitoring station A)…………………………………………………………………………………………………… 2-22

Figure 2.7. Relationship between DOC and total Fe in drainage waters at the Blanches and Maloney's sites. Strong positive correlation (exponential regression) at Blanches, combined with surficial sediment chemistry data, suggests reductive dissolution of Fe associated with anaerobic decomposition of organic matter was an important process mobilising surface Fe into drainage waters at this site………………………………………………………………………………………………………………………… 2-24

Figure 2.8. Cumulative daily flux estimates for a) Blanches and b) Maloney's drainage systems for 30 days following the February 2001 flood. Historic limit to natural drainage based on 0.5 m AHD. \(^\wedge\) = based on 24 hr mean at floodgates. (Note; no titratable acidity recorded at Blanches, see Fig 2.6b)……………………………………………………………………………………………………………………………………………… 2-27
Figure 2.9. The estimated oxygen depletion potential of the water discharging from drained ASS backswamps into the South Arm channel and the flow volume of the South Arm channel for ~11 days after the flood peak. (Note: the dashed line indicates greater uncertainty in upper catchment flow data due to increasing tidal influence. See Materials and methods section for details on calculations used to estimate the oxygen depletion potential of drainage waters)…………………………... 2-28

Figure 3.1. a) Clarence River catchment and b) lower floodplain and study area location at Shark Creek…………………………………………………………………………………………………………………………3-6

Figure 3.2. Eastern Shark Creek ASS backswamp (Milford 1997) study area, showing historic vegetation boundaries, contemporary M.quinquenervia encroachment, survey transects and surveyed individual M.quinquenervia locations……………………………………………………. 3-8

Figure 3.3. Changes in the chemical composition of groundwater from the sulfuric horizon beneath individual M.quinquenervia no.1. Ratios based on molar concentrations. Note; isolated tree growing in open swamp area, see Fig. 3.2……………………………………………………………………. 3-13

Figure 3.4. Changes in the chemical composition of groundwater from the sulfuric horizon beneath individual M. quinquenervia no.2. Ratios based on molar concentrations. Note; isolated tree growing in open swamp area, see Fig. 3.2……………………………………………………………………. 3-14

Figure 3.5. Increase in the theoretical contribution of Fe^{2+} to the titratable acidity of groundwater beneath M. quinquenervia no. 1 and 2. Assumes 2 mol H^+ produced for each mol of Fe^{2+} oxidised.. 3-14

Figure 3.6. a) Changes in mean soil EC_{a} surrounding M.quinquenervia no.3 and b) M. quinquenervia no.2 and c) changes in soil EC_{a}V-EC_{a}H surrounding M. quinquenervia no.3 and d) M. quinquenervia no.2. Note that the M. quinquenervia are located at the centre point of each survey grid. Based on EM38 grid survey, sample points n = 121. Linear interpolation between points………………………………………………………………………………………………. 3-15
Figure 3.7. Positive correlation between the mean soil EC$_a$ increase at the base of individual, isolated M. quinquenervia growing in open swamp areas and a) Crown Volume Index, and b) Basal area. $^A = $ EC$_a$ increase based on the difference between the mean of four EM38 measurements at the base of each tree and at 20 m radially away from tree. $^B = $ based on the formula [height.$(diameter)^2$] (Biddiscombe et al. 1985.) $^C = $ measured at 1.3 m and includes all stems. Note that some individual trees had up to nine main stems…………………………………. 3-16

Figure 3.8. Changes in soil profile a) ORP$_f$, b) pH$_f$ and c) EC (1:5 extract) either side of M. quinquenervia no.2. The top of each chart represents the ground surface. Interpolation based on profiles located at 20, 10, 5 and 2 m either side of the tree centre (n = 128)…………………………… 3-17

Figure 3.9. Changes in soil TAA, $S_{Cv}$, Soluble Al, CI$^-$ and SO$_4^{2-}$ with depth, from profiles taken at 10, 5 and 2 m either side of M. quinquenervia no.2. Symbols are the mean and error bars the range of both profiles. Depths increments are the mean of both profiles………………………………….. 3-18

Figure 3.10. Changes in the chemical composition of groundwater from the sulfuric horizon along transects perpendicular to the treeline of three encroaching M. quinquenervia forests. Ratios based on molar concentrations. All forests encroached after 1942. For location of transects ‘a’ and ‘b’ see Fig. 3.2. Tuckean transect located in an ASS backswamp on the Richmond River floodplain……… 3-20

Figure 3.11. Changes in EC$_a$V, EC$_a$H (measured at 10 m intervals) and sulfuric horizon groundwater chemical composition across M. quinquenervia encroachment sequence, transect e – f. Dates refer to the period in which encroachment occurred………………………………………. 3-22

Figure 3.12. Changes in mean soil EC$_a$ at transect c - d. The extent of M. quinquenervia encroachment was controlled by a fence and a drain. Both sides were open swamp in 1942. Numbers 1 to 4 show soil profile sampling locations. Based on EM38 grid survey, sample points n = 90, linear interpolation between points…………………………………………………………… 3-23

Figure 3.13. Increasing mean EC$_a$ at transects c - d and e - f is accompanied by a decreasing trend
in ECₐV - ECₐH, suggesting an association with enhanced near surface solute concentrations…….. 3-24

**Figure 3.14.** Changes in soil profile chemical composition with depth at soil sampling locations 1, 2 (open swamp) and 3, 4 (encroached *M. quinquenervia* forest) at transect c - d. The extent of *M. quinquenervia* encroachment was controlled by land management features (i.e. a fence and drain). Both sides were open swamp in 1942. See Fig. 3.12 for soil sampling locations. ^ = EC in 1:5 water extract…………………………………………………………………………………………... 3-25

**Figure 3.15.** Shark Creek acid sulfate soil backswamp showing the major vegetation types (after Johnston *et al.* 2003b) and the area of backswamp in which the elevation and EM38 transects were located……………………………………………………………………………………………… 3-41

**Figure 3.16.** Surface elevation distribution in the encroached *M. quinquenervia* forest and open swamp area at Shark Creek ASS backswamp……………………………………………………………………………………………………… 3-42

**Figure 3.17.** Relationships between surface elevation and a) ECₐH and b) mean ECₐ in areas of encroached *M. quinquenervia* forest and open swamp at Shark Creek ASS backswamp………………… 3-44

**Figure 3.18.** Positive correlation between soil ECₐH and surface soil (0 - 2 cm) soluble Al concentrations. All data are from Shark Creek ASS backswamp. Source: Johnston *et al.* (2003b) and Chapter 4……………………………………………………………………………………….. 3-45

**Figure 3.19.** Efflorescence of acidic solutes on surface and near surface roots of *M. quinquenervia*. Note that the efflorescence is also occurring on the soil surface in places where the roots are immediately below the surface. Photo taken during November 2002 during a period when the groundwater table was approximately 0.6 m below the soil surface. Marker pen for scale……… 3-45

**Figure 3.20.** An X-ray diffractogram of the surface salt efflorescence. Main peak responses clearly correspond to d-spacings associated with gypsum…………………………………………………… 3-46
Figure 4.1. The mean biomass of surface vegetative cover on the soil blocks for the different vegetation types. Error bars are ± the standard deviation………………………………………………………… 4-11

Figure 4.2. The mean chemical composition of the different in situ surface vegetative covers comparing a) total carbon, b) water soluble carbohydrate, c) NDF – ADF, d) lignin, e) total Al, and f) total Fe. Error bars are ± the standard deviation…………………………………………………………… 4-12

Figure 4.3. Changes in mean in situ surface soil (0 - 2 cm) a) pH and b) Eh over time after inundation associated with the different vegetation types. Error bars are ± the standard deviation………………………………………………………… 4-13

Figure 4.4. Changes in mean surface water a) Eh, b) pH, c) Fe^{2+}, d) dissolved oxygen, e) dissolved organic carbon, and f) EC over time after inundation associated with the different vegetation types. Error bars are ± the standard deviation……………………………………………………………... 4-15

Figure 4.5. Correlation between the lignin:WSC ratio of the surface vegetation and the minimum surface water Eh after inundation of each soil block. ^ = Water soluble carbohydrate……………... 4-16

Figure 4.6. Changes in the pH and Eh of surface waters over time after inundation in two M. quinquenervia tubs (M1 = closed diamond, M3 = open diamond). Sampling times correspond to the linear sequence shown in Fig. 4.4. The straight line represents the theoretical boundary between the stability areas of Fe^{2+}(aq) (grey area) and Fe(OH)_3 (plain area) for flooded soils (assuming an Fe^{2+}(aq) activity of 1 mmol at 25 °C – after Ponnamperuma et al. 1967). Day 11 (highlighted) coincided with a large measured decrease in Fe^{2+}(aq) (Fig. 4.4c) and the appearance of Fe (III) flocs in the tubs……………………………………………………………………………... 4-17

Figure 4.7. Changes in mean surface water a) titratable acidity, b) dissolved Al, c) Cl and d) SO_4^{2-} over time after inundation associated with the different vegetation types. Error bars are ± the standard deviation. ^ = This left Y-axis relates to M. quinquenervia only. ^ = This right Y-axis relates to C. dactylon and P. clandestinum only……………………………………………………………... 4-18
**Figure 4.8.** Linear correlation between the sum of acidic metal cations (Fe$^{2+}$ and dissolved Al) and titratable acidity in surface waters. Assumes that dissolved Al is in Al$^{3+}$ form and that 2 mol and 3 mol of H$^+$ are generated per mol of Fe$^{2+}$ and Al$^{3+}$ respectively. Data presented are mean values for each vegetation type. 4-19

**Figure 4.9.** The theoretical relative contributions of a) Fe$^{2+}$ and b) dissolved Al to the titratable acidity of surface waters associated with the different vegetation types. Assumes dissolved Al is in Al$^{3+}$ form and that 2 mol and 3 mol of H$^+$ are generated per mol of Fe$^{2+}$ and Al$^{3+}$ respectively. Data presented are mean values. 4-20

**Figure 4.10.** Surface soil pH / Eh signatures for each of the soil blocks during the experiment. The approximate areas occupied by different types of bacteria are also shown (after Baas Becking et al. 1960), where the grey area represents sulfate reducing bacteria, the hatched area represents iron bacteria and the plain area represents *Thiobacteria* spp. 4-21

**Figure 4.11.** Changes in surface water a) Cl$^-$:SO$_4^{2-}$ ratios and b) Cl$^-$:dissolved Al ratios. Data presented are mean values. Maloneys post-flood and Blanches post-flood data (including their date of inundation) derived from Johnston et al. (2003a). 4-22

**Figure 4.12.** Positive linear correlation between initial surface soil concentrations and resultant surface water concentrations of a) Cl$^-$ and b) soluble Al.$^\wedge$ = Surface water concentrations are from day 8 after inundation. Note: dissolved Al data from M2 is omitted due to experimental error. 4-23

**Figure 4.13.** Positive linear correlation between EC$_{aH}$ and a) surface soil (0 - 2 cm) soluble Al and b) surface soil (0 - 2 cm) Cl$^-$ concentrations. Individual *M. quinquenervia* and *C. dactylon* soil blocks are identified. Black squares are data derived from Johnston *et al.* (2003b). 4-24

**Figure 4.14.** Relationship between pE, Fe$^{2+}$ activities and pH for surface waters from the different tubs relative to the theoretical stability range for goethite and amorphous ferric hydroxide. Data
shown for *M. quinquenervia* and *C. dactylon* are mean values. Field surface waters and sulfuric horizon groundwater from the Shark Creek backswamp are also presented. Stability constants derived from Satawathananont *et al.* (1991)………………………………………………………... 4-25

**Figure 5.1.** Clarence River catchment (inset) and lower floodplain study site locations and associated ASS backswamps. ASS backswamp boundaries after Milford (1997)………………... 5-5

**Figure 5.2.** Blanches and Maloneys study sites, showing the location of submersible data loggers / flow / drain water level monitoring stations (A - B), piezometers, drains, floodgates and ASS backswamp margin. ASS backswamp boundaries after Milford (1997)…………………………… 5-6

**Figure 5.3.** Comparing a) tidally influenced daily drain water level variations adjacent each backswamp and b) mean and maximum daily groundwater gradients at Blanches and Maloney’s drains. Both data sets are based on a period when the backswamp water level was below the ground surface (~0.12 m AHD Blanches; ~0.2 m AHD Maloneys) and above mean minimum low water (~0.2 m AHD). For a) drain water levels were measured at monitoring station B (see Fig. 5.2). For b) gradients were calculated by subtracting drain water levels at monitoring station B from piezometer well no. 1 (2 m from drain at both sites)………………………………………………. 5-17

**Figure 5.4.** Backswamp drain water and groundwater levels and daily acidity flux estimates during 2001 for a) Blanches and b) Maloneys drain in relation to c) rainfall……………………………………. 5-20

**Figure 5.5.** Cumulative flux estimates of acidity, SO$_4^{2-}$, total Fe, dissolved Fe and dissolved Al for a) Blanches and b) Maloneys drainage systems during 2001 in relation to mean daily backswamp water level. (See Results and discussion for an explanation of the acid export window). MLW is ~mean minimum tidally influenced low water level in drain (monitoring station B)……………………. 5-22

**Figure 5.6.** Hourly acidity flux estimates at Blanches drain during the sole acid export event in relation to estuary, drain and groundwater levels and rainfall………………………………………. 5-26
**Figure 5.7.** Hourly acidity flux estimates at Maloney’s drain in relation to estuary, drain and groundwater levels and rainfall. Note the strong tidal modulation of flux, large in-drain tidal amplitude and development of effluent groundwater gradients during the ebb tide phase. 5-27

**Figure 5.8.** Relationship between daily acid flux and maximum daily groundwater gradients at Blanches and Maloney’s. Blanches is based on the sole acid export event, between 23 November and 15 December 2001 (Fig. 5.4). Maloney’s is based on a period between 26 April and 8 August 2001. 5-28

**Figure 5.9.** Schematic representation of acid flux dynamics in a) high K\text{sat} / high gradient, and b) low K\text{sat} / low gradient ASS backswamps, with respect to lithofacies and groundwater losses by evapotranspiration and groundwater outflow. 5-29

**Figure 5.10.** Tidal forcing during a floodgate opening event at Maloney’s caused rapid aquifer response over large distances from the drain due to high sulfuric horizon K\text{sat}. 5-31

**Figure 5.11.** The lower sulfuric horizon K\text{sat} at Blanches limits aquifer response to tidal forcing. Substantial increases in the height of the shallow groundwater in the piezometer wells occurred only after overtopping of the ground surface took place, causing infiltration down the profile. 5-32

**Figure 6.1.** Schematic representation of a) the development of effluent groundwater gradients ($S^\prime$) through tidal modulation of drain water levels, where $H_e$ is the equilibrium water table level in adjacent acid sulfate soils at distance (D) from the drain and $H_{min}$ is the minimum low tide water level in the drain, and b) the potential effect of a weir on reducing effluent groundwater gradients. 6-5

**Figure 6.2.** a) Clarence River catchment and b) lower floodplain and study area location adjacent Shark Creek. Acid sulfate soil backswamp boundary after Milford (1997). 6-7

**Figure 6.3.** Study site drainage network and locations of drain monitoring stations, piezometer wells, floodgates, weir and weather station. 6-8
Figure 6.4. Cumulative flux estimates of acidity, \( \text{SO}_4^{2-} \), dissolved Fe and dissolved Al at Maloneys drain during 2001 (pre-weir) in relation to mean daily water levels in the acid sulfate soil backswamp. The total flux of acidity in 2001 was \( 1.07 \times 10^6 \) mol H\(^+\). Most flux occurs while the backswamp water level is within a narrow elevation range which corresponds to the shallow groundwater zone above tidally influenced low water in the drain. \( ^{\text{A}} = \) the 24 hr mean of piezometer wells 1 and 2. \( ^{\text{B}} = \) mean minimum tidally influenced low water level in drain at station B…………………………………………………………………………………………………….. 6-18

Figure 6.5. Mean daily drain water pH values in relation to mean daily drain water levels at monitoring station A, before installation of the weir during 2001. pH values shown are the 24 hr mean from the submersible data logger at monitoring station A………………………………………………………….. 6-19

Figure 6.6. Mean daily drain water pH values in relation to maximum daily groundwater gradients. pH values are the 24 hr mean from the submersible data logger at monitoring station A. Data shown is from periods when the mean daily groundwater level was below the surface, between December 2000 and March 2003. Influent groundwater gradients develop during dry periods. \( ^{\text{A}} = \) the difference between the mean daily groundwater level and the minimum daily drain water level at drain monitoring station B, assuming a horizontal distance of 2 m………………….. 6-20

Figure 6.7. a) Tidal fluctuations in Shark Creek cause modulation of drain water levels at monitoring station B, influencing the development of effluent groundwater gradients in the ASS backswamp which consequently b) play an important role in regulating acid flux rates from groundwater seepage. The approximate upper levels of the backswamp ground surface are indicated by the dashed line………………………………………………………………………… 6-21

Figure 6.8. Correlation between daily acid flux estimates and maximum daily groundwater gradients. Based on a period between 26\(^{\text{th}}\) of April to 8\(^{\text{th}}\) of August 2001 (pre-weir) when the groundwater level was between 0.22 and -0.2 m AHD. Maximum daily groundwater gradients are based on the difference between the mean daily groundwater level and the minimum daily drain
water level at drain monitoring station B, assuming a horizontal distance of 2 m................. 6-22

**Figure 6.9.** a) Acid flux estimates, b) discharge volumes, c) flow weighted concentrations of H$^+$ and d) flow weighted concentrations of dissolved Al in relation to mean daily backswamp water levels during the pre and post-weir periods. The post-weir period differentiates between data collected when the weir was functioning normally (post-weir, closed) and when the two flap gates on the weir were open to assist outflow (post-weir, open)....................................................... 6-23

**Figure 6.10.** A comparison of pre-weir observed and modelled data for a) mean daily backswamp water levels, b) maximum daily groundwater gradients and c) acid flux rates in relation to d) observed rainfall. Maximum daily groundwater gradients and modelled acid flux are only calculated for periods when the mean daily backswamp water level was <0.22 m AHD........... 6-27

**Figure 6.11.** A comparison of post-weir observed and modelled data for a) mean daily backswamp water levels, b) maximum daily groundwater gradients and c) acid flux rates in relation to d) observed rainfall. Modelled data assumes the weir was absent, using identical methods to Fig. 6.10. Periods when the two flapgates on the weir were open are also shown................................. 6-28

**Figure 6.12.** Daily acid flux rates in relation to the difference between the mean daily backswamp water level and daily tidal minima in Shark Creek, comparing observed data from both the pre-weir and post-weir periods with modelled data from Fig. 6.11 for the post-weir period in 2003. Pre-weir observed and post-weir modelled data are based on periods when the mean daily groundwater level was <0.22 m AHD................................................................. 6-29

**Figure 6.13.** Correlation between cumulative PET (potential evapotranspiration) and surface soil (0 - 5 cm below ground surface) a) EC (1:5 water extract), b) pH (1:5 water extract), c) sulfate and d) aluminium (water extractable) during a prolonged dry period from August 2001 to May 2002. Error bars are standard deviation. Cumulative PET measured from 180 days prior to sampling. Numbers in brackets are the mean daily backswamp water elevation for 60 days prior to sampling. 6-31
Figure 7.1. a) Clarence River catchment and b) lower floodplain and study area locations and associated ASS backswamps. ASS backswamp boundaries after Milford (1997).................. 7-6

Figure 7.2. Blanches and Maloney's study sites, showing the location of submersible data loggers / flow / drain water level monitoring stations (A - B), piezometers, drains, floodgates and ASS backswamp margin. ASS backswamp boundaries after Milford (1997)............................ 7-8

Figure 7.3. Correlation between drain water pH (as measured by the submersible data logger at station A) and titratable acidity at Maloney's drain two days before, during and three days after a floodgate opening event (of four days duration), which is shown in detail in Fig. 7.15.................. 7-13

Figure 7.4. Cumulative frequency distribution of a) mean daily drain water pH and b) mean daily dissolved oxygen at Blanches and Maloney's drains between December 2000 and October 2003. Data for both sites are based on measurements made by SDL located at monitoring stations A...... 7-14

Figure 7.5. An overview of seasonal hydrological conditions during the monitoring period, displaying the mean daily groundwater levels (well no. 2), mean daily drain water pH and rainfall recorded at the Maloney's study site. Distinct wet periods with low drain water pH, when groundwater levels were consistently above local low tide minima (dashed line), and dry periods with generally high drain water pH are identified.......................................................... 7-15

Figure 7.6. Changes in drain water pH in relation to drain water levels at Blanches drain during two separate floodgate opening events of a) 48 hrs and b) 96 hrs duration. The total volume (ML; 1 ML = m³.10³) of estuarine water inflow during each day of the floodgate opening event is shown in bold type........................................................................................................ 7-16

Figure 7.7. Changes in a) mean daily drain water pH at Blanches drain monitoring stations A and B in relation to b) floodgate opening events and inflow / outflow volumes..................... 7-17
Figure 7.8. Increases in drain water pH at Maloney's drain (station B) in relation to the cumulative inflow volume per flood tide cycle during a four day floodgate opening event. Both pH and inflow volume are based on hourly measurements and data points correspond to inflow periods only. All data is based on the floodgate opening event shown in Figure 7.15. The pH increase was calculated by difference from the initial drain pH immediately prior to floodgate opening. $r^2$ is derived from a second order logarithmic regression………………………………………………………………………………….. 7-18

Figure 7.9. a) Drain and groundwater levels, b) drain water pH and c) dissolved oxygen in relation to d) rainfall at Maloney's study site during a period before, during and after a floodgate opening event………………………………………………………………………………………………... 7-19

Figure 7.10. Changes in drain water $H^+$ concentrations in relation to EC, before and during three individual floodgate opening events. Short arrows indicate the direction of change during the floodgate opening phase. The EC:$H^+$ signature of sulfuric horizon groundwater (from the Maloney's site), and non-acid estuary water (measured during a dry period) are also shown. Dashed lines represent the theoretical change in $H^+$ that would occur in relation to EC due to neutralisation of acidity by 1:1 addition of estuary water (based on alkalinity and EC data presented in Figure 7.17). The $H^+$ concentration of drain and estuary waters is based on pH and the sulfuric horizon groundwater is derived from titratable acidity……………………………………………………… 7-21

Figure 7.11. Drain water levels and moderation of diurnal fluctuations in dissolved oxygen saturation during a floodgate opening event at Blanches drain, in relation to solar radiation……….. 7-22

Figure 7.12. Changes in drain water DO in relation to drain water levels at Blanches drain during two separate floodgate opening events of a) 72 hrs and b) 114 hrs duration. The total volume (ML; 1 ML = m$^3$.10$^3$) of estuarine water inflow during each day of the floodgate opening event is shown in bold type…………………………………………………………………..……………… 7-23

Figure 7.13. Positive linear correlation between mean daily drain water dissolved oxygen levels at Blanches drain (station A) and the daily inflow:outflow volume ratio. Note that inflow only
occurred during floodgate opening events. Based on measurements between 15/3/01 to 19/5/01.

Flow volumes measured at station A……………………………………………………………….. 7-24

**Figure 7.14.** Net drain discharge volume in relation to the mean daily longitudinal drain water gradient at Blanches drain. Net inflows associated with floodgate opening are indicated by the arrows………………………………………………………………………………………………. 7-25

**Figure 7.15.** Changes in a) drain and groundwater levels, b) drain water pH, c) drain outflow volumes and d) acid flux rates before, during and after a four day floodgate opening event at Maloney's drain. Negative values for outflow volume represent tidal ingress………………………. 7-27

**Figure 7.16.** Sulfuric horizon groundwater a) titratable acidity, b) Cl, c) dissolved Fe and d) ORP in relation to distance from the drain before, during and after the floodgate opening event shown in Figure 7.15. Samples collected from a transect parallel to the piezometer transect shown in Figure 7.2…………………………………………………………………………………………………... 7-28

**Figure 7.17.** Correlation between Clarence River estuary water EC and alkalinity (expressed as bicarbonate equivalent). Samples collected during a low flow period in January 2004…………….. 7-29

**Figure 7.18.** Cumulative frequency distribution of a) mean daily drain water EC, b) acid flux in relation to mean daily drain water EC and c) flow volumes in relation to mean daily drain water EC at Blanches and Maloney's drains. EC data for both sites is based on measurements from monitoring station A………………………………………………………………………………... 7-30

**Figure 8.1.** a) Location of Clarence River catchment, b) the lower Clarence River floodplain - showing unconsolidated Quaternary sediments and upland areas, c) Romiaka and d) Shark Creek study sites…………………………………………………………………………………………... 8-6

**Figure 8.2.** Romiaka transect R1 a) stratigraphy, piezometer well locations and piezometer slotting zone, b) soil EC (1:5 extract) and c)mean EC in relation to distance from the drain. Soil
Figure 8.3. a) Tidal forcing in shallow groundwater over a 10 day period at transect R1 and b) hourly rainfall.

Figure 8.4. Water level dynamics in Tidal drain 1 and piezometers at transect R1 over a 30 day period from 1 to 30 June 2000.

Figure 8.5. Romiaka transect R2 a) Stratigraphy, piezometer well locations and piezometer slotting zone and b) soil EC (1:5 extract) in relation to distance from the drain. Soil EC contours based on linear interpolation (n = 48) of sampling undertaken before floodgate opening.

Figure 8.6. a) Tidal forcing in shallow groundwater over an 11 day period at transect R2 immediately before and during floodgate opening, b) changes in groundwater gradients at 4 and 10 m from the drain, c) changes in drain water groundwater EC and d) rainfall.

Figure 8.7. Water level dynamics in the Transition drain and transect R2 piezometers during a) periods of floodgate closure (n = 22 days) and b) periods of floodgate opening (n = 57 days).

Figure 8.8. Correlation between EC<sub>a</sub> and groundwater EC adjacent the Transition drain, before and during floodgate opening.

Figure 8.9. Changes in groundwater EC adjacent Romiaka Non-tidal drain, Transition drain and Tidal drain 2 a) before floodgate opening, b) after 16 days of floodgate opening, c) after 57 days of floodgate opening, and d) 60 days after floodgates were closed following flooding. The groundwater EC is inferred using EM38 measurements (see Fig. 8.8). Linear interpolation between points (n = 77). See Fig. 8.1c for location of x and y.
Figure 8.10. a) Stratigraphy at Shark Creek transect M1 and b) mean EC₄ at transect M3 before and after floodgate periods of opening, in relation to distance from the drain. The floodgate opening size was restricted to prevent any overtopping of the backswamp surface, thus the increases in EC₄ are due to sub-surface flow of saline drain water into the aquifer (see Fig. 8.13)...

8-22

Figure 8.11. Changes in soil EC (1:5 extract) with depth at profiles M1-1, M1-4 and M1-5. Sampled prior to floodgate opening...

8-23

Figure 8.12. a) Tidal forcing of shallow groundwater at Shark Creek during a four day floodgate opening event and b) tidally modulated changes in drain water and groundwater EC (10 m from the drain)... 8-24

Figure 8.13. Drain and groundwater level dynamics at Shark Creek a) four days before floodgate opening, b) during floodgate opening and c) four days immediately after floodgate opening. Based on the floodgate opening event shown in Fig. 8.12...

8-25

Figure 8.14. Changes in the chemical composition of shallow groundwater at Shark Creek backswamp in relation to distance from the drain, before and after periods of floodgate opening. Ratios are based on molar concentrations. Note: the floodgate opening size was restricted and no overtopping of the backswamp surface occurred during the opening periods...

8-26

Figure 8.15. Mean daily drain water pH values in relation to maximum daily groundwater gradients. pH values are the 24 hr mean from the SDL at monitoring station A. Data shown is from periods when the mean daily groundwater level (mean of M1-1 and M1-2) was below the ground surface, between December 2000 and March 2003. Influent groundwater gradients develop during dry periods. A = the difference between the mean daily groundwater level and the minimum daily water level at drain monitoring station B, assuming a horizontal distance of 2 m...

8-27

Figure 9.1. A schematic representation of a hydrograph showing the approximate timing and sequence of events occurring after deep flooding of an ASS backswamp in relation to changes in
drainage water quality. The precise timing of changes and the actual elevations (i.e. natural levee heights, backswamp surface levels and local low tide) will vary between sites........................................ 9-2

**Figure 9.2.** Maloneys ASS backswamp a) stratigraphy and surface elevation ranges, and b) mean daily drain water pH in relation to mean daily backswamp water levels. The approximate water level elevation ranges of three distinct hydrological zones are indicated (dashed lines) along with the dominant acid flux pathways, discharge volumes and drain water pH associated with each zone. MLW is the mean tidally influenced low water level in the bisecting drain. Soil stratigraphy and surface elevations are based on data from chapter 3. Drain water pH based on data collected in chapters 5 and 6................................................................. 9-6

**Figure 9.3.** A conceptual model of the influence of sulfuric horizon $K_{sat}$ and the elevation difference between sulfuric horizons and the local tidal minima in bisecting drains upon acid flux pathways and rates, for a given drainage depth / density. MLW is the mean tidally influenced low water level in the bisecting drain................................................................. 9-8

**Figure 9.4.** A comparison of estimated acid flux rates (no. in brackets, as kg H$_2$SO$_4$ yr$^{-1}$) of several drained sulfidic backswamps, in relation to the $K_{sat}$ of their sulfuric horizons and the elevation difference between the sulfuric horizons and local tidal minima. MLW is ~mean tidally influenced low water level in the bisecting drains. Measurements of $K_{sat}$ and upper sulfuric - local MLW are based on available data which use varying sampling methodologies and sampling intensities. Source data: Maloneys Drain - (Johnston *et al.* 2004), Blanches Drain - (Johnston *et al.* 2004; Johnston unpub. data), Partridge Ck – (White 1998; Aaso 2001; Johnston *et al.* 2003c), McLeod’s Ck – (White *et al.* 1993; Wilson *et al.* 1999; Cibilic 2003), Tuckean – (Sammut *et al.* 1996; Johnston unpub. data)................................................................. 9-9
Publications associated with this thesis


Guidelines for managing floodgates and drainage systems on coastal floodplains.’

(NSW Agriculture: Wollongbar)


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Chapter 1

Introduction

1.1. Format of thesis

This thesis examines the hydrology, biogeochemistry and management of several drained acid sulfate soil backswamps on the lower Clarence River coastal floodplain. It has a particular focus on the chemical characteristics and hydrological behaviour of surface water, groundwater and drainage waters within these backswamps. The core chapters of the thesis (2 to 8) consist of a series of papers prepared for publication in scientific journals. Each chapter is presented as a self-contained study with its own specific aims and objectives.

Chapter 1 provides background information relevant to the rest of the thesis. The formation of coastal acid sulfate soils is briefly reviewed along with some of their important chemical and physical properties. The drainage of coastal floodplains and subsequent alteration of floodplain hydrology is also examined. Some known and some speculative effects of these hydrological changes are discussed. The problem definition and focus of the thesis is presented along with a schematic summary of the contents of each individual chapter.

The core chapters of this thesis are divided into two main parts. Part I (chapters 2 to 5) contains studies whose main focus is the quantification and assessment of existing hydrological and biogeochemical processes occurring in drained sulfidic backswamps. These chapters focus on topics where there are knowledge gaps or some degree of uncertainty. Part II (chapters 6 to 8) contains studies which focus on the implications of
making changes to the current management of floodplain drainage systems and examine the effects of these changes on groundwater hydrology, acid export and drain water quality. The management changes examined include opening floodgates to allow tidal exchange with estuarine water and retention of drain water using a weir.

Chapter 9 is a summary and conclusion, synthesising the main results of the research, as well as making suggestions for future investigations.

1.2. The formation of coastal acid sulfate soils

Acid sulfate soil is a term applied to soil materials that contain appreciable quantities of sulfide minerals, and/or the reaction products resulting from oxidation of these minerals. Acid sulfate soils (ASS) are found in coastal sediments in many parts of the world (Brinkman 1982). The formation of coastal sulfidic sediments is part of the global sulfur cycle. Iron pyrite (FeS$_2$) is one of the main types of sulfide mineral in these sediments (van Breemen 1973) and it can form via a number of complex pathways (Rickard et al. 1995). A simplified representation of the reaction is described in Eq. (1.1), after Dent (1986).

$$\text{Fe}_2\text{O}_3 (s) + 4\text{SO}_4^{2-} (aq) + 8\text{CH}_2\text{O} + \frac{1}{2} \text{O}_2 (g) \rightarrow 2\text{FeS}_2 (s) + 8\text{HCO}_3^- (aq) + 4\text{H}_2\text{O}$$  \hspace{1cm} (1.1)

The accumulation of pyrite requires a number of conditions to be met, which after Pons and van Breemen (1982) include,

- a source of sulfate (i.e. seawater).
- a source of iron minerals (i.e. sediment).
- metabolisable organic matter.
- sulfate reducing bacteria.
- a generally anaerobic environment, with some limited aeration.
Some leaching of alkalinity (HCO$_3^-$) formed during sulfate reduction (see Eq. 1.1) is also essential for the accumulation of potential acidity. The reactions represented in equation (1.1) also take time and thus a slower accretion rate is more favourable for pyrite accumulation. The above conditions are best met in low energy, organic rich, tidal environments, such as mangrove swamps and tidal marshes (Pons and van Breemen 1982). The accretion of coastlines during the Holocene post-glacial marine transgression provided favourable conditions for accumulation of sulfidic sediment in many locations throughout the globe. Coastal systems dominated by fluvial inputs with rapid sedimentation rates tended to limit the degree of pyrite accumulation (Lin and Melville 1994). Whereas, highly saline systems in which the rate of sedimentation approximated the rate of sea level rise favoured the development of thicker sulfidic deposits with higher pyrite concentrations (Pons and van Breemen 1982).

Under reducing conditions the pyrite and other sulfide minerals in the sediment are relatively stable. Such sediments are often referred to as ‘potential acid sulfate soil’. The degradation of these sulfide minerals through oxidation processes releases substantial quantities of acidity, which influences the chemistry of surrounding soil and groundwater. Acidic, oxidised horizons (or ‘actual acid sulfate soil’) often overlie unoxidised, sulfidic sediments within the same soil profile. There are a variety of definitions and classification schemes for ASS. Some are based on an understanding of pedogenic processes specific to ASS (i.e. Dent 1986), whereas others rely on the depth to diagnostic soil horizons with specific chemical and/or physical criteria (i.e. Fanning and Witty 1993; Soil Survey Staff 1998), which can be restrictive in certain cases (Joukainen and Yli-Halla 2003). From a functional point of view acid sulfate soils may be regarded as occurring when the actual or potential acidity derived from sulfide minerals is in excess of the acid neutralising capacity of the sediment.
1.2.1. South eastern Australia and the Clarence River coastal floodplain

South eastern Australia is characterised by an embayed, high energy coastline (Roy et al. 1980). The relatively long and narrow coastal strip, located between the Pacific Ocean and the parallel Great Dividing Range, is interrupted at regular intervals by short coastal rivers with relatively small catchments. The lower portions of these coastal valleys were flooded with sea water and infilled with fluvial and marine sediments during the Holocene post-glacial marine transgression. Three main types of Holocene embayment infill are identified by Roy et al. (1980), including drowned river valleys, open ocean and barrier estuaries (Fig. 1.1).

Figure 1.1. A schematic representation of the stages of infilling (A - D) of a barrier estuary in NSW. Source: Roy 1984.
The Clarence River is identified as a mature barrier estuary (Roy et al. 1980; Roy 1984) which has evolved from an estuarine basin to an alluvial floodplain over the past ~10000 years (Fig. 1.1). Infilling of the lower river valley during the Holocene was characterised by seaward expansion of a fluvial delta within a broad, low energy inner basin behind an expanding sand barrier of marine origin at the estuary mouth (Fig. 1.2). The lower valley is bisected by a prominent bedrock ridge which divides the estuary into an inner and outer basin (Hashimoto and Hudson 2000 - Fig.1.2). The deposition of estuarine muds within the low energy inner basin led to the formation of extensive intertidal environments, ideal for the accumulation pyrite.

**Figure 1.2.** A schematic illustration of the sequential infilling of the Clarence River estuarine basin during the Holocene. Source: Hashimoto and Hudson 2000.
Previous studies have suggested that pyritic sediments in parts of the inner basin of the Clarence floodplain were likely to have been deposited in more saline conditions when the estuary entrance was relatively open, prior to the closure of the coastal sand barrier (Lin and Melville 1993). In mature barrier estuaries such as the Clarence, continued fluvial deposition has caused capping of the estuarine muds and sulfidic sediments with non-sulfidic material to varying depths (Lin and Melville 1993), and led to the creation of a broad floodplain. The lower Clarence floodplain morphology is characterised by well developed natural levees (approximately 1 - 5 m AHD; Australian Height Datum) grading into partially occluded backswamp plains with elevations mostly <0.5 m AHD. ASS profile development in such geomorphic settings typically displays strong stratigraphic trends related to topography (Walker 1972; Willett and Walker 1982). Fluvial capping is generally thinnest in the backswamps, which can contain sulfidic sediments relatively close (<1 m) to the contemporary ground surface.

The Clarence River catchment is about 22700 km$^2$ and is the largest coastal catchment in NSW. The floodplain is over 2600 km$^2$ and underlain by an estimated 530 km$^2$ of ASS (Tulau 1999). A notable feature of this broad floodplain is the occurrence of several large (~10 - 20 km$^2$) backswamps within the inner basin (Everlasting Swamp, Shark Creek swamp, Coldstream swamps), which have been mapped as containing sulfidic sediments close (<1 m) to the ground surface (Fig. 1.3). The Clarence River catchment geology includes a variety of igneous, metamorphic and sedimentary rock types from the Clarence-Morton Basin and New England Fold belt (McElroy 1969). The climate is sub-tropical and mean annual rainfall on the Clarence River floodplain ranges from 1100 to 1500 mm and generally decreases with distance from the coast. Rainfall distribution is highly seasonal and a distinct wet period occurs from December to May. The river discharge displays a
Figure 1.3. The distribution of ASS within <1 m of the ground surface in the lower Clarence River floodplain and the location of Everlasting Swamp, Shark Creek and Coldstream ASS backswamps. High risk ASS boundaries from Milford (1997) and Morand (1997).

A high degree of intra and inter-annual variability and the median flow rate is 2930 ML day\(^{-1}\) (Manly Hydraulics Laboratory 2000). Seasonal overbank flooding is relatively common and can cover low parts of the floodplain in 2 - 4 m of water. The salinity gradient along the estuary changes dramatically according to the seasonally varying discharge. While much of the estuary can be fresh during wet periods, upstream migration of the salt wedge
beyond Grafton (Fig. 1.3) is common during dry periods (Manly Hydraulics Laboratory 2000). The semi-diurnal tides extend upstream of Grafton and the mean spring tides range from 1.23 m near the coastal port of Yamba, to 0.6 m near Grafton (Manly Hydraulics Laboratory 2000).

1.3. Important chemical and physical properties of acid sulfate soils

The physical and chemical processes of ASS have been described as among the most complex of any soil in the world (Bouma et al. 1993). The oxidation of pyrite by exposure to oxygen causes the release of acidity, sulfate and iron, represented by the following Eq. (1.2), (Dent 1986).

\[
\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1.2)
\]

Exposure of pyrite to oxygen can occur via lowering of water table, allowing oxygen into the sediment, or through excavation of the sediment. Multiple oxidation pathways exist and a variety of autotrophic iron and sulfate bacteria play important roles in the different oxidation steps (van Breemen 1993). Pyrite oxidation rates tend to be faster at lower pH. Fe\textsuperscript{3+} is also a very important oxidant of pyrite (Luther et al. 1992) and if the pH is <4, rapid oxidation of pyrite by Fe\textsuperscript{3+}\textsubscript{(aq)} can occur catalytically under the influence of *Thiobacillus ferrooxidans* (van Breemen 1973). Complete oxidation of one mole of pyrite yields 4 moles of acid, as represented by the following Eq. (1.3), (Dent 1986).

\[
\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{7}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (1.3)
\]

Dissolution of clay silicate minerals occurs in strongly acid soils. This can be aided by ferrolysis associated with alternating oxidising / reducing soil conditions (Brinkman 1970). Dissolution of clay minerals causes the release of release of aluminium and other metals. Dissolved, monomeric forms of aluminium have received particular attention due to their
toxicity for many aquatic species (Sammut et al. 1995; Hyne and Wilson 1997). Concentrations of dissolved aluminium and other dissolved metals in ASS, are typically inversely proportional to soil and/or groundwater pH (Dent 1986; van Breemen 1993; Blunden 2000). The pH attained by the soil following oxidation of sulfide minerals is not only dependant upon the initial concentration of sulfides, but also upon the amount of acid neutralising components in the sediment, including exchangeable bases, carbonates and easily weatherable silicate minerals.

The distribution of pyrite and other sulfide minerals in the soil matrix is highly heterogeneous (Dent 1986; Andriesse 1993). Zones of organic matter accumulation, such as old root channels, often contain particularly high concentrations of pyrite. Old root channels and macropore can also act as preferential pathways for oxygen entry into the soil (Bronswijk et al. 1993). There can also be substantial variation in pyrite crystal size and morphology (Bush and Sullivan 1999) which can influence pyrite oxidation rates (Bronswijk et al. 1993). Greigite has also been reported in ASS (Bush and Sullivan 1996).

A wide range of iron and sulfur minerals are commonly formed following pyrite oxidation. Common oxidation products include jarosite (used as a visual indictor of past pyrite oxidation in soil profiles), and various other Fe oxide minerals including ferrihydrite, schwertmannite, goethite and hematite. Several trace metals can substitute for iron within pyrite or other related sulfide minerals, including Ni, Co, Cu, Zn, Pb, As, and these can also be released during oxidation reactions.

Both of the primary products from pyrite oxidation, Fe and S, are redox sensitive. Many of the redox transformations involving Fe and S species are mediated by a variety of bacteria.
Reduction reactions are highly dependant on an adequate source of labile organic matter and subsequently are often limited in sub-surface mineral soils (van Breemen 1993). However, labile organic matter is generally far more abundant in surface soils. The reduction of Fe and SO$_4^{2-}$ and reformation of sulfides is relatively common in surface soils following re-flooding and leads to the consumption of protons and a corresponding rise in soil pH (Ponnamparuma 1972; van Breemen 1975). Plant toxicity associated with excess Fe$^{2+}$ and H$_2$S in surface soils also commonly occurs following re-flooding. The biogeochemical significance of Fe (III) reduction has become increasingly recognised and can play a major role in carbon cycling in anaerobic aquatic sediments (Stumm and Sulzberger 1992; Lovley 1993; Roden and Wetzel 1996; Thamdrup 2000; Straub et al. 2001).

Shallow groundwater in ASS commonly has very low pH (<3 - 4), high concentrations of SO$_4^{2-}$ and acidic metal cations such as Fe$^{2+}$ and Al$^{3+}$. Fe$^{2+}$ and Al$^{3+}$ can be responsible for a large fraction of the titratable acidity in ASS drainage waters (Cook et al. 2000a). Oxidation of mobile, aqueous Fe$^{2+}$ to ferrihydrite (FeOOH) (via Fe$^{3+}$) can potentially occur at some distance from the source of pyrite, which causes the generation a further 2 moles of acidity (van Breemen 1973), represented by Eq. (1.4).

$$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{FeOOH} + 2\text{H}^+ \quad (1.4)$$

If the pH is <4.5 aluminium is mainly in the form Al$^{3+}$ and can potentially generate a further 3 moles of acidity by hydrolysis. Al$^{3+}$ is phytotoxic at relatively low concentrations (i.e. 1 - 2 mg L$^{-1}$; Dent 1986) and can severely inhibit plant growth.

The concentration and vertical distribution of acidic solutes within ASS profiles varies on a
seasonal basis (Walker 1972; Dent 1986; Eriksson 1993). Seasonally fluctuating water tables not only play a major role in the oxidation of new pyrite and release of additional oxidation products (Blunden 2000), but also the subsequent redistribution of these products. Rainfall and wet periods can result in downward leaching or export of soluble acidic products via drainage water (Minh et al. 1997). Evaporative flux from the capillary fringe during dry periods can also cause upward accumulation of acidic solutes in the soil profile (Minh et al. 1998). This process can lead to the acidification and creation of sulfuric horizons within essentially non-sulfidic sediments which lay above an oxidising sulfidic horizon (Lin and Melville 1993; Lin et al. 1995). Acidity arising from interflow of acidic groundwater can be difficult to distinguish from acidity derived from \textit{in situ} oxidisation of sulfides (Hamming and van den Eelaart 1993).

Sulfidic soils often undergo substantial physical and structural changes upon oxidation and drying (Dent 1986). Saturated, unoxidised, estuarine sulfidic clays typically have very high volumetric water contents, low bearing strength and generally very low hydraulic conductivity, except through old root channels and macropores. Loss of water leads to a one way process of ‘ripening’ in which irreversible collapse of structure and shrinkage occurs, resulting in fissuring and cracking (Dent 1986). Soluble products from pyrite oxidation can also help flocculate clays and promote the development of a more permeable, aggregated soil structure. The process of ripening is self-promoting, as a more permeable structure favours entry of oxygen and continued pyrite oxidation. Continued ripening can lead to the creation of sulfuric horizons with relatively high hydraulic conductivity compared to the underlying unoxidised sulfidic material, which has long term consequences for the management of acid groundwater.
The hydraulic properties of ASS are highly heterogenous and change over time due to the ripening processes mentioned above (Bouma et al. 1993). They typically vary with depth in the soil profile according to the degree of ripening and structural development within the individual horizons (Dent 1986; Blunden 2000). Anisotropy is also common and the hydraulic conductivity can be higher in the vertical plane (Blunden 2000). Macropores are also a relatively common feature, particularly in oxidised horizons. They can act as preferential pathways for both solute transport and oxygen diffusion. Very high hydraulic conductivity values have been reported in some oxidised ASS horizons in Indonesia associated with dense macropore networks comprised of old root channels and cracks (Hamming and van den Eelaart 1993). The orientation, geometry, volume, pore size distribution and connectivity of macropores profoundly affects groundwater movement rates (Bevan and Germann 1982; Bouma 1991). Macropore systems can experience very high velocity flows. The capacity of tubular macropores to carry water is proportional to the factor $r^4$ ($r$ = radius), and thus a relatively small number of larger pores can transmit large quantities of water even though their contribution to total pore volume is small (Bouma 1991).

1.4. Drainage of coastal floodplains and modification of hydrology

Large drainage networks have been progressively constructed on the coastal floodplains of northern NSW since European occupation. Drains were constructed mainly to reduce the impacts of frequent flooding, to convert low swampy land into agricultural land and to remove stormwater from agricultural land. In many cases natural channels and tidal creeks were straightened and converted into drains and many new open ditch drains were excavated.
The history of European occupation and agriculture on northern NSW coastal floodplains is intimately related to the incremental expansion of drainage schemes. By the 1890’s drainage works had already begun in many locations (Bodycott 1993). A series of severe floods during the late 1940’s and 1950’s led to the development of a coordinated, State Government sponsored flood mitigation scheme (Pressey and Middleton 1982). This scheme constructed extensive drainage works on the coastal floodplains of northern NSW throughout the 1960’s and 1970’s, greatly expanding and augmenting the existing network of drainage infrastructure (Pressey and Middleton 1982; Middleton et al. 1985). The use of more modern equipment (i.e. draglines) during this period led to constructed drains becoming much larger, wider and deeper than the original works. Floodgates (passive flapgates) were installed near the discharge point of most of these constructed drains. Their function was to allow drainage from the floodplain whilst preventing the ingress of either floodwaters or saline estuarine waters. They effectively allow drainage to low tide levels during dry periods. There are over 1700 km of floodgated drains and water courses on the Clarence River floodplain (Clarence River County Council, unpublished data).

1.5. Some effects of drainage and modified hydrology

1.5.1. Floodplain hydrology and water balance

The water balance of coastal floodplain backswamps is dominated by inputs from rainfall and upper catchment flooding and outputs via evapotranspiration and drainage (White et al. 1997). Prior to drainage construction, natural river levees helped retain a proportion of the flood and surface waters in ASS backswamps. Natural drainage rates from these inundated backswamps were often very slow due to the low outlet channel density, high channel roughness and sinuosity, low hydraulic gradients (White et al. 1997) and the existence of tidal depositional barriers near the outlet mouths. This combination of factors
meant that once backswamp water levels fell below the minimum elevation of natural levees and drainage lines, further loss of surface water was largely by evapotranspiration.

The construction of artificial drainage networks has caused a major and fundamental change to the hydrology of coastal floodplains, particularly in former wetlands and ASS backswamp systems (Pressey and Middleton 1982). One of the main hydrological results of constructed drainage has been increasing the rate of removal of surface waters from the floodplain, causing a reduction in natural retention / storage times of about an order of magnitude (i.e. ~100 days to ~10 days; White et al. 1997). This rapid shedding of surface water also increases the time period over which evapotranspiration can then act directly on the shallow groundwater - effectively increasing the depth to which evapotranspiration can lower the groundwater table during the dry season (Cook et al. 1999). This indirect contribution of drainage to lowering of groundwater levels has potential to enhance sulfide oxidation by increasing the exposure of sulfidic sediments to oxygen. Drains can also cause some direct interception and loss of shallow groundwater (Blunden 2000). This can increase the initial rate of groundwater drawdown, particularly in soils with high K_{sat} (Cook et al. 1999). The rate of drawdown of shallow groundwater by direct drainage is highly dependant upon the hydraulic properties of the intercepted soils horizons and other key factors including drain depth and density (Cook et al. 1999; Cook et al. 2002).

1.5.2. Generation and export of sulfide oxidation products

While there were clear historical warnings about the likely acidity problems associated with over-drainage of ASS backswamps (Walker 1963; Walker 1972), these were largely ignored. On the Clarence River floodplain anecdotal observations of acidification occurring in ASS backswamps following drain construction were made in the 1920’s
Lower groundwater levels enhance the opportunities for oxygen to enter sulfidic sediments, increasing oxidation and causing the release of acidity, soluble Fe, $\text{SO}_4^{2-}$ into soil and shallow groundwater as per Eq. (1.2). There is debate about what levels of acidity in floodplain ASS backswamps are essentially pre-European and what is due to the influence of constructed drainage and there are few definitive studies of this topic for eastern Australia (Lin et al. 1995; van Oploo et al. 1998).

Regardless of their contribution to sulfide oxidation, constructed drains collect and efficiently transport ASS backswamp surface waters and shallow groundwater past the natural levee system into adjacent estuarine channels. There have been many recent studies documenting how constructed drainage in ASS backswamps has facilitated the export of acidity, acidic metal cations and deoxygenated water into adjacent estuaries (i.e. Johnston 1995; Sammut et al. 1996; Wilson et al. 1999, Cook et al. 2000a; Blunden 2000). There is some historical documentation of fish kills occurring in eastern Australian estuaries prior to the 1950’s, though details regarding the precise causes (e.g. acidification, deoxygenation) of these historic events is very limited (NSW Agriculture and Fisheries 1989). While acidification / deoxygenation processes can and do occur naturally on undrained floodplains (Hart et al. 1987; Hamilton et al. 1997), the expansion of constructed drainage is likely to have altered the frequency, magnitude and duration of such events (Sammut et al. 1993).

1.5.3. Vegetation changes

One of the major impacts of drainage and shortening the hydroperiods (i.e. the duration of
inundation) of floodplain ASS backswamps was a change in, and in some cases complete loss of, wetland vegetation communities (Goodrick 1970; Pressey and Middleton 1982). There is limited data on original floodplain backswamp vegetation and in many cases this is confined to brief structural descriptions (i.e. open swamp, swamp forest, reeds and rushes) annotated on original portion survey maps (Smith 1999a; Cibilic 2003).

The role of hydroperiods in determining wetland vegetation species composition is well established (Mitsch and Gosselink 1993; Roberts and Marston 2000). Decreased depth and duration of inundation and increased drying has led to downslope ecotone migration of vegetation communities in some ASS backswamps (Pressey and Middleton 1982; NSW Agriculture and Fisheries 1989). Substantial increases in the area of flood intolerant pasture species have been noted in some areas, often in conjunction with a reduction in the original area of reeds and rushes (NSW Agriculture and Fisheries 1989; Smith 1999a; Cibilic 2003). In addition to drainage, the grazing of cattle and frequent burning is also likely to have influenced ASS backswamp vegetation species composition. Many ASS backswamps on northern NSW coastal floodplains had substantial accumulations of peat or highly organic surface soils. There are numerous examples of surface peat layers in ASS backswamps having been reduced or completely lost via fire following drainage (Smith 1999b).

1.6. Problem definition and focus of thesis.

There is now wide recognition that current drainage of coastal ASS can have severe consequences for estuarine water quality. There is substantial community pressure to reduce these negative off-site consequences. This pressure is driving management initiatives whose main aim is to improve environmental outcomes (i.e. Tulau 1999;
Johnston et al. 2003d). Many of these initiatives focus on changing the management of drainage systems and/or floodgates. In order to improve environmental outcomes, there is a need to have a sound conceptual understanding of some of the important processes contributing to the off-site impacts and to be able to predict the likely effects of management changes. Management attempts which lack a sound understanding of key processes are likely to be ad-hoc, reactive and meet with mixed success.

1.6.1. Areas of uncertainty

There has been limited study of some of the potential interrelationships between the altered hydrology and the biogeochemistry of drained sulfidic backswamps. There is potential for dynamic and complex interactions to occur between the increased rates of surface and groundwater removal, increased concentrations of redox sensitive species (Fe and S) in surface soils and groundwater, and changes to vegetation composition. Some specific areas of uncertainty and knowledge gaps are outlined below.

(a) The enhanced drainage of anoxic surface water from ASS backswamps after flooding and links this may have with deoxygenation events occurring in the estuary during the flood recession phase. Rapid removal of water from floodplains has potential to alter the flux of anoxic water and organic matter to adjacent channels (Sparks 1995). There is potential for interactions to occur between surface floodwaters in drained ASS backswamps, changed vegetation and increased concentrations of redox sensitive species (Fe, S) in surface sediments. A study by NSW Agriculture and Fisheries (1989) identified that decomposition of flood intolerant pasture species after inundation followed by rapid removal of floodplain backswamp surface waters by constructed drainage was a potentially important contributor to low dissolved oxygen events in the Macleay estuary. In contrast, a
recent comparison of available historic and contemporary data for the Richmond River concluded that “Floodplain management practices, including further draining and disturbance of acid sulfate soils appear to have had no appreciable effect on the processes that control the degree of oxygen saturation in the estuary” (Eyre 1997, pp. 177). However, historical studies of estuarine dissolved oxygen are limited (i.e. Rochford 1952) and to date there is very little flood event based data. There is a need to assess the changes in ASS backswamp surface water chemistry following a flood event and to quantify the magnitude of the impact of constructed drainage on estuarine deoxygenation.

(b) The acid flux dynamics of drained ASS backswamps. Field based studies of hydrological pathways of acid transport to drains with high temporal resolution analysis of acid flux are relatively limited. Most existing studies of acid flux rates from drained ASS backswamps in Australia have either had coarse temporal resolution (i.e. monthly, using water balance methods - Sammut et al. 1996; Wilson et al. 1999), or have acid flux estimates based on pH alone (i.e. Sammut et al. 1996), which is known to be of limited efficacy (Cook et al. 2000a). Hydrological pathways of acid flux have not always been clearly defined (i.e. Wilson et al. 1999). Studies with higher temporal resolution (i.e. Cook et al. 2000a; Cook et al. 2000b) have provided more detailed assessment of acid flux pathways in relation to site specific hydrological behaviour. There can be large variability in the water quality between drainage systems situated in ASS backswamps (Johnston 1995), but the reasons for these differences are not always clear. Relationships between the hydrological pathways of acid export and variations in site specific soil / hydrological characteristics require further attention.

(c) The vegetation changes in ASS backswamps after European occupation and drainage have been relatively poorly documented. Little attention has been given to quantifying the
aerial expansion of woody tree species (i.e. *Melaleuca quinquenervia*) in ASS backswamps and examination of any implications this may have for the chemical composition of surface water or groundwater and soil geochemistry.

(d) The effects of changes to drainage system management upon groundwater hydrology, acid export and drain water quality. Retaining drain water with weirs can reduce the effluent groundwater hydraulic gradients driving acid groundwater seepage (Blunden 2000), but the effects of this strategy on reducing acid export have not been quantified. There is a need to further investigate the effects of floodgate opening and tidal water exchange on improving in-drain water quality and also to evaluate the potential for this to cause lateral intrusion of salt from the drain into adjacent soil (Blunden 2000).

1.6.2. Statement of theses

The primary theses are (i) that the dominant processes affecting surface drainage water quality in ASS backswamps arise from interactions between hydrology, soils and vegetation, (ii) that the hydraulic conductivity of sulfuric horizons and local tidal dynamics in adjacent drains play a primary role in groundwater seepage and thus acid export, and (iii) that improvements in drainage water quality can be achieved by making informed changes to the current hydrological management of drains in ASS backswamps.

This thesis aims to address some of the areas of uncertainty and data gaps outlined above and to quantify some of the improvements in drainage water quality made by changing the current hydrological management of ASS backswamps.
1.6.3. Part I: The quantification and assessment of existing hydrological and biogeochemical processes in drained acid sulfate soil backswamps.

Chapters 2 to 5 focus on the areas of uncertainty and knowledge gaps identified in section 1.6.1.. The issues and topics addressed by each chapter are outlined below with the aid of schematic diagrams.

Chapter 2 examines drainage water quality and drainage rates following major flooding. It relates the changes in water quality to biogeochemical processes occurring in the backswamps and assesses the contribution of artificial drainage of ASS backswamps to an observed estuarine deoxygenation event (Fig. 1.4).

Figure 1.4. A schematic representation of some of the main processes and topics examined in chapter 2 and chapter 4. Numbers in parenthesis relate to the relevant chapter.

Chapter 3 quantifies the aerial extent of Melaleuca quinquenervia encroachment in a drained ASS backswamp and examines effects of this encroachment on the geochemistry
of shallow groundwater and sulfidic sediment (Fig. 1.5).

Chapter 4 examines changes in the surface water quality (deoxygenation, redox processes and acidification) associated with re-flooding of surface soil from an ASS backswamp with different *in situ* vegetative cover (i.e. grass species and *Melaleuca quinquenervia*) in a temperature controlled laboratory environment (Fig. 1.4 and 1.5).

![Figure 1.5](image.png)

**Figure 1.5.** A schematic representation of some of the main processes and topics examined in chapter 3 and chapter 4. Numbers in parenthesis relate to the relevant chapter.

Chapter 5 examines the acid flux dynamics of two different ASS backswamps. It focuses on high temporal resolution acid flux rates, hydrological pathways of acid flux and the frequency, duration and intensity of drain water acidification. Important hydrological factors controlling export rates and pathways are identified (Fig. 1.6).
1.6.4. **Part II: Examining the effects of changes to the management of drainage systems.**

Chapters 6, 7 and 8 evaluate some effects of changing the management of drainage systems upon drain water quality, shallow groundwater hydrology and groundwater chemistry. The types of management changes examined include (a) the retention of water within drains, and (b) the tidal exchange of estuarine water with drain water via opening floodgates. The issues and topics addressed by each chapter are outlined below with the aid of schematic diagrams.

Chapter 6 evaluates the effectiveness of using an in-drain retention structure (a weir) to reduce acid flux from a drained ASS backswamp (Fig. 1.6).
Chapter 7 examines some effects of opening floodgates on in-drain water quality, particularly acidity and dissolved oxygen, as well as inflow and outflow volumes and acid flux (Fig. 1.7). Some interactions with shallow groundwater are also examined.

Chapter 8 examines the effects of floodgate opening on lateral seepage of saline water from drains into adjacent shallow aquifers (Fig. 1.7). Two sites with contrasting geomorphology and soil hydraulic properties are compared.
Chapter 2

Artificial drainage of floodwaters from sulfidic backswamps: effects on deoxygenation in an Australian estuary

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2.1. Abstract

The Clarence River estuary experienced extensive oxygen depletion and fish kills following overbank flooding in 2001. This paper examines the chemical composition and volume of surface water draining from two floodplain sulfidic backswamps into the Clarence River estuary after the flooding. Water draining from the backswamps was severely deoxygenated (<5 µmol L\(^{-1}\) O\(_2\)), developed high chemical oxygen demand (~5000 µmol L\(^{-1}\)) and became enriched in iron (~350 µmol L\(^{-1}\)) during the weeks following the flood. The chemistry of this anoxic drainage water was influenced by anaerobic decomposition of backswamp vegetation, iron and sulfur biogeochemistry in backswamp surface sediments and shallow groundwater input from acid sulfate soils. This study shows that artificial drainage of sulfidic backswamps increased the volume of anoxic surface water with high deoxygenation potential exported to the estuary, increasing the severity and duration of estuarine oxygen depletion in the latter stages (>6 days post-peak) of flood recession. In the absence of artificial drainage, most of the floodwaters with high deoxygenation potential would have been retained in the landscape and not exported to the estuary as observed during this flood.
2.2. Introduction

Coastal floodplains and their associated wetlands play an important role in regulating flood flows, sediment and nutrient fluxes and exert a strong influence on the quality of receding floodwaters (Hart et al. 1987; Mitsch and Gosselink 1993; Sammut et al. 1996; Hamilton et al. 1997). Development of rural settlements and agriculture on Australia’s eastern coastal floodplains has led to construction of drainage to mitigate the adverse effects of large floods and intense rainfall events. There is growing community concern about the impacts of coastal drainage systems on estuarine water quality and fisheries (NSW Agriculture and Fisheries 1989; Slavich 2001).

Drainage of coastal floodplains has increased the occurrence of water acidification and deoxygenation events in adjacent estuaries (Sammut et al. 1994; Sammut et al. 1996; White et al. 1997). These events have been linked to oxidation and drainage of acid sulfate soils (Sammut et al. 1996; Wilson et al. 1999; Cook et al. 2000a), changes in the type of floodplain vegetation (Pressey and Middleton 1982; Middleton et al. 1985; NSW Agriculture and Fisheries 1989), and changes in the rate of delivery of flood waters to the estuary (Pressey and Middleton 1982; White et al. 1997).

Prior to drainage construction, natural river levees retained a part of the flood and storm waters in low backswamp basins on the floodplain. The natural drainage rate from inundated backswamps was often very slow due to the low outlet channel density, high channel roughness and sinuosity, low hydraulic gradients (White et al. 1997) and the existence of tidal depositional barriers near the outlet mouths. Artificial drainage and flood mitigation strategies have modified many of these characteristics so that drainage from backswamps into the estuary is now much faster.
Sulfidic estuarine sediments and acid sulfate soils (ASS) often lie beneath a thin alluvial veneer in the backswamps of coastal floodplains (Walker 1972). The shallow depth to ASS in backswamps is significant because of its influence upon the quality of drainage waters (Sammut et al. 1996; Wilson et al. 1999) and the chemistry of surface sediments (Walker 1972; van Breemen 1973; Dent, 1986). Artificial drainage has encouraged sulfide oxidation and enhanced the accumulation of Fe (III) oxides, SO$_4^{2-}$ and Al in surface sediments of ASS backswamps (Walker 1972; Rosicky et al. 1999). Deep drains in ASS backswamps are also an ideal sub-environment for the formation and accumulation of monosulfidic black oozes (MBO) rich in acid volatile sulfur species (Sullivan and Bush 1999).

When ASS backswamps are flooded there are likely to be interactions between the decomposition of organic matter and surface accumulations of redox sensitive species, such as Fe and SO$_4^{2-}$, which may influence surface water chemistry (Ponnamperuma 1972; Olivie-Lauquet et al. 2001; Lamers et al. 2002). Microbially mediated Fe (III) reduction is an important process catalysing carbon oxidation in anaerobic sediments (Lovley and Phillips 1986; Stumm and Sulzberger 1992; Lovley 1993; Roden and Wetzel 1996; Thamdrup 2000; Straub et al. 2001) and reduction rates are highly dependent upon the abundance of poorly crystalline Fe (III) oxides (Roden and Wetzel 2002).

The combined impact of the above processes on estuarine deoxygenation events is poorly documented. There is a need to characterise the chemistry and volumes of flood drainage waters from ASS backswamps and quantify their temporal variation to better understand how these processes contribute to deoxygenation and acidification events. This paper aims to (1) describe temporal changes to drainage water chemistry after flooding from two drained coastal floodplain ASS backswamps, (2) examine processes responsible for these
changes, (3) estimate the flux of oxygen depleting compounds from the two drains to the estuary, and (4) estimate the contribution of artificial drainage of ASS backswamps to the observed estuarine deoxygenation event.

2.3. Material and methods

2.3.1. Study Areas

The Clarence River catchment (Fig. 2.1) has an area of 22700 km$^2$ and the Clarence River estuary is a mature barrier system (Roy 1984). The floodplain is over 2600 km$^2$ and underlain by an estimated 530 km$^2$ of acid sulfate soils (Tulau 1999). There are over 1700 km of floodgated drains and water courses on the Clarence River floodplain. The two study areas were Blanches and Maloney's (Fig. 2.1). Both drain water from ASS backswamps on the lower Clarence River floodplain into the estuary. The backswamps are infilled Holocene estuarine embayments (Roy 1984; Lin and Melville 1993) with surface elevations mostly < 0.2 m Australian Height Datum (AHD; 0 AHD ~mean sea level). Both contain ASS with large reserves of acidity in the sulfuric horizons and are underlain by sulfidic sediment ~1 m from the ground surface (Lin and Melville 1993; Morand 1997). The hydraulic conductivity of the sulfuric horizons is about 15 times higher at Maloney's than Blanches (Johnston et al. 2002a; Johnston et al. 2004), resulting in large differences in the acid flux dynamics of the respective drains. Maloney's drain typically displays high acid flux rates and chronic acid discharge, whereas Blanches drain has lower acid flux rates and infrequent, highly episodic discharge of acidity (Johnston et al. 2004).
Blanches is located on Everlasting Swamp (Fig. 2.2) and drains an ASS backswamp area of ~600 ha, plus a proportion of an upland catchment. The main drain is over 3.5 km long and up to 10 m wide and discharges water through a two cell box culvert with outward opening floodgates. This drain was constructed through the natural levee in the 1960’s and discharges directly into the main Clarence River channel. Everlasting Swamp was originally a seasonal, tidally influenced, brackish to fresh water wetland dominated by reeds and rushes and has undergone major changes to natural hydrology and vegetation since the early 1900’s (Smith 1999a).
Maloneys is located in the lower eastern Shark Creek backswamp (Fig. 2.2). The main drain is over 1.5 km long, up to 8 m wide and has a catchment containing 208 ha of ASS backswamp and 300 ha of upland. The drain discharges through a natural levee into Shark Creek via a single cell pipe culvert with an outward opening floodgate. The hydrology of the backswamp has been modified by drainage. Originally there were no natural channels...
through the distributary levee at this site. This means that prior to drain construction, water loss from the backswamp would have been largely restricted to evapotranspiration once surface waters fell below the height of the natural levee (>1 - 3.5 m AHD).

The limit to natural drainage at both study site backswamps, prior to artificial drainage, was conservatively estimated as ~0.5 m AHD. This figure is based on previous studies (White et al. 1997), available historical data and local tidal dynamics (local mean high water at both sites is ~0.45 m AHD), and is used to estimate the proportion of flux due to constructed drainage. Once mean drain water levels fell below ~0.5 m AHD, further surface water drainage from the backswamps was regarded as induced by constructed drainage. In some backswamp systems this natural limit may well have been higher, particularly those systems with high natural levees and few natural drainage lines (e.g. eastern Shark Creek).

2.3.2. Meteorological monitoring

Temperature and rainfall were recorded hourly with two EIT E-Tech weather stations, one located at the Maloneys study site and the other at Grafton Agricultural Research Station (Fig. 2.1). Rainfall data used in this study is an arithmetic mean from both weather stations.

2.3.3. Backswamp vegetation

Contemporary backswamp vegetation at Blanches is dominated by open pasture. At Maloneys, open pasture comprises one third of the backswamp area and the remainder is Melaleuca quinquenervia forest. Open pasture areas at both sites consisted mostly of native grass species including Paspalum distichum, Pseudoraphis spinescens and Cynodon dactylon with scattered occurrences of rushes Eleocharis acuta and Juncus usitatus. Visual estimates of ground cover foliage were made according to McDonald et al. (1990) in the
ASS backswamp at both sites along 400 m transects perpendicular to the piezometers (Fig. 2.2) four days before and three weeks after flooding.

2.3.4. River, drain and groundwater quality

Hourly measurements of drain water dissolved oxygen (DO), pH, Electrical Conductivity (EC) and temperature were made with Greenspan CS304 submersible data loggers (SDL). Two SDLs were installed in each drain, one near the floodgates and one near the backswamp margin, designated monitoring stations A and B, respectively (Fig. 2.2). Each SDL was housed in a slotted 0.1 m diameter PVC pipe, positioned as close to centre channel as possible. DO was measured via a diffusion rod, pH using a double junction Ag/Cl electrode and EC via a toroidal sensor. The SDLs were cleaned, maintained and calibrated every 28 - 32 days and were calibrated 4 days prior to the February 2001 flood event. During the post-flood period SDLs were cleaned approximately every 8 - 10 days to minimise fouling and check for calibration drift.

Spot measurements of in situ drain water DO, pH, EC, temperature and redox potential were recorded at the time and location of sample collection using freshly calibrated portable field equipment (TPS 90FLMV). Redox potential was measured with a platinum tipped Ag/AgCl reference electrode and values are reported relative to the standard hydrogen electrode (Eh), corrected for temperature and adjusted to pH 7 according to Bohn (1971). Comparison of spot measurements with logged SDL values indicates that the logged data from the Blanches floodgates site were accurate, with a mean difference in pH of 0.12 units (n = 11), in EC of 0.07 dS m$^{-1}$ and in DO of 8 µmol L$^{-1}$. 

2-9
Data collected by NSW Fisheries (Pollard 2001; Westlake and Copeland 2002) following the February flood showed extensive estuarine deoxygenation (DO <15 µmol L\(^{-1}\)) associated with pH values ~6.0 occurring over a 20 km stretch of the South Arm channel (Fig. 2.1) for at least 3 weeks after the flood peak. The South Arm channel receives waters from ~6000 ha of artificially drained ASS backswamp (Milford 1997; Morand 1997), principally from the Shark Creek and Coldstream sub-catchments, but has a much lower volume than the main Clarence River channel. A limited number of spot measurements of river water quality were made in this study using freshly calibrated portable field equipment (TPS 90FLMV). Measurements were confined to the South Arm channel, at a location 2 km upstream of Maclean and were restricted to the upper 2 m of the water column 10 m out from the river bank.

Groundwater was collected from the sulfuric horizons at both sites from shallow auger holes as part of an associated study (Johnston et al. 2002b).

2.3.5. Sample collection, treatment and analysis

Drain water samples were collected at the floodgate culverts and at the backswamp SDL approximately every 2 - 4 days, beginning several days after the flood peak and continuing for about 30 days. Sampling intensity was highest immediately following the flood. When discharge became affected by tidal influence, sampling coincided with outflow periods to ensure accurate representation of discharge water. Water samples were collected from 0 to 0.3 m below the surface at centre channel using a clean 10 L plastic bucket thoroughly pre-rinsed with the drain water to be collected. From this a minimum of three 250 ml sub-samples were taken in clean (acid rinsed, distilled water flushed) polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times. Visible air bubbles were
excluded prior to sealing the cap and samples then placed in cold storage (~4°C) for transport. One 250 ml sub-sample was analysed for titratable acidity to pH 5.5 on the same day as sample collection (APHA (1995), 2310B - including the peroxide oxidation step). At least one 250 ml sub-sample per day was selected for further chemical analysis and frozen within 4 hrs of collection to minimise chemical / biochemical changes. Samples selected for chemical analysis were transported frozen, thawed at 4°C, sub-samples extracted and analysed for Chemical Oxygen Demand (COD) (di-chromate digestion, colorimetric - APHA (1995), 5220D), Total Fe and Total Al (ICPMS - APHA (1995), 3120), Dissolved Fe and Dissolved Al (0.2 µm cellulose acetate filtration, ICPMS - APHA (1995), 3120), Cl⁻ (FIA - AHPA (1995), 4500 Cl), SO₄²⁻ (APHA (1995), SO₄²⁻ - E), dissolved organic carbon (DOC) (combination Infra-red - APHA (1995), 5310B) and Acetate (Dionex Liquid Chromatography; AS14A column, eluent 8 mM sodium carbonate/1 mM sodium bicarbonate flow at 1 ml min⁻¹, conductivity detection).

2.3.6. Drain discharge estimates
Flow velocity in the drains was measured using a Doppler sensor (Starflow - 6526-51) with a velocity range of 0.021 m s⁻¹ to 4.5 m s⁻¹. The scan interval was set for 30 seconds and the hourly mean, maximum and minimum logged, enabling the time at which drain discharge commenced to be accurately determined. The Starflow unit also measured water level using a hydrostatic pressure sensor vented to the atmosphere. Velocity data used to estimate discharge were derived from the Starflow unit located at the floodgate culvert (Station A, Fig. 2.2). Each Starflow unit was positioned in the centre of the culvert (centre of one cell at Blanches). Culvert dimensions and Starflow locations were surveyed to AHD. Checks were undertaken using a calibrated current meter in the Doppler field of view under a range of flow conditions (>1 to ~0.1 m s⁻¹) and yielded flow velocities within ± 10% of the Doppler
sensor. Daily drain discharge ($Q_d$) equals the sum of the hourly discharge volumes ($q_h$), which was derived using Eq. (2.1),

$$q_h = V_h A_h \quad (2.1)$$

where $V_h =$ mean hourly flow velocity, $A_h =$ mean hourly cross-sectional area of water in culvert. Additional water level measurements were recorded every hour inside and outside the floodgates and near the backswamp margin using a Dataflow capacitance probe and 392 logger (precision ± 0.001 m; accuracy ± 0.01 m) housed in a 5.5 cm diameter slotted PVC pipe and surveyed to AHD.

2.3.7. Drain flux estimates

Daily flux estimates for DOC, COD, Total Fe, dissolved Fe, Total Al, $\text{SO}_4^{2-}$ and titratable acidity were made by multiplying $Q_d$ by the daily concentration ($C_d$) of that parameter. For sampling days $C_d$ was the chemical composition of the drain water outflow sample. For non-sampling days $C_d$ was estimated by linear interpolation between adjacent sampling day concentrations. Total flux estimates are the sum of daily flux for 30 days after the flood peak and are expressed relative to the area of ASS backswamp in the drainage sub-catchment of each study site. In calculating the oxygen depletion potential of drainage water, $C_d$ was conservatively estimated as 0.5 x COD (chemical oxygen demand). This was to account for the COD test overestimating biologically mediated oxygen demand in waters through inclusion of reduced inorganics and oxidation resistant organic compounds (Krenkel and Novotny 1980). The oxygen content of receiving river waters was assumed to be 156 $\mu$mol L$^{-1}$ (5 mg L$^{-1}$). Based on these two figures, an estimate of the volume of river water that could potentially be deoxygenated per unit volume of drain water was obtained.
2.3.8. Estimates of river flow and deoxygenation potential of ASS backswamp drainage

A first order estimate of flow volumes in the South Arm channel for 2 weeks after the flood peak was made using a rating curve for the Clarence River main channel and hourly water level data from a Grafton gauging station (Clarence River County Council, unpublished data). The total flow volume in the South Arm channel, including all inputs from the Coldstream River and Shark Creek, was estimated to be 0.2 x the main Clarence River flow, based on relative differences in channel size.

A first order estimate of the daily oxygen depletion potential of water discharging from drained ASS backswamps into the South Arm channel was derived by scaling up the COD flux data from both study sites according to the following Eq. (2.2),

\[ \theta_s = \frac{(Q_b + Q_m)}{2A} \]  

(2.2)

where \( \theta_s \) is the estimated daily oxygen depletion potential of waters discharging into the South Arm channel from drained ASS backswamps (m\(^3\) day\(^{-1}\)), \( Q_b \) and \( Q_m \) are the daily oxygen depletion potential flux estimates from the Blanches and Maloney's drains respectively (m\(^3\) ha\(^{-1}\) - based on the area of drained ASS backswamp in each sub-catchment) and \( A \) is the known area of drained ASS backswamps that discharge into the South Arm channel, all of which were inundated during the flood (6000 ha - Milford 1997; Morand 1997). This analysis assumes the study sites were reasonably representative of other drained ASS backswamps discharging into the South Arm channel, on the basis of extensive ground and aerial observations.

2.3.9. Surface sediment

Surface (0 - 2 cm) backswamp sediment samples were collected by push corer or by hand in open pasture areas of the ASS backswamp at Blanches and Maloney's. Each sample
comprised of 10 small sub-samples taken from a randomly selected 2 m² area until a volume of about 250 cm³ was obtained. This was placed in an airtight container, put into cold storage and frozen within several hours of collection. Selected sub-samples from Blanches were defrosted and immediately analysed for AVS (acid volatile sulfur - Sullivan and Bush 1998). The remaining samples were oven-dried at 85°C, crushed to pass a 2 mm sieve and then analysed for reduced inorganic sulfur species S_{Cr} (Sullivan et al. 1998), SO_{4}^{2-} (ion chromatography - APHA (1995), 4110B), oxalate-extractable Fe and citrate / dithionate-extractable Fe (Rayment and Higginson 1992). Oxalate-extractable Fe can be regarded as an estimate of the more active, poorly crystalline fraction of Fe minerals (such as ferrihydrite or schwertmannite) that are readily available for biomediated reduction (Lovley and Phillips 1986).

2.4. Results

2.4.1. Flooding

There were two large floods in the Clarence River in 2001, the first in early February and the second in early March. The February 2001 flood was accompanied by high rainfall in the upper catchment (200 to 400 mm; Bureau of Meteorology, unpublished data) and the lower floodplain received about 200 mm (Fig. 2.3). The last major flood in the Clarence prior to this event was in 1996. Backswamp groundwater levels were low at both study sites prior to the onset of rainfall (<0.7 m below ground level). There was little surface water in either backswamp until overtopping floodwaters were received.

The Clarence River peaked around 4 m AHD near Lawrence on 4 February 2001. At Blanches, rising floodwaters overtopped the natural levee at Sportsman’s Creek and progressively filled Everlasting Swamp on 3 February to a depth of about 4 m (Fig. 2.3).
Floodwater covered the backswamp vegetation to a depth >1 m for at least 4 days and most of the backswamp surface remained inundated until the onset of the second flood.

Compared to the Blanches study site, Maloney’s backswamp experienced relatively shallow flooding of shorter duration. At Maloney’s, floodwaters did not overtop the natural distributary levee on Shark Creek until ~8 km upstream from the study site floodgates, where the levee is lower. This resulted in a slow infilling of the east Shark Creek backswamp to a maximum depth of ~0.8 m before floodwaters began to recede (Fig. 2.4). This fundamental difference in the depth and duration of flooding at the two study sites had important effects upon the extent of vegetation decomposition and resultant post-flood drainage water chemistry.

2.4.2. Effects of flooding on vegetation

Effects of flooding on vegetation at each site varied according to the differences in inundation depth and duration. While *P. distichum*, and *P. spinescens* can tolerate wet conditions, rapid onset of deep inundation or high water temperatures will often lead to mortality (NSW Agriculture and Fisheries 1989). *Cynodon dactylon* is even less tolerant of inundation (NSW Agriculture and Fisheries 1989). Open pasture areas at both Blanches and Maloney’s had >80% ground cover immediately before flooding. Three weeks after flooding at Blanches this had reduced to <10% cover and vegetation had decomposed to a black organic slurry devoid of green vegetative material. In contrast, three weeks after flooding at Maloney’s the open pasture ground cover remained >80% and continued to grow and flourish as the shallow overlying flood waters receded. There was minimal (<10%) understorey groundcover beneath the *M. quinquenervia* forest at Maloney’s, however leaf litter was abundant.
2.4.3. River water quality

Large fish kills were first observed in the South Arm channel on the morning of 9 February associated with a DO concentration of ~10 µmol L\(^{-1}\) and a near neutral pH (~6.5). Surviving fish species, observed at the South Arm channel spot monitoring site, displayed behaviour consistent with hypoxia including surface gulping, sedate, sluggish movement and rapid opercular ventilation. The Eh of water in the South Arm channel fell from >500 to <200 between 9 and 12 February and changed colour from brown to black between 12 and 14 February. It remained black for several weeks and had a distinctive unpleasant odour. Aerial observations conducted on 17 February revealed a prominent plume of black water discharging from the South Arm channel into brown turbid water of the mainstream Clarence on the ebb tide.

![Figure 2.3. a) Clarence River\(^A\) and Blanches Drain hydrographs (note different scales), b) time series pH and DO at the floodgate SDL (monitoring station A) and c) hourly rainfall. Water level in m AHD (Australian Height Datum, 0 AHD ~ mean sea level). \(^A\) = Outside Blanches drain floodgates.](image)
Data from a SDL located in Sportsman’s Creek, 2 km from the confluence with the Clarence River, showed floodwater DO concentrations between 150 - 250 µmol L\(^{-1}\) on the rising limb and peak of the hydrograph (Manly Hydraulics Laboratory 2001). The site is close to the main channel and the data regarded as representative of mainstream Clarence River water, particularly in the early stages of the flood where water at the site was derived directly from the Clarence River. This data is important because it shows the initial floodwaters in the Clarence River were well oxygenated.

2.4.4. Drain water chemistry

Drainage waters at both sites had very low DO concentrations from 4 - 6 days after the flood peak. At Blanches drain there was a sharp initial drop in DO on 3 February during the early stages of backswamp infilling (Fig. 2.3). MBO has been found in the basal sediments of the drains at both study sites (data not shown) and this rapid decline in DO matches the known behaviour of suspended MBO (Sullivan and Bush 1999). While suspension of MBO may explain this initial drop, a precise cause cannot be determined on the basis of available data. However, the effect was short lived and the DO associated with the main infilling floodwaters recovered to around 190 µmol L\(^{-1}\) and then underwent a gradual decline over a four day period to almost zero (Fig. 2.3). The DO concentrations in Blanches drain remained below 5 µmol L\(^{-1}\) during the following four weeks, except for three short peaks in early March associated with intentional floodgate opening and ingress of more oxygenated river water (Fig. 2.3). A significant feature of the water discharging from Blanches drain was a distinctive colour change from brown and turbid to black around 11 February. This colour change was associated with an order of magnitude increase in dissolved Fe concentrations plus further lowering of Eh and was accompanied by a strong unpleasant odour and a thin oily surface film. The drain water at Blanches remained black in appearance until the onset
of the second flood.

At Maloneys drain floodgates there was an increase in DO concentrations (to 150 µmol L^{-1}) associated with the initial infilling floodwaters. A sharp drop to <15 µmol L^{-1} then occurred over a 24 hr period associated with an increase in EC (Fig. 2.4). It is possible that this decrease may be due to in-drain suspension of MBO as discussed above. The EC at the Maloneys floodgate SDL decreased rapidly during the latter stages of backswamp infilling (Fig. 2.4) due to dilution from river water. This river water also caused a mild recovery in drain water DO concentrations.

![Figure 2.4](image)

**Figure 2.4.** a) Shark Creek ^A and Maloneys Drain hydrographs (note different scales), b) time series pH and DO at the floodgate SDL and c) time series EC at the floodgate SDL (monitoring station A). ^A = Outside Maloneys drain floodgates.
However, the onset of outflow and high discharge velocities (>1.8 m s\(^{-1}\)) on 7 and 8 February were associated with further rapid declines in DO. Scour channels measured in the basal drain sediments at this site after the floods suggest that some mobilisation of MBO is likely to have occurred (data not shown). The dissolved oxygen concentrations in drain water remained mostly below 15 µmol L\(^{-1}\) for the following four weeks.

The Eh of the drain water decreased rapidly after flooding at both sites (Fig. 2.5b), but was lower at Blanches drain with minimum recorded values close to 0 mV. The initial temperature of the floodwaters was around 23\(^{\circ}\)C. Water temperatures on the floodplain increased rapidly (~33\(^{\circ}\)C measured in Blanches backswamp surface waters) in response to a period of high daily temperatures and drain waters remained >25\(^{\circ}\)C for most of the monitoring period (Fig. 2.6a). The pH of Blanches drain water following flooding was generally between 6 - 7 (Fig. 2.3). In Maloneys drain the pH varied substantially with initial values near 5.5 - 6 followed by a period of marked tidally modulated troughs. Minimum pH values near 3.5 were recorded in early March in Maloneys drain (Fig. 2.4).

There were very different temporal trends in dissolved organic carbon and to a lesser extent chemical oxygen demand, in the drain waters at the two sites (Figs. 2.5c and d). Although drain water at both sites had similar initial DOC concentrations, a sharp increase occurred in Blanches drain, whereas DOC at Maloneys drain remained relatively static. It is highly likely that these DOC trends are related to the substantial differences between the two sites in ground cover loss and vegetation decomposition. There were also distinct differences in the chemical properties of backswamp surface water between the two sites. DOC, COD and total Fe were almost an order of magnitude higher in the backswamp surface water at Blanches, whereas dissolved Fe and acetate were around two orders of magnitude higher (Table 2.1).
Figure 2.5. Post-flood changes in Blanches and Maloney's drainage water a) discharge volumes, b) Eh, c) dissolved organic carbon, d) chemical oxygen demand, e) total Fe and f) dissolved Fe. All concentration data is based on samples taken at the floodgates (monitoring station A).

At both sites total Fe in the drain waters increased by two orders of magnitude within three
weeks of flooding (Fig. 5e). Dissolved Fe in the water at Blanches drain increased an order of magnitude between 10 and 12 February associated with the pronounced colour change in drain water from brown to black discussed previously (Fig. 5f). Though sampling limitations precluded Fe speciation assays, given the greater solubility and relative stability Fe (II) under reducing conditions (Stumm and Morgan 1981), it is probable that a significant fraction of the dissolved Fe measured in drainage waters were Fe (II) compounds, possibly chelated with organic acids. The black colour observed in drainage waters may be related to such Fe (II) / organic acid complexes (Theis and Singer 1974).

Table 2.1. Chemical analyses of backswamp surface waters at Blanches and Maloney's study sites following the February flood.

Water depth at sampling locations was ~0.2 m. All concentrations in mmol L⁻¹ except where stated.

<table>
<thead>
<tr>
<th></th>
<th>Blanches (19/02/01)⁵</th>
<th>Maloney's (21/02/01)⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.03</td>
<td>6.27</td>
</tr>
<tr>
<td>EC (dS m⁻¹)</td>
<td>1.09</td>
<td>0.18</td>
</tr>
<tr>
<td>Chemical Oxygen Demand</td>
<td>25.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>22.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Total Fe</td>
<td>1.58</td>
<td>0.16</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>1.10</td>
<td>0.02</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1.27</td>
<td>0.26</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>5.63</td>
<td>0.95</td>
</tr>
<tr>
<td>Total Al</td>
<td>0.024</td>
<td>0.006</td>
</tr>
<tr>
<td>Acetate</td>
<td>2.62</td>
<td>0.01</td>
</tr>
</tbody>
</table>

⁵ Date sampled.
Figure 2.6. Post-flood changes in Blanches and Maloneys drainage water a) mean daily temperature at the floodgate SDL, b) titratable acidity (to pH 5.5), c) Cl⁻:SO₄²⁻ ratios (molar) and d) total Al. All concentration data is based on samples taken at the floodgates (monitoring station A).

At Blanches, increases in Total Fe in drain water were positively correlated ($r^2 = 0.82$, exponential regression) with increasing DOC (Fig. 2.7). This suggests that the process mobilising Fe into drainage waters at Blanches was associated with the mobilisation of organic carbon into solution. A likely process is the reductive dissolution of accumulated surface Fe (III) fuelled by anaerobic decomposition of organic matter (Lovley 1993; Roden and Wetzel 1996; Thamdrup 2000). In contrast, increases in Fe and DOC in the drain water at Maloneys were poorly correlated, suggesting Fe was mobilised by a different mechanism. Inputs of shallow ASS groundwater are likely to have been a more important source of
mobile Fe in drainage waters at this site (Johnston et al. 2004).

No titratable acidity to pH 5.5 was detected in any samples taken in Blanches drain following the flood. Drain water at Maloney’s had low initial values of titratable acidity, followed by a sharp increase on 14 February (Fig. 2.6b), which was associated with large increases in dissolved Fe and dissolved Al.

**Table 2.2. Chemical analyses of shallow ASS groundwater at Blanches and Maloney’s study sites.**

Samples collected from within 1 m of the ground surface. All concentrations are means expressed in mmol L$^{-1}$. Ratios based on molar concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Blanches (n = 7)</th>
<th>Maloney’s (n = 25)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titratable Acidity - H$^+$</td>
<td>9.1</td>
<td>13.9</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>52</td>
<td>17</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>38</td>
<td>19</td>
</tr>
<tr>
<td>Total Fe</td>
<td>3.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Total Al</td>
<td>5.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>1.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Cl:SO$_4^{2-}$</td>
<td>1.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

While both sites have shallow sulfidic soils and acidified shallow groundwater with similar chemical composition (Table 2.2) there were marked differences in the Cl$^-$:SO$_4^{2-}$ ratios of drainage water following inundation (Fig. 2.6c). Low, stable ratios at Maloney’s drain indicate that the sources of drainage waters at this site are associated with the oxidation of sulfides (Mulvey 1993) and that these sources remained relatively constant during the outflow stages of the flood. In contrast the Cl$^-$:SO$_4^{2-}$ in Blanches drain water steadily
increased during the outflow stages of the flood due to increasing Cl\textsuperscript{-}, but relatively stable SO\textsubscript{4}\textsuperscript{2-} concentrations. This apparent attenuation of SO\textsubscript{4}\textsuperscript{2-} relative to Cl\textsuperscript{-} is most likely related to SO\textsubscript{4}\textsuperscript{2-} reduction and sulfide mineral reformation occurring in the Blanches backswamp during this period (see below).

Higher total and dissolved Al concentrations at Maloney's drain also suggest an increasing influence of shallow ASS groundwater drainage at this site (Fig. 2.6d). Blanches maintained relatively stable, low Al concentrations in accordance with the circumneutral pH. Acetate is a primary fermentation product associated with anaerobic decomposition of organic matter and concentrations in backswamp surface waters at Blanches were high (2.62 mmol L\textsuperscript{-1}) (Table 2.1). However, acetate in discharge waters at the floodgates (2½ km from the backswamp) were consistently below detection limits (0.001 mmol L\textsuperscript{-1}) which may indicate \textit{in situ} oxidation or complexation in floodwaters prior to discharge.

\textbf{Figure 2.7.} Relationship between DOC and total Fe in drainage waters at the Blanches and Maloney's sites. Strong positive correlation (exponential regression) at Blanches, combined with surficial sediment chemistry data, suggests reductive dissolution of Fe associated with anaerobic decomposition of organic matter was an important process mobilising surface Fe into drainage waters at this site.
2.4.5. Surface sediment chemistry

Surface sediment chemistry in the ASS backswamps at both sites is strongly influenced by the underlying sulfides. Upward flux and surface accumulation of sulfide oxidation products, particularly Fe and SO$_4^{2-}$, is a well documented process in ASS (Dent 1986). Very high concentrations (>1 mol kg$^{-1}$) of poorly crystalline Fe (III) (oxalate-extractable) occur in surface (0 - 2cm) backswamp sediments at Blanches along with significant SO$_4^{2-}$ (Table 2.3). Significant, but much lower concentrations occur in surface sediments at Maloney's. After flooding in Blanches backswamp, there was an order of magnitude increase in concentrations of reduced iron sulfide minerals (S$_{Cr}$) in surface sediments, plus significant concentrations of AVS (Table 2.3). This was accompanied by a considerable rise in pH, from <4.0 before flooding to ~6.5 after flooding. These data demonstrate significant Fe and SO$_4^{2-}$ reduction took place at Blanches in the period following flooding and is consistent with the known behaviour of flooded ASS with high organic matter content (van Breemen 1993). Comparative post-flood soil data are unavailable for the Maloney's site.

Table 2.3. Iron and sulfur fractions in backswamp surface sediments at Blanches and Maloney's study sites.

Sample depth 0 - 2 cm. Post-flood samples were collected during May 2001 while the backswamp surface was still inundated after flooding. s.e. is standard error. nd = no data available.

<table>
<thead>
<tr>
<th></th>
<th>Blanches</th>
<th>s.e.</th>
<th>Maloney's</th>
<th>s.e.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalate-extractable Fe (III)$^A$</td>
<td>1120</td>
<td>263</td>
<td>206</td>
<td>8</td>
</tr>
<tr>
<td>SO$_4^{2-}$ $^A$</td>
<td>19</td>
<td>6.9</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Pre-flood S$_{Cr}$ (%)</td>
<td>0.06</td>
<td>0.01</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Post-flood S$_{Cr}$ (%)</td>
<td>0.74</td>
<td>0.12</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Post-flood AVS (%)</td>
<td>2.5</td>
<td>0.64</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

$^A$ mmol kg$^{-1}$. 

2-25
2.4.6. Drain discharge and flux estimates

Total flux estimates of oxygen depletion potential, DOC, SO$_4^{2-}$, Fe, Al and acidity at Blanches and Maloney's drains for 30 days after the flood are provided in Table 2.4. The timing of this flux is represented in Fig. 2.8. Drain discharge rates decreased in the latter stages of flood recession (Fig. 2.5a), but the rapidly increasing concentrations of many measured parameters resulted in high flux quantities during this period. The cumulative daily flux data presented in Fig. 2.8 clearly demonstrate that at both study sites the majority of the oxygen depleting compounds, DOC and Fe were exported to the estuary after artificial drainage lowered swamp water levels below natural drainage limits. Data in Fig. 2.8 suggest that artificial drainage increased the DOC flux by about 2.4 times at both study sites.

Table 2.4. Total discharge and total flux estimates for the Blanches and Maloney's study site drains for 30 days following the February flood.

All flux estimates (kg ha$^{-1}$) are expressed in relation to the area of ASS backswamp in each drain sub-catchment.

<table>
<thead>
<tr>
<th></th>
<th>Blanches</th>
<th>Maloney's</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge ($10^3$ m$^3$)</td>
<td>4900</td>
<td>1300</td>
</tr>
<tr>
<td>Oxygen depletion potential $^A$</td>
<td>62</td>
<td>37</td>
</tr>
<tr>
<td>Dissolved Organic Carbon flux</td>
<td>200</td>
<td>87</td>
</tr>
<tr>
<td>SO$_4^{2-}$ flux</td>
<td>216</td>
<td>332</td>
</tr>
<tr>
<td>Total Fe flux</td>
<td>25</td>
<td>29</td>
</tr>
<tr>
<td>Dissolved Fe flux</td>
<td>9.6</td>
<td>10</td>
</tr>
<tr>
<td>Total Al flux</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Acidity flux $^B$</td>
<td>0</td>
<td>53</td>
</tr>
</tbody>
</table>

$^A$ Estimated volume of river water deoxygenated ($m^3.10^3$ ha$^{-1}$), expressed in relation to the area of ASS backswamp in each drain sub-catchment (see Materials and methods).

$^B$ Based on titratable acidity to pH 5.5, expressed as CaCO$_3$ equivalent. (Note; no titratable acidity recorded at Blanches, see Fig. 2.6b).
Figure 2.8. Cumulative daily flux estimates for a) Blanches and b) Maloney's drainage systems for 30 days following the February 2001 flood. Historic limit to natural drainage based on 0.5 m AHD. ^ = based on 24 hr mean at floodgates. Note; no titratable acidity recorded at Blanches, see Fig 2.6b.
A first order estimate of the oxygen depletion potential of water discharging from drained ASS backswamps into the South Arm channel in relation to the flow volume of the South Arm channel during the first two weeks of the flood is presented in Fig. 2.9. This suggests that by 7 February the drainage discharge from ASS backswamps could account for ~60% of the deoxygenation of water flowing down the South Arm channel, and by 9 February the oxygen depletion potential of drainage discharge exceeded the flows down this channel. This estimate corresponds well with field observations which show severe deoxygenation occurring in the South Arm channel on 9 February, and suggests that the artificial drainage of ASS backswamps made a significant contribution to the anoxia observed in this part of the estuary.

Figure 2.9. The estimated oxygen depletion potential of the water discharging from drained ASS backswamps into the South Arm channel and the flow volume of the South Arm channel for ~11 days after the flood peak. Note: the dashed line indicates greater uncertainty in upper catchment flow data due to increasing tidal influence. See Materials and methods section for details on calculations used to estimate the oxygen depletion potential of drainage waters.
2.5. Discussion

Anaerobic decomposition of organic matter after flooding is a natural part of floodplain carbon cycling processes. However, artificial drainage of ASS backswamp surface waters following the February 2001 flood altered the dynamics of this process in two significant ways. Firstly, the transport of surface water by artificial drainage substantially increased the total flux of high COD water from the backswamps to the estuary (Fig. 2.8). Secondly, the timing of this input to the estuary coincided with the latter stages of flood recession when river discharge volumes were falling and the dilution capacity of the estuary was diminishing (Fig. 2.9). Instead of anoxic water remaining impounded behind the natural levee system in the ASS backswamps, where carbon mineralisation processes could be completed, artificial drainage bypassed this process and effectively ‘transferred’ it to the estuary.

Large changes occurred in the chemical composition of floodwaters within 5 - 10 days of contact with the floodplain ASS backswamps. The high COD in drain waters is most likely related to the abundance of organic compounds and fermentation products resulting from anaerobic decomposition of floodplain organic matter and to a lesser extent reduced inorganic species, such as Fe (II). DOC can theoretically account for a mean of 92% and 61% of the COD in drain waters at Blanches and Maloneys respectively, assuming complete oxidation to CO$_2$ and 1 mol of oxygen is consumed for every 1 mol of carbon oxidised (Krenkel and Novotny 1980). While there was evidence of both SO$_4^{2-}$ and Fe reduction at Blanches, sampling limitations precluded the measurement of H$_2$S and CH$_4$, thus any contribution they may have made (if present) to the oxygen depletion potential of drainage waters remains unknown.
While Fe appears to have influenced carbon metabolism in surface flood waters (see below), particularly at the Blanches site, its role in direct O\textsubscript{2} consumption from the drain water was less significant. Fe (II) can deplete dissolved oxygen in receiving waters (van Breemen 1993). However, even assuming that all of the Fe present in drain water samples was Fe\textsuperscript{2+} and 1 mol of oxygen consumed for every 4 mol of Fe\textsuperscript{2+} oxidised (Cook \textit{et al.} 2000a), this only accounts for a mean of about 1% of the COD at both Blanches and Maloney’s.

Other processes associated with floods can consume dissolved oxygen and may have contributed to the deoxygenation event. These processes include macerated upland organic matter, allochthonous DOC inputs from upland floodwaters, flood-elevated nutrients (Eyre and Twigg 1997) and suspended sediment oxygen demand. However, initial floodwaters were well oxygenated and estuarine anoxia occurred in parts of the estuary with small channel size and large areas of drained ASS backswamps, during a period when large volumes of water were draining off the floodplain. This suggests that floodplain drainage had a more significant role than these other deoxygenation processes. It is also plausible that mobilisation of MBO may have also contributed to the event, particularly during the early stages of flood recession when drain velocities were high (Sullivan \textit{et al.} 2002). However, the extent of this contribution is unknown on the basis of available data.

The deep, prolonged flooding at Blanches led to extensive death and decomposition of pasture species in the backswamp, in turn promoting high DOC concentrations in drain water. High acetate combined with low Eh and almost no dissolved oxygen in shallow backswamp flood waters confirms anaerobic metabolism was a major pathway of carbon oxidation. Shallow flooding and the subsequent lack of death or decomposition of pasture species at Maloney’s may be largely responsible for the lower and more stable DOC
concentrations observed at this site. The fact that two thirds of the backswamp at Maloney's was *M. quinquenervia* forest may have also influenced DOC concentrations, as previous studies have indicated slow rates of litter decay in flooded *M. quinquenervia* forests (Greenway 1994).

High temperatures in backswamp floodwaters at both sites reduced DO saturation potential and are likely to have had a positive influence on carbon oxidation rates by favouring microbial metabolism (Stumm and Morgan 1981; Olivie-Lauquet *et al.* 2001). The seasonal timing of flood events and post-flood temperatures are thus likely to exert a significant influence upon backswamp floodwater chemistry.

Iron and sulfur redox transformations in surface soils of the ASS backswamps were a key process affecting drainage water chemistry. There is substantial evidence that microbially mediated Fe (II) - Fe (III) redox cycling and Fe (III) and SO\(_4^{2-}\) reduction played an important role in the oxidation of carbon in anaerobic backswamp waters and sediment at Blanches. Evidence includes the order of magnitude increase in iron sulfide minerals in surface sediments following flooding, the very high concentrations of poorly crystalline Fe (III) oxides in surface sediments (Table 2.3), the strong positive correlation between Fe and DOC (Fig. 2.7), the significant concentrations of dissolved Fe in backswamp surface (Table 2.2) and drainage water (Fig. 2.5f), and the attenuation of SO\(_4^{2-}\) relative to Cl\(^-\) in drainage water (Fig. 2.6c).

The low pH, high titratable acidity, low Cl\(^-\):SO\(_4^{2-}\) ratios and high Al in drain waters at Maloney's suggest there was a greater input of shallow ASS groundwater at this site. In contrast, Blanches drain water chemistry data, including neutral pH, high Cl\(^-\):SO\(_4^{2-}\) ratios,
low Al, and no titratable acidity, strongly suggest minimal inputs of ASS groundwater during the period of observation. These suggestions accord with other research conducted at both sites, which showed large differences in the magnitude of ASS groundwater inputs to the respective drains (Johnston et al. 2004).

2.6. Conclusions

Artificial drainage of floodplain ASS backswamps contributed significantly to the magnitude and duration of the deoxygenation event in the Clarence River estuary. At both study sites, most oxygen depleting compounds were exported to the estuary after the natural limits to backswamp drainage were exceeded. Products of organic matter decomposition once largely confined to backswamps were discharged to the estuary in enhanced quantities and ‘contaminant’ flux was skewed towards the latter stages of flood recession (>6 days post peak) when estuarine dilution capacity was falling. Adverse impacts of this process on estuarine biota and water quality are likely to have increased above natural levels.

Contact with floodplain ASS backswamps profoundly altered the chemistry of floodwaters. Antecedent carbon accumulation, depth of flooding and subsequent amount of organic matter decomposition, plus the high post-flood temperatures all appear to have been important factors. Anaerobic decomposition of organic matter was a primary process affecting drainage waters. Some of this carbon metabolism appears to have been coupled with microbi ally mediated Fe and \( \text{SO}_4^{2-} \) reduction and catalysed by Fe (II) - Fe (III) redox cycling. Inputs of shallow ASS groundwater were also important at one of the study sites. The accumulation of easily reducible Fe and \( \text{SO}_4^{2-} \) minerals in backswamp surface soils as a result of ASS drainage may be altering carbon oxidation rates and pathways during periods of anaerobic surface conditions by providing increased concentrations of alternate electron
acceptors, though this requires further research to substantiate.

Without significant changes to the modified hydrology of floodplain ASS backswamps, drainage enhanced estuarine deoxygenation events of similar magnitude are likely to occur episodically in the future, particularly if flooding takes place during warm periods when there is sufficient accumulation of labile carbon in backswamp areas.

2.7. Acknowledgments

We thank the study site landowners for their assistance and cooperation. We thank several anonymous referees for their helpful suggestions with the manuscript. We also thank Clarence River County Council and the Department of Infrastructure, Planning and Natural Resources for assistance and access to data, Graham Lancaster and Southern Cross University Environmental Analysis Laboratory for sample analysis and Salirian Claff for AVS analysis. This study was funded by Land and Water Australia, Acid Soil Action, Sugar Research and Development Corporation, Acid Sulfate Soils Program and NSW Agriculture.
Chapter 3

Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to <i>Melaleuca quinquenervia</i> encroachment

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3.1. Abstract

Extensive encroachment of the native tree species, *Melaleuca quinquenervia* (Cav.) Blake, has occurred on a coastal floodplain sulfidic backswamp in eastern Australia. Almost 50% of the open swamp area *circa* 1870 is now monospecific *M. quinquenervia* forest. Encroachment has been associated with shortened hydroperiods and land management changes following drainage for agriculture. Large differences in shallow groundwater and sediment geochemistry were observed beneath both individual *M. quinquenervia* trees and encroaching forests compared to open swamp. Groundwater beneath *M. quinquenervia* had enhanced titratable acidity and acidic metal cations, increased concentrations of other ionic species (Cl\(^-\), SO\(_4^{2-}\)), altered ionic ratios and increased dissolved organic carbon. Soil beneath *M. quinquenervia* displayed enhanced accumulation of acidity and soluble ions, with concentration profiles suggesting vertical redistribution towards the surface. Deepening of the sulfide oxidation front in the soil beneath encroached *M. quinquenervia* suggests enhanced sulfide oxidation may be occurring. Changes in soil pH, redox potential and Fe mineral precipitation / dissolution were also evident. These changes appear to be the result of interactions between *M. quinquenervia* physiology and the unique groundwater and sediment geochemistry of the surrounding sulfidic / sulfuric horizons. Mechanisms to explain the observed changes are discussed along with potential management implications.
3.2. Introduction

Sulfidic sediments and acid sulfate soils (ASS) underlie substantial areas of backswamp on the coastal floodplains of eastern Australia (White et al. 1997). Many of these backswamp landscapes have been artificially drained (Tulau 1999) and sulfuric horizons are often found within 1 m of the surface (Walker 1972; Lin and Melville 1993). Groundwater levels are generally shallow (<1 m) and fluctuate seasonally. Acid groundwater is often brackish to moderately saline (Walker 1972) with high concentrations of $\text{SO}_4^{2-}$ and acidic metal cations, principally Fe and Al. Large amounts of acidity, Fe and Al are exported from sulfidic backswamps into adjacent estuaries via artificial drainage systems (Sammut et al. 1996; Wilson et al. 1999; Blunden and Indraratna 2000). The consequences of this export for estuarine biota and ecological function are widely recognised as a major issue and significant resources are currently focused on developing and implementing management strategies to reduce acid outflows.

Before drainage, many sulfidic backswamps were seasonal to semi-permanent wetlands, with surface waters impounded behind the natural levee system after flooding and inundation (Pressey and Middleton 1982). However, artificial drainage and flood mitigation works have reduced the hydroperiod by approximately an order of magnitude (Middleton et al. 1985; White et al. 1997). This change in hydrology and rapid removal of surface waters after flooding, combined with land management practices such as grazing and burning, has led to significant changes in wetland vegetation species assemblages (Pressey and Middleton 1982; Middleton et al. 1985; Pressey 1989; NSW Agriculture and Fisheries 1989). While seasonal and long term hydrology play critical roles in wetland vegetation succession, the pre-drainage vegetation in these ASS backswamps has generally been poorly documented. Available anecdotal information combined with current
succession patterns, suggest that some ASS backswamps, particularly those with deeper surface water and prolonged hydroperiods, were dominated by open swamp containing emergent reeds such as *Phragmites australis* (NSW Agriculture and Fisheries 1989) with fringing stands of swamp forest containing *Melaleuca quinquenervia* and *Casuarina glauca* on slightly higher elevation margins.

*Melaleuca quinquenervia* (Cav.) Blake is a woody tree species native to eastern Australia commonly found in many coastal wetland environments. It can grow to about 25 m tall, has a wide distribution, is well adapted to seasonal waterlogging and can tolerate a diverse range of soil, hydrological, salinity, fire and climatic regimes (Laroche 1999). It is a hardy, opportunistic species with many pioneering adaptations that facilitate rapid propagation and dispersal, particularly in disturbed areas, and has become a serious exotic weed in large areas of the Florida everglades (DiStephano and Fisher 1983; Laroche 1999). While there is limited research data on transpiration rates, it was originally introduced to some areas due to a perceived capacity to dry out wetlands (Morton 1966).

Vegetation can modify the biogeochemistry of the rhizosphere environment through many processes. These include enhanced carbon inputs, root ion exchange and ion exclusion mechanisms, root exudates, radial oxygen diffusion from roots (Armstrong 1975), hydraulic redistribution of soil water (Caldwell and Richards 1989; Dawson 1993; Burgess *et al.* 1998), rhizosphere microbial associations and nutrient cycling (Gobran and Clegg 1996; El-Shatnawi and Makhadmeh 2001).

Commercial tree planting been proposed as a management option to decrease acid export in coastal ASS backswamps (George 1999). There is a lack of information about the
effects this may have upon the unique sediment geochemistry in ASS backswamps, particularly in cases where trees were not a dominant part of the original pre-drainage vegetation. This current study demonstrates substantial alteration of shallow groundwater and sediment geochemistry has accompanied *M. quinquenervia* encroachment in an ASS backswamp. This phenomenon has not been documented before in ASS backswamps in Australia and has significant implications for long term management and attempts to reduce acid flux from these systems.

This paper has three aims: (1) To quantify the aerial extent of *M. quinquenervia* encroachment in an artificially drained ASS backswamp following European occupation, (2) to document and assess and the changes to groundwater and soil geochemistry associated with *M. quinquenervia* encroachment, and (3) to review processes that may explain the observed changes in groundwater and sediment geochemistry.

### 3.3. Materials and Methods

#### 3.3.1. Study site

The study area is an 8 km$^2$ artificially drained sulfidic backswamp located in Shark Creek, a small tributary on the lower Clarence River floodplain (29°30′ S, 153°15′ E) (Fig. 3.1). The backswamp is an infilled Holocene estuarine sub-embayment. The stratigraphy and geomorphic evolution of this backswamp is detailed in Lin and Melville (1993). The backswamp surface elevation is mostly <0.2 m Australian Height Datum (AHD; 0 AHD ~mean sea level) and is bounded by sandstone upland to the east and a narrow distributary levee adjacent Shark Creek to the west. The backswamp soils are Sulfuric/Sulfidic Oxyaquic Hydrosols (Australian Soil Classification, Isbell 1996) (Hydraquentic Sulfaquents - Soil Taxonomy, Soil Survey Staff 1998). Sulfidic sediments of estuarine
origin are typically found 0.8 to 1 m below the ground surface in the backswamp (Lin and Melville 1993; Johnston et al. 2002a). These are overlain by highly acidic sulfuric horizons with Fe (III) mineral and jarosite mottles, which are comprised of mainly non-sulfidic sediments, deposited in a brackish lagoonal environment (Lin and Melville 1993). Soil texture in the sulfuric and sulfidic horizons is predominantly silty clay to clay. The main landuse is grazing, though there is some sugar cane along the natural levee. The climate is sub-tropical and mean annual rainfall on the Clarence River floodplain ranges from 1100 to 1500 mm with a highly seasonal distribution and a distinct wet period from December to May.

**Figure 3.1.** a) Clarence River catchment and b) lower floodplain and study area location at Shark Creek.
3.3.2. Historic vegetation boundary mapping

Mapping and reconstruction of historical vegetation boundaries was based on analysis of original portion maps and aerial photograph interpretation combined with ground truthing. Copies of original portion maps, containing the first available survey record for each parcel of land in the study area (circa 1870), were obtained from NSW Department of Land and Water Conservation. Portion maps clearly marked the boundary between ‘open swamp’ and ‘swamp forest’. Surveyors notes on the portion maps about ‘land improvements’ indicated minimal clearing of swamp forest had occurred by the time of survey. Portion maps were collated and the boundaries between ‘open swamp’ and ‘swamp forest’ overlain on a contemporary map of the backswamp ASS based on Milford (1997). The extent of *M. quinquenervia* forest apparent in aerial photographs taken in 1942 and 1998 was assessed and boundaries added to the contemporary map. This resulted in determination of five vegetation zones, (1) swamp forest ~1870, (2) open swamp ~1870, (3) *M. quinquenervia* encroachment ~1870 - 1942, (4) *M. quinquenervia* encroachment 1942 - 1998 and (5) remaining open swamp (Fig. 3.2).

3.3.3. Shallow groundwater survey

All groundwater samples were collected during 2001 - 02, when the water table was within the sulfuric horizons. This was a period of below average rainfall and receding backswamp water tables. Groundwater samples were extracted from the sulfuric horizons in freshly excavated, 0.05 m diameter unlined wells using a hand pump. Groundwater in each well was pumped continuously for several minutes immediately after excavation until largely free of suspended sediment. The very high saturated hydraulic conductivity of sulfuric horizons at this site (due to macroporosity - Johnston *et al*. 2004) ensured rapid well infilling with surrounding groundwater during pumping.
Figure 3.2. Eastern Shark Creek ASS backswamp (Milford 1997) study area, showing historic vegetation boundaries, contemporary *M. quinquenervia* encroachment, survey transects and surveyed individual *M. quinquenervia* locations.
The pH, Electrical Conductivity (EC), redox potential (ORP) and temperature were immediately measured using freshly calibrated portable field equipment (TPS 90FLMV). Redox potential was measured with a platinum tipped Ag/AgCl reference electrode and all ORP values are reported as recorded without correction. A minimum of two 250 ml sub-samples were collected in clean (acid rinsed, distilled water flushed) polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times. Visible air bubbles were excluded prior to sealing the cap and samples placed in cold storage (~4°C). One 250 ml sub-sample was analysed for titratable acidity to pH 5.5 (APHA (1995), 2310B - including the peroxide oxidation step) within 24 hrs of sample collection. An extract from this sub-sample was also analysed for Ferrous iron (0.22 µm filtration, Spectrophotometrically, Phenanthroline method - HACH (1991), 8146) within 24 hrs of collection. One 250 ml sub-sample was selected for further chemical analysis, and analysed for total Fe and total Al (ICPAES - USEPA 6010), dissolved Fe and dissolved Al (0.45 µm filtration, ICPAES - USEPA 6010), Cl\⁻ and SO\(^{4-}\) (Ion chromatography - AHPA 4110). Selected samples were also analysed for dissolved organic carbon (APHA (1995), 5310 B) and total arsenic (ICPAES - USEPA 6010).

3.3.4. EM38 survey

Line transect and grid surveys were conducted using a Geonics EM38 electromagnetic induction soil conductivity meter, which was operated in accordance with the manufacturers instructions (McNeill 1986). The EM38 has a coil spacing of 1 m and measures apparent soil electrical conductivity (EC\(_a\)) in mS m\(^{-1}\) in either a vertical (EC\(_a\)V) or horizontal (EC\(_a\)H) dipole orientation. In the vertical orientation the EM38 is more responsive to changes in EC\(_a\) below 0.45 m, while in the horizontal orientation the maximum response is to the surface and declines with depth. Due to this difference in
respective depth response functions, $EC_a V - EC_a H$ can provide a useful measure of the trend in soil $EC_a$ with depth (Slavich 1990). The mean of the vertical and horizontal readings provides a more effective integration of soil profile $EC_a$ than either measurement alone (Slavich 1990). A number of studies have successfully used EM38 measurements to determine rootzone salinity in areas with shallow saline water tables (Slavich and Peterson 1990; Bennett and George 1995).

3.3.5. Soil survey

Two soil survey transects were sampled, one bracketing an individual *M. quinquenervia* (no. 2) and the other perpendicular to the tree line of an encroaching *M. quinquenervia* forest (c - d) (Fig. 3.2). At each soil sampling location a pair of soil cores 1 m apart were collected using a gouge auger to a depth of ~1.5 m. Profiles were described according to McDonald et al. (1990) and the soil surface surveyed to AHD. Samples from each pair of cores were collected at 0.02 m, 0.1 m and every 0.1 m thereafter to a depth of 1.5 m below ground surface and combined in ~equal quantities to create single samples in order to reduce errors arising from spatial heterogeneity. Samples were carefully handled to avoid oxidation of sulfides. A further profile was gouge augered at each soil sampling location and the field pH ($pH_f$) and ORP (ORP$_f$) determined at the same depth intervals as above by inserting electrodes (double junction Ag/AgCl) into freshly excavated moist soil, with full electrode calibration and KCl electrolyte replacement between each profile. The approximate bulk density of selected sub-samples was determined (Melville 1998). Soil samples were oven-dried at 85°C within 48 hrs of collection and crushed to pass a 2 mm sieve. The EC of a 1:5 water extract was determined for each sample (Rayment and Higginson 1992) and select samples analysed for reduced inorganic sulfur species ($S_{Cr}$ - Sullivan et al. 2000) and total actual acidity (TAA - Ahern et al. 1998; Lin et al. 2000), water soluble Cl$^{-}$ and $SO_4^{2-}$ (Ion
chromatography - APHA (1995), 4110) and water soluble Al (ICPAES - USEPA 6010). Select samples were also analysed for total organic carbon (Rayment and Higginson 1992).

3.3.6. Leaf analysis

Fresh leaf litter was collected over three weeks in two 1 m² fine mesh litter traps located in the encroached *M. quinquenervia* forest adjacent transect ‘a’ and transect ‘c - d’. All twigs and small branches were removed from these samples. Two samples of fresh, living leaves were collected using hand shears from several live trees in the same vicinity. Two forest floor litter samples were collected, each from a 0.04 m² area located near the litter traps. Samples were oven-dried at 45°C, crushed in a hammer mill to pass a 2 mm sieve and analysed for water soluble Cl⁻ (SPAC 14), total S (Leco combustion), total Al and total Fe (ICPAES - USEPA 6010).

3.3.7. Evapotranspiration of groundwater

The additional amount of groundwater evapotranspired by *M. quinquenervia* relative to open pasture was estimated using the non-steady state chloride mass balance model as described in Slavich *et al.* (2002). In shallow water table environments the model estimates net flux of groundwater into the rootzone from changes in chloride storage over a monitoring period. Soil chloride data from profile no. 1 (transect c - d) was used to represent the open swamp before encroachment by forest and profile no. 4 (transect c - d) to represent soil conditions after 60 years of forest growth. This analysis assumes that the increased soil chloride beneath the *M. quinquenervia* forest was due to enhanced upward flux of groundwater following encroachment, the initial groundwater chloride concentrations and soil chloride storage was the same as profile no. 1, and that loss of chloride to surface floodwaters is small relative to the change in storage.
3.4. Results

3.4.1. Vegetation boundary analysis

The results of historic vegetation boundary reconstruction are summarised in Fig. 3.2. Circa 1870, open swamp comprised 77% of the ASS backswamp area. The remaining 23% was closed forest, found mostly in higher elevation areas along the levee system and in fringing pockets adjacent upland country. By 1998 the remaining open swamp area had almost halved in size to about 39% of the ASS backswamp. This reduction in area of open swamp was due solely to expansion in the aerial extent of *M. quinquenervia* forest, with most of the encroachment occurring between 1942 and 1998. Ground observations revealed the areas where *M. quinquenervia* encroachment had taken place since 1942 were dense, monospecific stands of similar size class. Remaining open swamp comprised native grasses including *Paspalum distichum, Pseudoraphis spinescens, Cynodon dactylon* with scattered occurrences of rushes *Eleocharis acuta* and *Juncus usitatus*.

3.4.2. Individual trees

Soil EC$_a$, groundwater and soil chemistry were assessed adjacent to several isolated, individual *M. quinquenervia* that were growing in open swamp areas surrounded by native pasture species.

The ionic strength of shallow groundwater was substantially higher directly beneath two different, individual *M. quinquenervia*, with the EC, titratable acidity, Cl$^-$ and Fe$^{2+}$ all enhanced relative to the surrounding open swamp (Fig. 3.3 and 3.4). Increases in DOC were also apparent (Fig. 3.3 and 3.4), but there was no obvious change in dissolved aluminium (data not shown). A higher pH and lower redox potential occurred immediately beneath the two trees compared to surrounding open swamp. Ionic ratios indicate enhanced
Fe relative to both $\text{Cl}^-$ and $\text{SO}_4^{2-}$ directly beneath the trees (Fig. 3.3 and 3.4).

Assuming 2 mol $\text{H}^+$ is produced for each mol of $\text{Fe}^{2+}$ oxidised (van Breemen 1993) the theoretical contribution that $\text{Fe}^{2+}$ made to the titratable acidity of groundwater increased substantially beneath each tree (Fig. 3.5). While there are differences in absolute concentrations, the primary trends in ionic composition, ratio changes and physico-chemical characteristics shown in Figs. 3.3 and 3.4 are similar beneath both trees.
Figure 3.4. Changes in the chemical composition of groundwater from the sulfuric horizon beneath individual *M. quinquenervia* no. 2. Ratios based on molar concentrations. Note; isolated tree growing in open swamp area, see Fig. 3.2.

Figure 3.5. Increase in the theoretical contribution of Fe$^{2+}$ to the titratable acidity of groundwater beneath *M. quinquenervia* no. 1 and 2. Assumes 2 mol H$^+$ produced for each mol of Fe$^{2+}$ oxidised.
Two EM38 grid surveys conducted around isolated, individual *M. quinquenervia* growing in open swamp areas showed a clear concentric pattern of increasing mean EC$_a$ with individual trees being the loci (Fig. 3.6a and b). The radial extent of the mean EC$_a$ increase was relatively localised with the greatest changes occurring within 5 m of each tree. Data showing EC$_a$V - EC$_a$H demonstrates the EC$_a$ increases were greater in the horizontal dipole orientation than the vertical (Fig. 3.6c and 3.6d). This suggests a change in the vertical distribution of conducting ions with relatively greater increases near the soil surface (Slavich and Petterson 1990). Again the radial extent of this change is in close proximity to both trees.

**Figure 3.6.** a) Changes in mean soil EC$_a$ surrounding *M. quinquenervia* no.3 and b) *M. quinquenervia* no.2 and c) changes in soil EC$_a$V-EC$_a$H surrounding *M. quinquenervia* no.3 and d) *M. quinquenervia* no.2. Note that the *M. quinquenervia* are located at the centre point of each survey grid. Based on EM38 grid survey, sample points n = 121. Linear interpolation between points.
Linear regression analysis between mean EC\textsubscript{a} and groundwater EC, titratable acidity, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and Fe\textsuperscript{2+} at \textit{M. quinquenervia} no. 1 and no. 2 displayed high correlation coefficients (Table 3.1). These data demonstrate that mean EC\textsubscript{a} is a very useful surrogate for assessing changes in groundwater ion / acidic solute concentrations in this backswamp landscape. Positive correlation ($r^2 > 0.75$) was also observed between the size of isolated, individual trees growing in open swamp areas and the magnitude of the localised EC\textsubscript{a} increase evident at the base of the tree (Fig. 3.7).

**Table 3.1. Linear regression analysis ($r^2$) between mean soil EC\textsubscript{a} and the chemical composition of groundwater from the sulfuric horizons adjacent \textit{M. quinquenervia} no. 1 and 2.**

<table>
<thead>
<tr>
<th>Groundwater</th>
<th>\textit{M. quinquenervia} no.1 ($r^2$)</th>
<th>\textit{M. quinquenervia} no. 2 ($r^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>0.91</td>
<td>0.85</td>
</tr>
<tr>
<td>Titratable acidity</td>
<td>0.81</td>
<td>0.72</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>0.71</td>
<td>0.57</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>Fe\textsuperscript{2+}</td>
<td>0.71</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**Figure 3.7.** Positive correlation between the mean soil EC\textsubscript{a} increase at the base of individual, isolated \textit{M. quinquenervia} growing in open swamp areas and a) Crown Volume Index, and b) Basal area. $^{\text{A}}$ = EC\textsubscript{a} increase based on the difference between the mean of four EM38 measurements at the base of each tree and at 20 m radially away from tree. $^{\text{B}}$ = based on the formula $\text{[height} \times \text{diameter}^2]$ (Biddiscombe \textit{et al.} 1985.) $^{\text{C}}$ = measured at 1.3 m and includes all stems. Note that some individual trees had up to nine main stems.
The soil survey transect bracketing individual *M. quinquenervia* no. 2 shows there were substantial changes in soil geochemistry spatially associated with the tree. These include:

a) A decrease in redox potential directly beneath the tree between -0.4 and -1.0 m AHD (Fig. 3.8a). The low ORP values at this depth range 2 m either side of the tree coincided with a distinct sulfurous odour (presumably H₂S) that was absent from other profiles.

b) Decreased pH in the near surface soils directly adjacent to the tree (Fig. 3.8b). A slight pH increase also occurred in the sulfuric horizon between -0.3 and -0.6 m AHD directly beneath the tree.

c) Significant increases in EC were evident beneath the tree, particularly near the surface and to a lesser extent at depth (Fig. 3.8c). This pattern of localised EC increase near the surface corresponds with the EM38 data (Fig. 3.6).

![Figure 3.8](image_url)

*Figure 3.8. Changes in soil profile a) ORP, b) pH, and c) EC (1:5 extract) either side of *M. quinquenervia* no.2. The top of each chart represents the ground surface. Interpolation based on profiles located at 20, 10, 5 and 2 m either side of the tree centre (n = 128).*
d) Increased Cl, TAA, SO$_4^{2-}$, soluble Al were evident in near surface soils at 2 m and to a lesser extent at 5 m radially from the tree (Fig. 3.9).

e) The sulfide oxidation front was ~0.1 m deeper in the soil profile at 2 m either side of the tree compared to 5 m and 10 m (Fig. 3.9).

Figure 3.9. Changes in soil TAA, $S_{Co}$, Soluble Al, Cl$^-$ and SO$_4^{2-}$ with depth, from profiles taken at 10, 5 and 2 m either side of M. quinquenervia no.2. Symbols are the mean and error bars the range of both profiles. Depths increments are the mean of both profiles.

Reddish brown Fe (III) oxide mineral deposits occurring as root channel pore linings were clearly evident in the sulfuric horizon at soil profiles located 5, 10 and 20 m radially from
the tree. In contrast there was an almost complete absence of Fe (III) oxide minerals lining root channel pores in the sulfuric horizon directly beneath the tree (2 m), corresponding to the zone of decreased soil redox potential. This observation is an important indicator of geochemical change occurring directly beneath the tree.

3.4.3. Encroaching tree lines

Soil EC$_a$, groundwater and soil chemistry were also assessed along transects perpendicular to encroaching *M. quinquenervia* tree lines. Results show similar changes to those observed beneath individual trees only the magnitude of change is generally greater. However, there are some different trends, primarily in pH, redox potential and mineral precipitation.

The ionic strength of shallow groundwater was much higher beneath encroaching *M. quinquenervia* forests when compared to adjacent open swamp (Fig. 3.10). Fig. 3.10 compares results from two transects at the Shark Creek study site (‘a’ and ‘b’- Fig. 3.2) with a third transect from an ASS backswamp on the Richmond River floodplain, NSW (Tuckean swamp). The Tuckean transect was also located perpendicular to a *M. quinquenervia* forest that had encroached since 1942. Substantially higher titratable acidity, EC, Cl$^-$, dissolved Fe and dissolved Al are evident beneath the encroached *M. quinquenervia* forest along each transect. A decreasing pH trend is also apparent. Higher DOC levels were observed under *M. quinquenervia* forest compared to open swamp at transects ‘a’ and ‘b’, but not at the Tuckean site. There was also enhanced dissolved Fe, and to a lesser extent enhanced SO$_4^{2-}$, relative to Cl$^-$ beneath the encroached forest (Fig. 3.10).
All available groundwater data from open swamp and encroached *M. quinquenervia* forests in the study area are summarised in Table 3.2. Based on this data, all of the ionic species measured had concentrations significantly higher in the encroached forest compared to the open swamp ($P < 0.01$). Mean concentrations of titratable acidity, dissolved Fe and dissolved Al were between 7 - 10x higher beneath encroaching forests compared to open swamp. A five fold enhancement of dissolved Fe and dissolved Al relative to Cl$^-$ was also evident beneath encroached *M. quinquenervia* forests along with lower Cl$^-$/SO$_4^{2-}$ ratios (Table 3.2).

Figure 3.10. Changes in the chemical composition of groundwater from the sulfuric horizon along transects perpendicular to the treeline of three encroaching *M. quinquenervia* forests. Ratios based on molar concentrations. All forests encroached after 1942. For location of transects ‘a’ and ‘b’ see Fig. 3.2. Tuckean transect located in an ASS backswamp on the Richmond River floodplain.
Table 3.2. The chemical composition of groundwater from the sulfuric horizons in open swamp areas and encroached *M. quinquenervia* forest at Shark Creek ASS backswamp.

Encroachment occurred during the period between 1942 - 1998. All concentrations in mmol L\(^{-1}\).

Ratios based on molar concentrations. s.e. is standard error.

<table>
<thead>
<tr>
<th></th>
<th>Open swamp (n = 25)</th>
<th>M. quinquenervia forest (n = 9)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>s.e.</td>
<td>Mean</td>
</tr>
<tr>
<td>pH</td>
<td>3.55</td>
<td>0.04</td>
<td>3.25</td>
</tr>
<tr>
<td>EC (dS m(^{-1}))</td>
<td>3.4</td>
<td>0.2</td>
<td>10.3</td>
</tr>
<tr>
<td>Titratable acidity</td>
<td>6.1</td>
<td>0.3</td>
<td>43.1</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>12.6</td>
<td>1.7</td>
<td>33.8</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>15.1</td>
<td>2.5</td>
<td>46.5</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>0.9</td>
<td>0.1</td>
<td>8.2</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>1.3</td>
<td>0.1</td>
<td>11.1</td>
</tr>
<tr>
<td>Cl(^-):SO(_4^{2-})</td>
<td>1.6</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Cl(^-):Dissolved Fe</td>
<td>24.4</td>
<td>3.7</td>
<td>4.8</td>
</tr>
<tr>
<td>Cl(^-):Dissolved Al</td>
<td>14.9</td>
<td>3.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

* P <0.05; ** P <0.01; *** P <0.001.

Groundwater sampling was also undertaken along transect e - f, where a more detailed history of *M. quinquenervia* encroachment was determined from aerial photographs. Groundwater along this encroachment sequence showed steadily decreasing Cl\(^-\):SO\(_4^{2-}\) ratios and increasing DOC with time after encroachment (Fig. 3.11). A much larger titratable acidity and lower pH also occurred immediately beneath the forest, along with higher dissolved aluminium and arsenic concentrations.

An EM38 grid survey (transect c - d), showed higher soil EC\(_a\) immediately beneath an encroaching *M. quinquenervia* forest (Fig. 3.12). The extent of *M. quinquenervia* encroachment at this location was controlled by land management features (i.e. a fence and a drain) and the EC\(_a\) change conformed very closely to this artificially induced, straight
Figure 3.11. Changes in EC_V, EC_H (measured at 10 m intervals) and sulfuric horizon groundwater chemical composition across *M. quinquenervia* encroachment sequence, transect e - f. Dates refer to the period in which encroachment occurred.

boundary (Fig. 3.12). This location was open swamp between ~1870 and 1942, with
encroachment taking place after 1942 (Fig. 3.2). This data combined with the significant EC$_a$ increases evident at an individual tree scale (Fig. 3.6a and 3.6b), provides strong evidence that the EC$_a$ increase at transect c - d is directly related to *M. quinquenervia* forest establishment.

**Figure 3.12.** Changes in mean soil EC$_a$ at transect c - d. The extent of *M. quinquenervia* encroachment was controlled by a fence and a drain. Both sides were open swamp in 1942. Numbers 1 to 4 show soil profile sampling locations. Based on EM38 grid survey, sample points n = 90, linear interpolation between points.

EM38 readings made along the encroachment sequence (transect e - f, Fig. 3.11) show a large increase EC$_a$ immediately beneath the tree line. The magnitude of the EC$_a$ increase is greater in the horizontal dipole orientation, similar to that found beneath individual trees, suggesting enhanced near surface concentrations of conducting ions. A decrease in EC$_a$H is also evident in the pre-1942 encroachment zone. At both transects c - d and e - f, the higher EC$_a$ values beneath encroached *M. quinquenervia* forest were accompanied by a decreasing trend in EC$_a$V - EC$_a$H. This suggests the higher EC$_a$ values were associated with enhanced concentrations of conducting ions near the soil surface (Fig. 3.13), which accords with the EC$_a$ pattern beneath individual trees.
Figure 3.13. Increasing mean ECₐ at transects c - d and e - f is accompanied by a decreasing trend in ECₐV - ECₐH, suggesting an association with enhanced near surface solute concentrations.

Soil profiles beneath the encroached *M. quinquenervia* forest at transect c - d had lower pH, higher redox potential and significantly higher EC with depth compared to the open swamp area (Fig. 3.14). The magnitude of the EC increase was greatest in the near surface soils. TAA, Cl⁻, SO₄²⁻ and soluble Al were also substantially higher beneath the encroached *M. quinquenervia* forest with concentration profiles indicating near surface accumulation (Fig. 3.14). Total organic carbon was also higher in the upper ~0.4 m of the soil profile beneath the encroached *M. quinquenervia* forest. $S_{Ct}$ data indicate that the sulfide oxidation front was 0.15 - 0.2 m deeper in the soil profile beneath the encroached *M. quinquenervia* forest (Fig. 3.14). Using mean soil data from the open swamp and encroached forest and assuming a) deepening has occurred since encroachment, b) the reduced inorganic sulfur species are in the form of pyrite and c) 4 mol of H⁺ generated for each mol of FeS₂ oxidised (van Breemen 1993), this represents a theoretical generation of $9.7 \times 10^5$ mol H⁺ ha⁻¹. This alone can account for the observed difference in TAA ($9.3 \times 10^5$ mol H⁺ ha⁻¹) evident beneath the encroached forest compared to the open swamp.
Figure 3.14. Changes in soil profile chemical composition with depth at soil sampling locations 1, 2 (open swamp) and 3, 4 (encroached *M. quinquenervia* forest) at transect c - d. The extent of *M. quinquenervia* encroachment was controlled by land management features (i.e. a fence and drain). Both sides were open swamp in 1942. See Fig. 3.12 for soil sampling locations. $^\wedge$ = EC in 1:5 water extract.
The sulfuric horizon in the open swamp (profiles 1 and 2) had common, distinct reddish brown Fe (III) oxide mineral deposits, occurring as thin coatings lining pore channels and fissures, whereas there were few pale yellow jarosite mottles. In contrast, the sulfuric horizon in the M. quinquenervia forest (profiles 3 and 4) had few Fe (III) oxide mineral deposits, but many prominent, yellow jarosite mottles lining root channel pores, which occurred ~0.15 m (AHD) deeper in the profile compared to the open swamp.

3.4.4. Evapotranspiration of groundwater

The chloride mass balance model estimated an extra 1590 mm of groundwater was used from beneath the encroached M. quinquenervia forest compared to the open pasture. The aerial photographs indicate that the forest is approximately 60 years old. This means the average increase in groundwater use by M. quinquenervia was 27 mm yr\(^{-1}\) over the period of encroachment (1942 - 2002). This could result in a slight lowering of the long term average watertable depth under the forest. This interpretation is supported by the lowering of the pyrite oxidation front (Fig. 3.14).

3.4.5. Leaf sample analysis

Results of leaf sample analysis are presented in Table 3.3. Concentrations of Fe and Al were lowest in green living leaves, higher in senescent leaves and over an order of magnitude higher in forest floor leaf litter. Cl\(^{-}\) was highest in the green living leaves, while senescent leaves and forest floor leaf litter had lower, but similar concentrations. Total S did not vary substantially between the various litter fractions.
Table 3.3. Concentration of selected ions in green living leaves, senescent leaves and forest floor litter from encroached *M. quinquenervia*.

All concentrations in mmol kg\textsuperscript{-1} on a dry weight basis. s.e. is standard error.

<table>
<thead>
<tr>
<th></th>
<th>Green living leaves</th>
<th>Senescent leaves</th>
<th>Forest floor leaf litter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>s.e.</td>
<td>Mean</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>366</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td>Total S</td>
<td>176</td>
<td>11</td>
<td>125</td>
</tr>
<tr>
<td>Total Fe</td>
<td>2</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Total Al</td>
<td>20</td>
<td>2</td>
<td>33</td>
</tr>
</tbody>
</table>

3.5. Discussion

3.5.1. *M. quinquenervia* encroachment

Analysis of vegetation changes in Fig. 3.2 demonstrates there has been substantial expansion of *M. quinquenervia* into the open swamp areas following European occupation. The hydrology of the study area backswamp has been modified by drainage for agriculture, effectively shortening the hydroperiod. Originally there were no natural channels through the distributary levee in the study area. This means that prior to drain construction, water loss from the backswamp after flooding would have been largely restricted to evapotranspiration once surface waters fell below the height of the natural levee (>1 - 3.5 m AHD).

While *M. quinquenervia* is very tolerant of water logging and seasonal inundation, establishment of *M. quinquenervia* seedlings can be limited by excessively long or short hydroperiods (Myers 1983; Hofstetter and Sonenshien 1990). In an unpublished study of backswamp vegetation on the Clarence River floodplain, Pressey and Clancy (1980) suggested that *M. quinquenervia* and *C. glauca* often occurred as fringing bands on the margins of swamps. This pattern matches the distribution of swamp forest at the study area.
circa 1870 (Fig. 3.2). Fringing patterns of *Melaleuca* forest distribution (various species) have also been described on some seasonally inundated floodplains in northern Australia (Finlayson and Woodroffe 1996). One study on the lower north coast of NSW found a significant negative correlation between prolonged deep flooding and *M. quinquenervia* tree size (Winning and Clark 1996). Hofstetter and Sonenshien (1990) suggested that *M. quinquenervia* was more prevalent in wetlands where hydroperiods were shortened by human activities.

Although a direct causal link cannot be demonstrated on the basis of existing data, given the strong relationship between hydrology and wetland vegetation succession, it is plausible that the aerial expansion of *M. quinquenervia* at the study site may be related to artificial drainage and shortening of the hydroperiod. However, disturbance and fire can also greatly favour *M. quinquenervia* establishment (Morton 1966; Hofstetter and Sonenshien 1990; Laroche 1999), thus its aerial expansion may also have been influenced by changed land management practices such as grazing and burning. It is also probable that during the past ~6000 years following post-glacial marine transgression, extended dry or wet periods may have encouraged natural vegetation succession and periodic fluctuation in the ratio of swamp forest to open swamp.

3.5.2. *Alteration of groundwater and sediment geochemistry*

The chemical characteristics of acid sulfate soils are often spatially heterogeneous (Dent 1986) and can be influenced by local hydrology and micro-topography (Husson *et al.* 2000). An alternative hypothesis is that *M. quinquenervia* has preferentially colonised what were essentially pre-existing soil and groundwater conditions which had been caused by other factors. However, all survey techniques used in this study revealed highly localised
zones of intense changes in soil and groundwater chemistry occurring with randomly distributed, isolated, individual trees being the loci. Further, there was a positive correlation between individual tree size and the magnitude of the localised changes immediately adjacent the trees. There were also large changes in soil EC\textsubscript{a} corresponding precisely to linear land management features which had limited the extent of forest encroachment (Fig. 3.12). Combined, these data led to the rejection of the ‘preferential colonisation’ hypothesis and strongly suggest that \textit{M. quinquenervia} encroachment is causing substantial changes to groundwater and sediment geochemistry at the study site.

The rhizosphere consists of a complex mosaic of heterogeneous soil micro-environments (El-Shatnawi and Makhadmeh 2001), with many competing and complementary species of bacteria playing important roles in electron transfer reactions involving metals (Warren and Haack 2001). It is known that vegetation can exert species dependant influences upon rhizosphere pH and redox potential (Nye 1981; Chen and Barko 1988). Previous studies have demonstrated individual trees can influence pedogenesis and increase soil acidity and exchangeable aluminium (Ryan and McGarity 1983; Gobran and Clegg 1996). The changes to pH and redox potential in groundwater and soil beneath \textit{M. quinquenervia} have important implications for metal mobility, reactivity and bio-availability (Gambrell 1994; Warren and Haack 2001). The differences in the direction of change in pH and redox potential at >0.5 m depth below ground surface beneath individual trees compared to encroached forests are intriguing, and may be related to the competing effects of the various process in operation and differences in the scale their cumulative impacts. Data suggest multiple processes are responsible for the differences in groundwater and sediment geochemistry between open swamp and encroached \textit{M. quinquenervia} areas. These are discussed below.
3.5.3. **Enhanced water use and ion exclusion**

*M. quinquenervia* can tolerate a wide range of salinity conditions (Laroche 1999). Ion exclusion during water uptake is a well documented salt tolerance mechanism in both halophytes and non-halophytes (Flowers et al. 1977; Greenway and Munns 1980). Data suggest that a primary mechanism driving the increased ion concentrations in shallow groundwater and soil beneath *M. quinquenervia* forests is enhanced water use combined with ion exclusion. Evidence to support this hypothesis includes:

a) Increased Cl⁻ concentrations in groundwater and soil beneath both individual trees and encroached forests. The magnitude of this increase is greater beneath encroached forests.

b) The localised, concentric pattern of soil ECₐ increase with individual trees being the loci.

c) Strong positive correlation between tree basal area and the magnitude of ECₐ increase at the tree base. This is particularly relevant given that basal area has been shown to have a very high correlation with individual tree water use in other *Melaleuca* species (Hatton et al. 1998).

This hypothesis has documented parallels. In arid areas with shallow saline water tables, it has been demonstrated that establishment of tree plantations can lead to localised lowering of groundwater levels and increases in groundwater and soil ion concentrations beneath trees due to enhanced groundwater use (Heuperman 1995; Stolte et al. 1997; Barrett-Lennard and Malcolm 1999; Silberstein et al. 1999; Barrett-Lennard 2002). In one study the degree of shallow groundwater salinisation was positively related to tree density (Stolte et al. 1997) and in another, leaf density (Barrett-Lennard and Malcolm 1999).
At the study site, when the water table is within the sulfuric horizon, groundwater levels across the backswamp are uniform and piezometer data do not show localised lowering of groundwater tables beneath the encroached *M. quinquenervia* forest (data not shown). This is attributed primarily to the very high saturated hydraulic conductivity (*K*<sub>sat</sub>) of the sulfuric horizon soils (Johnston *et al.* 2004). The high *K*<sub>sat</sub> of the sulfuric horizons, whilst enhancing water availability for the trees, is likely to favour rapid groundwater movement with replenishment from neighbouring areas which will inevitably bring more ions (Silberstein *et al.* 1999). However, piezometer data do suggest that localised lowering of the water table can occur beneath the encroached *M. quinquenervia* forest once the water table falls into the sulfidic horizons during a dry period (data not shown). This difference in water table response is likely related to aquifer anisotropy and decreasing *K*<sub>sat</sub> in the sulfidic sediments (Johnston *et al.* 2002a).

While a number of authors have suggested that *Melaleuca* spp. are capable of high transpiration rates (Hofstetter 1991; Laroche 1999) definitive assessment of transpiration rates and comparison the shallow rooted pasture species in the open swamp areas is beyond the scope of this study.

While greater water use and ion exclusion may explain much of the observed changes, the enhancement of other ions (i.e. Fe, Al, SO<sub>4</sub><sup>2-</sup>) relative to Cl<sup>-</sup> suggests that other processes are also occurring. Selective ion exclusion during water uptake may be one possibility. Enhanced sulfide oxidation may be another.

3.5.4. Enhanced sulfide oxidation

The deepening of the sulfide oxidation front beneath an individual tree and an encroached
forest suggests *M. quinquenervia* encroachment may be enhancing the oxidation of sulfide minerals (primarily pyrite). Initial stages of pyrite oxidation result in the release of Fe\(^{2+}\), SO\(_4^{2-}\) and other co-precipitated metals according to Eq. (3.1) (van Breemen 1993):

\[
\text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{H}^+ + 2\text{SO}_4^{2-}
\]

Pyrite oxidation rates tend to increase with decreasing pH (van Breemen 1993) and a comparatively lower soil pH is evident in the soils near the sulfuric horizon boundary beneath the encroached *M. quinquenervia* forest (Fig. 3.14). While it is beyond the scope of this study to determine a precise mechanism, there are a number of possibilities which may explain the deepening of the sulfide oxidation front. It should be noted that the possibilities listed below are necessarily speculative and based on a review of known processes.

(1) Enhanced local drawdown of the groundwater beneath *M. quinquenervia* due to increased evapotranspiration during very dry periods when the water table is in the sulfdic horizon. This could theoretically lead to greater O\(_2\) diffusion and sulfide oxidation, contributing to the deepening of the sulfide oxidation front.

(2) Radial oxygen loss (ROL) from the roots is known to occur in many species of wetland plants in response to O\(_2\) deficient conditions in the rhizosphere (Armstrong 1975; Visser *et al*. 2000). ROL can cause localised increases in sediment redox conditions (Chen and Barko 1988) and lead to the creation of oxidised halos surrounding roots (Armstrong *et al*. 1990). ROL from living roots was thought to be the primary cause of enhanced pyrite oxidation in sulfide rich marsh sediments in a study by Hsieh and Yang (1997). Bolton (1999) noted that *M. quinquenervia* roots lack aerenchymatic tissues, which are normally
the primary means of oxygen transport to the roots in many wetland plants. Bolton (1999) proposed that *M. quinquenervia* may have a unique means of root aeration, via air filled spaces in the cork-like bark network which forms a sheath around the outside of submerged roots.

(3) Fe (III) is an important and highly effective oxidising agent in the microbially mediated degradation of sulfide minerals such as pyrite (Luther *et al*. 1992; van Breemen 1993; Sand *et al*. 2001) particularly at low pH (<4). More Fe (III) may be available in groundwater beneath the encroached *M. quinquenervia*. While speciation data suggests that most of the Fe in groundwater was present as Fe$^{2+}$, the large increase in the concentration of dissolved Fe plus the dissolution of Fe (III) mineral deposits (see below) accords with this possibility.

3.5.5. Metal mobility and mineral precipitation / dissolution

The enhancement of Fe and Al in groundwater relative to Cl$^-$ is likely to be related, at least in part, to changes in pH and redox potential. Both pH and redox potential exert a major influence on solid / solution reactions and the precipitation / dissolution of various mineral phases, with consequent implications for metal mobility.

The increased Al beneath the encroached *M. quinquenervia* forest may be due to lower pH and dissolution of clay minerals (van Breemen 1993) and a distinct peak is evident at the sulfide oxidation front (Fig. 3.14). Increased solution ionic strength can also increase mineral dissolution rates (Warren and Haack 2001) which may contribute to higher metal concentrations beneath encroached *M. quinquenervia* forests.
Although the increase in Fe in groundwater may be related to sulfide oxidation, data suggest localised reductive dissolution of Fe (III) minerals might also be occurring at the individual tree level. The visible decrease in Fe (III) mineral deposits in root channel pores in the sulfuric horizon combined with the increase in Fe$^{2+}$ and the enhancement of dissolved Fe relative to both Cl$^-$ and SO$_4^{2-}$ in the groundwater directly beneath individual trees (Figs. 3.3 and 3.4) support this suggestion. Increased carbon inputs (from root turnover, root exudates or litter leachate), as evident in the enhanced groundwater DOC (Figs. 3.3 and 3.4) and soil total organic carbon (Fig. 3.14), may be providing a source of organic ligands to drive microbially catalysed reductive dissolution of Fe (III) minerals lining root channel pores (Luther \textit{et al.} 1992; Lovley 1993; Liang \textit{et al.} 2000). The concurrent decrease in redox potential and pH increase in both the groundwater (Figs. 3.3 and 3.4) and the sulfuric horizon (Fig. 3.8a and 3.8b) beneath individual trees accords with this hypothesis (van Breemen 1993). Fe (III) hydroxyoxides are efficient scavengers of other trace metals and these may be released accompanying Fe (III) mineral dissolution and reduction (Warren and Haack 2001).

The more pronounced jarosite mottling in the sulfuric horizon beneath the encroached \textit{M. quinquenervia} forest compared to open swamp may be related to the lower soil pH and higher soil redox conditions (Dent 1986).

3.5.6. \textit{Surface accumulation of soluble ions}

The increase in soluble ions in the soil beneath individual trees and encroached forests was greatest near the soil surface (0 - 30 cm). This suggests a mechanism of vertical redistribution of ions that is absent in open swamp areas. One possibility is enhanced capillary rise beneath the \textit{M. quinquenervia} forest. Another possibility is leaf litter.
data in Table 3.3 and an assumed annual leaf litter fall rate of 0.7 kg m\(^{-2}\) yr\(^{-1}\) (based on Greenway 1994 and Finlayson et al. 1993) an estimate of the annual contribution of leaf litter to soil solute accumulation can be derived. Using profile 1 to represent open swamp and profile 4 to represent *M. quinquenervia* forest and assuming an identical initial soil accumulation prior to encroachment and complete loss from the leaves to the soil via leaching, litter accumulation from senescent leaves could theoretically account for 3% and 40% of the differences in soil Cl\(^-\) and Al, respectively.

Another potential source of ions may be the hydraulic lifting of water, whereby soil water is transported from areas of high water potential (i.e. from deeper in the soil profile) to the near surface rhizosphere by roots (Caldwell and Richards 1989; Dawson 1993). *M. quinquenervia* has a shallow rooting habit and while hydraulic lift has not been studied specifically in *M. quinquenervia*, it is known to occur in a wide range of plant species and environments (Caldwell et al. 1998). Hydraulic lifting of water is generally a localised phenomena, typically occurring in close radial proximity (<5 m) to the tree (Dawson 1993) which matches the pattern of localised solute accumulation observed around individual *M. quinquenervia*. Recent research suggests that ions may be transported along the roots with the lifted water via apoplastic pathways (J. Richards pers. comm.). This hypothesis is supported by visual observations. An efflorescence of white, soluble acidic salts occurred on the exposed bark of near surface roots of individual *M. quinquenervia* during a period when the water table was about 0.6 m below the surface.

3.5.7. Management implications

If there are no changes to the current land management and the artificial drainage regime, continued encroachment of *M. quinquenervia* into open swamp areas is likely to occur at
this site. Dense stands of young *M. quinquenervia* are evident on the margins of existing encroached forest in many locations.

The alteration of sediment and shallow groundwater geochemistry has significant implications for managing acid export. Increased concentrations of acidity and acidic metal cations in groundwater beneath encroached *M. quinquenervia* areas are likely to enhance the concentrations of soluble acidic products entering drains that bisect these areas. At sites where the dominant pathway of acid flux is groundwater seepage, such as east Shark Creek ASS backswamp (Johnston *et al.* 2004), this process may be contributing to existing acid and metal export loads. The potential for acidification of shallow surface water following inundation is likely to be increased due to the near surface accumulation of acidic solutes evident beneath *M. quinquenervia*.

### 3.5.8. Further research

A substantial number of questions arise from this study and possible areas of further research include;

- Establish the extent of *M. quinquenervia* encroachment post-European occupation in other coastal sulfidic backswamps.

- Examine the role of changes to drainage and fire regimes in coastal sulfidic backswamps upon *M. quinquenervia* encroachment.

- Determine whether similar changes are evident beneath other species of deep-rooted vegetation that have encroached in ASS backswamps (i.e. *Casuarina glauca*).

- Quantify the implications of enhanced groundwater acidity and near surface soil acidity for acid flux and drainage water quality.

- Identify and quantify the processes involved in the enhancement of soil and
groundwater acidity and rank their relative importance.

- Definitively determine if enhanced sulfide oxidation is occurring and identify the mechanism(s).
- Definitively establish the mechanism for the near surface accumulation of ions.
- Identify viable management strategies.

3.6. Conclusions

Extensive encroachment of *M. quinquenervia* in an artificially drained sulfidic backswamp has resulted in large changes to shallow groundwater and sediment geochemistry. The enhanced acidic metal cations and other solutes evident in soil and groundwater are likely to be the result of multiple processes, including increased water use combined with ion exclusion, complex rhizosphere - sediment interactions and possibly enhanced sulfide oxidation. Further research examining *M. quinquenervia* physiology and its rhizosphere - sediment interactions specific to drained sulfidic soils is required to determine precise causal mechanisms. Enhanced soil and groundwater acidification may be contributing to drainage system acid flux loads and without intervention continued encroachment is likely.

Acknowledgments

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Addendum to Chapter 3

Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to *Melaleuca quinquenervia* encroachment:
the influence of micro-topography

3.8. Abstract

In a review of Johnston *et al.* (2003b) it was suggested that variations in backswamp micro-topography could be an alternative factor capable of explaining the large differences in soil / groundwater acidity that were attributed to *M. quinquenervia* encroachment. This study was designed to test this hypothesis. Multiple line transect surveys were conducted in the different vegetation types (open swamp vs *M. quinquenervia*) with measurements of surface elevation and ECₐ (using an EM38) recorded at each survey point. While the vegetation types occupied relatively similar topography and elevation ranges, the mean elevation of encroached *M. quinquenervia* forest (0.13 m AHD) was slightly lower than the open swamp (0.16 m AHD). There was a negative correlation between ECₐ and micro-topography within the individual vegetation types, with the highest correlation coefficient occurring in open swamp area. However, the vegetation types had very distinct ECₐ populations, with *M. quinquenervia* having a mean ECₐ value of 2.0 dS m⁻¹ compared to 0.9 dS m⁻¹ in open swamp (significant at *P* <0.001). These data show that while micro-topography appears to have some influence on ECₐ, it is clearly not the dominant factor causing the large differences in soil / groundwater acidity apparent between the two vegetation types. The chemical composition and mineralogy of an acidic salt efflorescence observed on surface roots of *M. quinquenervia* was also examined.
3.9. Introduction

One of the referees of Johnston et al. (2003b) suggested that backswamp micro-topography could be an alternative factor capable of explaining the large differences observed in soil / groundwater acidity between encroached *M. quinquenervia* and open swamp. The primary argument of the referee was that the encroached trees were not causing changes to soil and groundwater geochemistry, but rather had preferentially colonised parts of the landscape with pre-existing soil and groundwater conditions. They suggested that these pre-existing differences in soil and groundwater conditions were most likely to be related to variations in micro-topography. Relationships between soil acidification and micro-topography have been demonstrated in some ASS backswamps (Husson et al. 2000). It is known that acidic solutes can accumulate in topographic lows in ASS backswamps (Kemsley 1997; Smith et al. 2003).

In addition, Johnston et al. (2003b) reported the an efflorescence of white, acidic salts occurring preferentially on the surface roots of individual *M. quinquenervia* at a time when the water table was ~0.6 m below the ground surface. However, the mineralogy or chemical composition of these salts was not reported.

This study aims to (1) test the hypothesis that variations in micro-topography can explain the large differences observed in soil / groundwater acidity between the different vegetation types (i.e. *M. quinquenervia* and open swamp dominated by pasture species), and (2) examine the mineralogy and chemical composition of a soluble salt efflorescence observed on the near surface roots of *M. quinquenervia.*
3.10. Materials and Methods

3.10.1. Study site

The study site is an artificially drained sulfidic backswamp located in Shark Creek, a small tributary on the lower Clarence River floodplain (29°30' S, 153°15' E) (see Chapter 3, section 3.3.1. for a detailed description). The backswamp is an infilled Holocene estuarine sub-embayment and there are currently two main vegetation types, as described by Johnston et al. (2003b) (see Fig. 3.2). These are encroached *M. quinquenervia* forest, and open swamp dominated by native grass species.

3.10.2. Elevation survey and EM38 sampling

Multiple line transects were established in each of the vegetation zones (open pasture, n = 14; *M. quinquenervia*, n = 13) over a ~2.5 km² portion of the ASS backswamp (Fig. 3.15). Each transect consisted of ~8 points with approximately 20 m spacing between points. Each point was surveyed for elevation to AHD using an automatic level and measuring staff. At each survey point measurements were made using a Geonics EM38 electromagnetic induction soil conductivity meter, which was operated in accordance with the manufacturers instructions (McNeill 1986). The EM38 has a coil spacing of 1 m and measures apparent soil electrical conductivity (ECₐ) in mS m⁻¹ in either a vertical (ECₐV) or horizontal (ECₐH) dipole orientation. In the vertical orientation the EM38 is more responsive to changes in ECₐ below 0.45 m, while in the horizontal orientation the maximum response is to the surface and declines with depth. The mean of the vertical and horizontal readings provides a more effective integration of soil profile ECₐ than either measurement alone (Slavich 1990). Johnston et al. (2003b) demonstrated that ECₐ is a powerful surrogate measurement for assessing relative changes in the concentrations of acidic solutes in groundwater and soil within this particular ASS backswamp.
3.10.3. Surface salt mineralogy and chemical analysis

Salt accumulations were collected from the surface roots of living *M. quinquenervia* trees located within Shark Creek backswamp by gently scraping the accumulations with a plastic spatula and transferring the material into a clean plastic container. At the time of collection the groundwater table was about 0.3 m below the ground surface. A sub-sample of this salt was gently hand-ground to a fine powder. An X-ray diffractogram was obtained for this
powdered sample using a Phillips PW 1820 diffractometer. The remaining sample (~1 gm) was placed in distilled water (1:50) and gently shaken for about 1 minute. A pH reading was then taken using freshly calibrated portable field equipment (TPS 90FLMV) and the remaining sample filtered (0.45 µm cellulose acetate), placed into a clean polyethylene bottle and immediately frozen to minimise biochemical changes. This sample was defrosted at 4°C and analysed for Cl\(^-\), SO\(_4^{2-}\), Fe, Al, Ca and Mg (ICPAES - USEPA 6010).

3.11. Results and discussion

3.11.1 Micro-topography and solute accumulation

Both the *M. quinquenervia* forest and open swamp areas occupied similar elevation ranges and had reasonably similar overall elevation distributions (Fig. 3.16). However, the mean elevation of encroached *M. quinquenervia* forest (0.13 m AHD) was slightly lower than the open swamp (0.16 m AHD). While this difference is relatively small (~10% of the total elevation range), it was statistically significant at \( P < 0.05 \) (Table 3.4).

![Figure 3.16. Surface elevation distribution in the encroached *M. quinquenervia* forest and open swamp area at Shark Creek ASS backswamp.](image)
Table 3.4. Mean surface elevations and soil EC\textsubscript{a} for open swamp areas and encroached *M. quinquenervia* forest areas at Shark Creek backswamp.

All values are means. Figures in brackets are standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>Open swamp (n = 98)</th>
<th><em>M. quinquenervia</em> (n = 84)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elevation (m AHD)</td>
<td>0.16 [0.06]</td>
<td>0.13 [0.05]</td>
<td>*</td>
</tr>
<tr>
<td>Mean EC\textsubscript{a} (dS m\textsuperscript{-1})</td>
<td>0.90 [0.21]</td>
<td>2.02 [0.42]</td>
<td>***</td>
</tr>
<tr>
<td>EC\textsubscript{a}H (dS m\textsuperscript{-1})</td>
<td>0.80 [0.21]</td>
<td>1.90 [0.43]</td>
<td>***</td>
</tr>
<tr>
<td>EC\textsubscript{a}V (dS m\textsuperscript{-1})</td>
<td>1.00 [0.21]</td>
<td>2.15 [0.41]</td>
<td>***</td>
</tr>
</tbody>
</table>

\*P <0.05, **P <0.01, ***P <0.001

While the difference in their mean elevations was small, the *M. quinquenervia* forest and open swamp have two very distinct EC\textsubscript{a}H and mean EC\textsubscript{a} populations (Fig. 3.17). The EC\textsubscript{a}H and mean EC\textsubscript{a} in encroached *M. quinquenervia* areas were substantially higher than open swamp for any given elevation (Fig. 3.17). The mean of the EC\textsubscript{a}H, EC\textsubscript{a}V and mean EC\textsubscript{a} were more than double in the encroached *M. quinquenervia* forest areas compared to open swamp (Table 3.4) and were significantly different at P <0.001. However, there was also a negative correlation between EC\textsubscript{a} and micro-topography evident within the individual vegetation types, with the highest correlation coefficient occurring in open swamp area (r\textsuperscript{2} = 0.38) (Fig. 3.17b). These data show that while micro-topography appears to have some influence on EC\textsubscript{a} and the accumulation of acidic solutes in soil and groundwater, it is clearly not the dominant factor responsible for the large differences in soil / groundwater acidity between the two vegetation types.

A compilation of available data from Johnston *et al.* (2003b) and Chapter 4 show a strong positive correlation between surface soil (0 - 2 cm) soluble Al concentrations and EC\textsubscript{a}H (Fig. 3.18). While this relationship is site specific, it further demonstrates the value of
EM38 measurements as a surrogate for assessing changes in the concentration of acidic solutes in surface soils within this particular ASS backswamp landscape.

Figure 3.17. Relationships between surface elevation and a) EC$_{a}$H and b) mean EC$_{a}$ in areas of encroached *M. quinquenervia* forest and open swamp at Shark Creek ASS backswamp.
3.11.2. Salt efflorescence on surface roots

A photograph of the surface salt efflorescence which preferentially accumulated on the surface roots of individual *M. quinquenervia* is shown in Fig. 3.19.

**Figure 3.18.** Positive correlation between soil EC$_{\text{cH}}$ and surface soil (0 - 2 cm) soluble Al concentrations. All data are from Shark Creek ASS backswamp. Source: Johnston *et al.* (2003b) and Chapter 4.

**Figure 3.19.** Efflorescence of acidic solutes on surface and near surface roots of *M. quinquenervia*. Note that the efflorescence is also occurring on the soil surface in places where the roots are immediately below the surface. Photo taken during November 2002 during a period when the groundwater table was approximately 0.6 m below the soil surface. Marker pen for scale.
Analysis of the X-ray diffractogram of this salt efflorescence reveals peak responses at d-spacings which correspond to gypsum \(\text{CaSO}_4^{2-} \cdot 2\text{H}_2\text{O}\), which was subsequently identified as the dominant mineral salt in the sample (Fig. 3.20).

![X-ray diffractogram of the surface salt efflorescence. Main peak responses clearly correspond to d-spacings associated with gypsum.](image)

**Figure 3.20.** An X-ray diffractogram of the surface salt efflorescence. Main peak responses clearly correspond to d-spacings associated with gypsum.

The dominance of Ca and \(\text{SO}_4^{2-}\) was confirmed by chemical analysis (Table 3.5), however there was also substantial \(\text{Cl}^-\) and some \(\text{Mg}\) present, suggesting the presence of other unidentified mineral salts. The 1:50 extract of the salt had a pH value of 3.96 (equivalent to 0.11 mmol H\(^+\) L\(^-1\)), suggesting the existence of some soluble form(s) of acidity. A small quantity of Fe and Al was also detected in the chemical analysis (Table 3.5), which may represent the adsorption of these acidic metal cations. Even if only half of these metal cations were in the form of Fe\(^{2+}\) and Al\(^{3+}\) (capable of producing 2 and 3 mol of H\(^+\) respectively), they could theoretically produce an acidity equivalent to 0.17 mmol H\(^+\) L\(^-1\), and can thus readily account for low pH of the sample extract.
Table 3.5. The chemical composition of a water extract (1:50) of the salt efflorescence on *M. quinquenervia* surface roots.

pH of distilled water prior to addition of salt = 5.56. All concentrations in mmol L⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>Salt sample (1:50 water extract)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.96</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>16.67</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>9.94</td>
</tr>
<tr>
<td>Ca</td>
<td>11.72</td>
</tr>
<tr>
<td>Mg</td>
<td>2.55</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>0.06</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>0.08</td>
</tr>
</tbody>
</table>

3.12. Conclusions

While micro-topography appears to have some influence on EC<sub>a</sub> at this site, it is clearly not the dominant factor causing the large differences in soil / groundwater acidity apparent between the two vegetation types. These data support the original conclusion of Johnston *et al.* (2003b), i.e. that the observed differences in soil and groundwater geochemistry between the vegetation types are related to the encroachment of *M. quinquenervia*. 
Chapter 4

Changes in surface water quality after inundation of acid sulfate soils with different vegetation cover

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**Collection of samples, laboratory analysis and interpretation of data**

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Interpretation of data: Johnston, Slavich

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Original draft: Johnston
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Preparation of computer graphics: Johnston
4.1. Abstract

Surface soils from an acid sulfate soil backswamp were inundated in a temperature controlled environment and surface water chemistry changes monitored. The soils had contrasting \textit{in situ} vegetative cover (i.e. grass species and \textit{Melaleuca quinquenervia} litter). While the different vegetation types had similar biomass and carbon content, there were large differences in the quality and lability of that carbon which strongly influenced decay / redox processes and the chemical composition of surface waters. The grass species had more labile carbon. Their surface waters displayed rapid and sustained O$_2$ depletion, sustained low Eh ($\sim$0 mV), high dissolved organic carbon (DOC) and moderate pH (5 - 6). Their soil acidity was partially neutralised, sulfides were re-formed and reductive dissolution of Fe (III) led to the generation of stored acidity in the water column as Fe$^{2+}$(aq).

In contrast, \textit{M. quinquenervia} litter was high in decay resistant compounds. Its surface waters had lower DOC, low pH ($<$4) and only underwent a short period of low O$_2$/ Eh. Its surface waters also had higher titratable acidity due to soluble Al and neutralisation of soil acidity was limited. Concentrations of Cl$^-$ and Al in surface waters were strongly correlated to initial soil contents, whereas the behaviour of Fe and SO$_4^{2-}$ varied according to pH and redox status. This study demonstrates that changes in vegetation communities in ASS backswamps which substantially alter either a) the pool of labile vegetative organic carbon or b) the concentration of acidic solutes in surface soil, can have profound implications for the chemical characteristics of backswamp surface waters.
4.2. Introduction

Large areas of acid sulfate soils (ASS) lay beneath Australia’s eastern coastal floodplains (Naylor et al. 1995). Floodplain backswamps which contain ASS undergo regular inundation during wet seasons and extensive drainage systems have been constructed to remove surface waters (White et al. 1997; Tulau 1999). Surface waters in ASS backswamps are frequently acidic and drainage from these areas can export large amounts of acidity, Fe and Al to adjacent estuarine waters (Sammut et al. 1996; White et al. 1997; Wilson et al. 1999; Cook et al. 2000a; Johnston et al. 2004). Drainage of anaerobic surface waters from ASS backswamps after flooding can also contribute to deoxygenation of estuarine waters (Johnston et al. 2003a).

Redox sensitive species, such as Fe and SO$_4^{2-}$, are abundant in ASS (Walker 1972; van Breemen 1973; Dent 1986) and can be important terminal electron acceptors during the anaerobic decay of organic matter. Johnston et al. (2003a) reported that the chemical composition of surface waters draining from two ASS backswamps after flooding was strongly influenced by coupling of Fe and SO$_4^{2-}$ reduction with anaerobic decay of in situ surface vegetation. Redox transformations of these species in inundated soils are usually mediated by bacteria and reduction reactions typically consume acidity (van Breemen 1973; Stumm and Morgan 1981). Accompanying changes in soil pH and Eh influence both mineral stability and metal solubility (Satawathananont et al. 1991; Warren and Haack 2001) and have a profound influence on the chemistry of overlying waters (Ponnamperruma 1972; van Breemen 1975).

Labile organic carbon provides the primary source of electron donors in soils and is thus a critical factor determining reduction processes and pathways in inundated acid sediments.
(van Breemen 1975; Blodau and Peiffer 2003). Other factors influencing reduction processes and pathways include microbial ecology, soil pH (van Breemen 1975) and the abundance of the terminal electron acceptors themselves, particularly amorphous Fe (III) oxides (Postma and Jakobsen 1996; Roden and Wetzel 2002).

Rates of organic matter decay in wetland environments are strongly influenced by the species of emergent vascular plants and the chemical composition of plant tissues (Polunin 1984; Webster and Benfield 1986). Carbon from non-woody plants species is typically more labile than carbon from woody plants (Webster and Benfield 1986). Decay rates can be retarded by high concentrations of lignin and other polyphenolic compounds (Webster and Benfield 1986; McClaugherty and Berg 1987), low pH and metal toxicity (Marschner and Kalbitz 2003). While bacteria dominate lignin degradation in aquatic environments (Benner et al. 1986), lignin decomposition is often slow under anaerobic conditions (Zimmermann 1990).

Large changes in the aerial extent of vegetation species have occurred within ASS backswamps on Australia’s east coast due to drainage and agriculture (Goodrick 1970; Pressey and Middleton 1982; Pressey 1989). Decreases in the natural hydroperiod of ASS backswamps (White et al. 1997) has generally favoured species adapted to more frequent drying (Pressey and Middleton 1982). In some ASS backswamps, large areas that were once dominated by reeds and rushes, such as Phragmites australis, have now been replaced by grass species including Cynodon dactylon and Paspalum distichum (NSW Agriculture and Fisheries 1989). Some of these grass species, particularly C. dactylon, have limited tolerance of inundation (Ashraf and Yasmin 1991).
Expansion in the area of the native tree species *Melaleuca quinquenervia* has also been documented in some drained ASS backswamps (Johnston *et al.* 2003b). Encroachment of *M. quinquenervia* was identified by Johnston *et al.* (2003b) as being responsible for altering groundwater geochemistry and increasing the concentrations of acidic solutes in near surface soils. Higher concentrations of acidic solutes in surface soils are likely to enhance the acidification and influence the chemical composition of inundating surface waters. The encroached areas of *M. quinquenervia* identified by Johnston *et al.* (2003b) had minimal understorey and surface vegetative carbon was dominated by leaf litter. Slow decay rates have been invoked to explain substantial accumulations of *M. quinquenervia* litter in floodplain environments in previous studies (Greenway 1994).

While Johnston *et al.* (2003b) demonstrated that changes to vegetation composition in ASS backswamps can potentially influence surface soil acidity, such changes are also likely to have altered the characteristics of the surface vegetative carbon pool. There is a need for further assessment of the interactions between these processes and the implications they may have for the chemical composition of surface waters following inundation. This paper examines the results of laboratory experiments involving inundation of surface soils from an ASS backswamp with contrasting vegetation types i.e. grass species and encroached *Melaleuca quinquenervia*. It aims to (1) assess and compare the changes in surface water chemistry (acidification, deoxygenation and reduction processes) following inundation of these soils, and (2) relate the observed changes to initial sediment chemistry and labile organic carbon from surface vegetation.
4.3. Materials and Methods

4.3.1. Soil collection and treatment

Surface soils were collected from an ASS backswamp (Shark Creek) on the Clarence River floodplain (29°30' S, 153°15' E). This backswamp is described in Johnston et al. (2003b) and Lin and Melville (1993). Typical profiles consist of an acidic, organic rich topsoil (~0.3 m deep) overlying highly acidic, mineral sulfuric horizons with Fe (III) mineral and jarosite mottles, which are underlain by sulfidic sediments of estuarine origin 0.8 to 1 m below the ground surface (Lin and Melville 1993; Johnston et al. 2003b).

Whole blocks of surface soil (0.15 - 0.18 m deep x 0.48 m wide x 0.68 m long) were carefully excavated and placed intact with an upright orientation into tight fitting plastic tubs (0.4 m deep). Despite attempts to ensure smooth sides on the blocks, some small air pockets remained between the base and sides of the soil blocks and the plastic tubs. All in situ surface organic matter on each soil block was retained. Three blocks (C1, C2, C3) were collected from open swamp areas (Chapter 3, Fig.3.2) and their dominant in situ surface vegetative cover was the grass species C. dactylon. These blocks were collected during a prolonged dry period and the grass was dry, brown and in a senescent phase. Three blocks (M1, M2, M3) were collected from areas of encroached M. quinquenervia forest, where the encroachment occurred after 1942 (Chapter 3, Fig. 3.2). The in situ surface vegetative cover in these blocks consisted of M. quinquenervia leaf litter and no vascular plant species were present.

An additional organic topsoil block (K1) was collected in accordance with the methods outlined above, from a different area of ASS on the Clarence River floodplain (Alumy Creek – see Tulau 1999). The in situ surface vegetative cover on this block consisted of
improved pasture species dominated by actively growing Kykuyu (*Pennisetum clandestinum*). The surface soil at this site was less acidic than that from the Shark Creek backswamp and the sulfide layer was >1.0 m from the ground surface.

A Geonics EM38 electromagnetic induction soil conductivity meter was used to measure apparent soil electrical conductivity (EC$_a$) in the field at each site (except K1) prior to collection of the soil blocks. The EM38 has a coil spacing of 1 m and measures EC$_a$ in mS m$^{-1}$ in either a vertical (EC$_a$V) or horizontal (EC$_a$H) dipole orientation. In the horizontal orientation the maximum response is to the surface soil and declines with depth.

The plastic tubs with soil blocks were placed in a temperature controlled laboratory environment with diffuse natural light and florescent lighting. The air temperature was monitored hourly during the experiment with an EIT E-Tech weather station (mean air temperature 25.7$^\circ$C, standard deviation 1$^\circ$C). Sufficient distilled water was prepared and allowed to equilibrate to laboratory temperature and atmospheric O$_2$. Each tub was flooded quickly (10 minutes) with distilled water until the surface was submerged to a depth of 0.2 m. Care was taken to avoid disturbing soil particles during the flooding process. The water surface in each tub remained exposed to the atmosphere for the duration of the experiment (26 days).

In one of the tubs (M2) the very top layer (1 - 3 cm) of the organic rich surface soil broke away from the main soil block and floated to the surface as an intact ‘raft’. This was discovered about 1 hr after initial inundation and the ‘raft’ was re-submerged. However, this re-submerging process forced water through the ‘raft’ which is likely to have encouraged leaching of solutes (acidic and non-acidic) into the surface water beyond what
would have occurred naturally. This experimental error is likely to have enhanced concentrations of dissolved Al, chloride and titratable acidity in the surface water of tub M2 and should be considered in subsequent data interpretation.

4.3.2. Surface vegetation cover sampling and analysis

All surface organic matter (including leaf litter and standing grass) was removed from two 0.1 m x 0.1 m quadrats on each soil block. Samples were oven-dried at 60°C for 96 hours, dry weights were obtained for each quadrat and the mean of both quadrats used to calculate biomass. The two samples from each soil block were then bulked and crushed in a hammer mill to pass a 2 mm sieve and analysed for water soluble Cl⁻ (SPAC 14), total Al and total Fe (ICPAES - USEPA 6010) carbon (LECO), nitrogen (LECO 3336), lignin (acid detergent - ANKOM Technology - 9.99), water soluble carbohydrate (WSC) (modification of Technicon Industrial Method 302 - 73A), acid detergent fibre (ADF) (ANKOM Technology - 9.99) and neutral detergent fibre (NDF) (ANKOM Technology - 9.98).

4.3.3. Soil sampling and analysis

Surface soils (0 - 2 cm) were sampled from each soil block prior to re-flooding and on days 8, 19 and 26 post-flooding. On each occasion sub-samples were collected from four random locations and bulked to form a single ~50 gm sample prior to drying. Soil samples were oven-dried at 85°C within 48 hrs of collection and crushed to pass a 2 mm sieve. The Electrical Conductivity (EC) and pH of a 1:5 water extract was determined for each sample (Rayment and Higginson 1992). All samples were analysed for reduced inorganic sulfur species (SCr⁻ - Sullivan et al. 2000) and total actual acidity (TAA - Ahern et al. 1998; Lin et al. 2000), water soluble Cl⁻ and SO₄²⁻ (Ion chromatography - APHA (1995), 4110) and water soluble Al (ICPAES - USEPA 6010), total carbon and organic carbon (Rayment and
The \textit{in situ} pH and redox potential of surface soils (0 - 2 cm) was determined regularly by direct probe insertion at two random locations in each soil block using freshly calibrated equipment (TPS 90FLMV). The mean of the two values was used. pH was measured using a double junction Ag/AgCl electrode and redox potential was measured with a platinum tipped Ag/AgCl reference electrode. All redox values presented in this paper are reported relative to the standard hydrogen electrode (Eh), but are not corrected for pH due to the uncertainty of the correction factor in reduced soils (Ponnamperuma 1972).

4.3.4. Water sampling and analysis

The surface water pH, EC, redox potential, dissolved oxygen (DO) and temperature of was measured regularly \textit{in situ} in each tub using freshly calibrated equipment (TPS 90FLMV). Probes were placed at mid-depth close to the centre of each tub during measurements. In addition, hourly measurements of surface water DO, pH, EC and temperature were made in tubs M1, M2, C1 and C2 with Greenspan CS304 submersible data loggers. DO was measured via a diffusion rod, pH using a double junction Ag/Cl electrode and EC via a toroidal sensor.

Water samples were collected from each tub at pre-determined intervals according to the following procedure. A 400 ml bulked sample of water was obtained by extracting smaller sub-samples of water from >6 random locations at mid-depth using a clean syringe with flexible plastic tubing. The syringe and tubing were thoroughly cleaned between each tub and flushed three times with the water to be sampled. From this sample a 200 ml sub-sample was analysed for titratable acidity to pH 5.5 (APHA (1995), 2310B - including the peroxide
oxidation step) within 24 hrs of sample collection. Another 30 ml sub-sample was immediately filtered (0.45 µm), placed into cold storage (~4°C) and analysed for Ferrous iron within several hrs of collection (Spectrophotometrically, phenanthroline method - HACH (1991) - 8146). A further 150 ml sub-sample was immediately filtered (0.45 µm) and transferred to a clean (acid rinsed, distilled water flushed) polyethylene bottle. Visible air bubbles were excluded prior to sealing the cap and this sample was immediately frozen for storage. Frozen samples were defrosted at ~4°C and analysed for Cl⁻ and SO₄²⁻ (Ion chromatography - AHPA (1995), 4110), dissolved Al (ICPAES - USEPA 6010) and dissolved organic carbon (combination Infra-red - APHA (1995), 5310).

Shallow surface waters were also sampled from the Shark Creek backswamp after rainfall caused inundation of the surface. Six samples were collected, three each from the different vegetation zones i.e. open swamp and *M. quinquenervia* forest. The *in situ* pH, EC, redox potential, DO and temperature of surface water was measured at the site of sample collection using freshly calibrated field equipment (TPS 90FLMV). Selected samples were collected in clean 250 ml polyethylene bottles and analysed according to the methods and procedures outlined above.

**4.4. Results**

**4.4.1. Surface vegetation cover**

The mean dry weight of *in situ* surface vegetation prior to inundation of the soil blocks is shown in Fig. 4.1. This includes all standing grass and leaf litter. Results are similar for each vegetation type (~3 to 4 kg/m²). The *M. quinquenervia* litter accumulation is comparable to values reported previously for floodplain environments in sub-tropical eastern Australia (Greenway 1994).
Figure 4.1. The mean biomass of surface vegetative cover on the soil blocks for the different vegetation types. Error bars are ± the standard deviation.

While the different vegetation types have similar total carbon contents (Fig. 4.2a) there are large differences in the biodegradability of that carbon. The biodegradability of the different pools of carbon within natural organic matter can be loosely divided into labile, semi-labile and stable fractions (Marschner and Kalbitz 2003). In this study WSC (consisting mainly of readily soluble sugars) was used as an indicator of the labile carbon fraction. This fraction was highest for the *P. clandestinum* (~4%), lower in *C. dactylon* (~1.5%), and lowest in *M. quinquenervia* (~0.7%) (Fig. 4.2b). The difference between ADF and NDF consists of plant cell wall material comprised of a heterogeneous collection of polysaccharides (mainly hemicellulose) and is used as an indicator of the semi-labile carbon fraction. This fraction was much higher (30 - 35%) in both *P. clandestinum* and *C. dactylon* compared to *M. quinquenervia* (7%) (Fig. 4.2c). Aromatic, polyphenolic compounds are typically associated with low biodegradability of organic matter (Webster and Benfield 1986; Marschner and Kalbitz 2003) and lignin concentrations are used as an indicator of this more recalcitrant, stable carbon fraction. Fig. 4.2d shows that the mean
Lignin content of *M. quinquenervia* litter (~40%) is far higher than either *C. dactylon* (~15%) or *P. clandestinum* (~6%). Mean C:N ratios were reasonably similar for all three vegetations types at 30, 53, 40 for *P. clandestinum*, *C. dactylon* and *M. quinquenervia* respectively. However, *M. quinquenervia* litter had far higher total Al and Fe contents compared to the grass species (Fig. 4.2e and 4.2f).

**Figure 4.2.** The mean chemical composition of the different *in situ* surface vegetative covers comparing a) total carbon, b) water soluble carbohydrate, c) NDF – ADF, d) lignin, e) total Al, and f) total Fe. Error bars are ± the standard deviation.
4.4.2. Reduction and acidity in surface soils

The different vegetation types exhibited markedly contrasting in situ pH and redox behaviour in their near surface soils after inundation. The pH was relatively stable and mostly <4 in the *M. quinquenervia* blocks, whereas substantial pH increases were evident in the soil blocks containing grass species within the first 10 days (Fig. 4.3a). Large decreases in Eh occurred in all soil blocks during the first week following inundation. These decreases were more rapid and of greater magnitude in *P. clandestinum>* *C. dactylon>* *M. quinquenervia* respectively (Fig. 4.3b). This pattern accords with the observed differences in the biodegradability of vegetative carbon.

![Figure 4.3](image)

Figure 4.3. Changes in mean in situ surface soil (0 - 2 cm) a) pH and b) Eh over time after inundation associated with the different vegetation types. Error bars are ± the standard deviation.

The mean chemical composition of surface soils before and at day 26 of the inundation experiment is shown in Table 4.1. While there was little change in mean organic carbon content, the day 26 samples display greater variability which may reflect increasing sub-sample heterogeneity due to vegetation decomposition. The \( S_{Cr} \) decreased to about half of the initial values in the *M. quinquenervia* soils though there was a high degree of initial variability. \( S_{Cr} \) increased by about 50% of initial values in the *C. dactylon* and *P. clandestinum* soils, but overall amounts remain small (Table 4.1). Tubs with *C. dactylon*...
and *P. clandestinum* produced a distinct sulfurous odour from about day 6 onwards whereas the *M. quinquenervia* tubs were relatively odourless by comparison. While it is possible that H$_2$S could have formed in the tubs containing grass species, this was not measured. There were much higher initial concentrations of solutes (i.e. Al, Cl$^-$ and SO$_4^{2-}$) in the surface soils of the *M. quinquenervia* blocks (Table 4.1). The general decrease in surface soil solutes by day 26 is likely due to diffusion into the water column. Fe concentrations and speciation within the soil was not measured. However, previous research at this site by Johnston *et al.* (2003a) found high concentrations (~200 mmol kg$^{-1}$) of oxalate extractable Fe (representing the poorly crystalline fraction) in surface soils (0 - 2 cm) from areas of open swamp.

<table>
<thead>
<tr>
<th></th>
<th><em>M. quinquenervia</em></th>
<th><em>C. dactylon</em></th>
<th><em>P. clandestinum</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic carbon (%)</td>
<td>17.0 [0.0]</td>
<td>15.0 [0.0]</td>
<td>14.0 [2.1]</td>
</tr>
<tr>
<td>S$_{Cr}$ (%)</td>
<td>0.46 [0.46]</td>
<td>0.09 [0.03]</td>
<td>0.03 [0.05]</td>
</tr>
<tr>
<td>TAA</td>
<td>477 [76]</td>
<td>320 [80]</td>
<td>160 [100]</td>
</tr>
<tr>
<td>Water soluble Al</td>
<td>18.9 [8.7]</td>
<td>3.3 [3.6]</td>
<td>0.5 [1.3]</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>17.7 [2.1]</td>
<td>4.8 [4.6]</td>
<td>2.0 [2.0]</td>
</tr>
</tbody>
</table>

4.4.3. Geochemistry of surface waters

The physico-chemical characteristics and geochemistry of surface waters in the tubs changed substantially over time after inundation. Decreases in Eh occurred in all surface waters within the first 5 days following inundation and were more rapid and of greater magnitude in *P. clandestinum* > *C. dactylon* > *M. quinquenervia* respectively (Fig. 4.4a). The
Eh decrease was sustained for the duration of the experiment in tubs containing grass species, whereas an Eh recovery (beginning day 8) occurred in the *M. quinquenervia* tubs. Decaying vegetation is the primary source of electron donors so it follows that there is likely to be a close relationship between the lability of vegetative carbon and the redox status of surface waters after inundation. Fig. 4.5 shows that as the ratio of lignin to WSC decreases (i.e. as carbon lability increases) the minimum Eh recorded in the surface waters of the tubs also decreases.

**Figure 4.4.** Changes in mean surface water a) Eh, b) pH, c) Fe$^{2+}$, d) dissolved oxygen, e) dissolved organic carbon, and f) EC over time after inundation associated with the different vegetation types. Error bars are ± the standard deviation.
Sustained, uniformly low pH values (mostly <4) were observed in *M. quinquenervia* tubs, whereas pH ranged from around 5 to 6 in grass species tubs (Fig. 4.4b). The water in each of the tubs with grass species turned black and highly turbid during the experiment whereas waters associated with *M. quinquenervia* were relatively clear.

![Figure 4.5](image)

**Figure 4.5.** Correlation between the lignin:WSC ratio of the surface vegetation and the minimum surface water Eh after inundation of each soil block. ^A^ = Water soluble carbohydrate.

Concentrations of Fe$^{2+}$ increased rapidly in the first 10 days following inundation in all tubs (Fig. 4.4c). Peak values of 1 mmol L$^{-1}$ were associated with *P. clandestinum*. While the high values remained relatively stable in tubs containing grass species, a sharp decline in Fe$^{2+}$ occurred in the *M. quinquenervia* tubs coincident with a recovery in DO concentrations and the aforementioned Eh increase. This decline in Fe$^{2+}$ (day 11) was associated with the visible precipitation of Fe (III) flocs on the sediment and sides of the plastics tubs and also coincided with a slight fall in pH. Its timing coincides with that predicted on the basis of pH / Eh data for stability of iron hydroxides in aqueous environments (Fig. 4.6). Schwertmannite is a poorly crystalline Fe mineral which is known
to form in Fe and SO₄²⁻ rich waters with a pH range from 2.8 - 4.5 (Bigham et al. 1996). Schwertmannite is a very common precipitate in drainage waters in the Shark Creek ASS backswamp (L.A. Sullivan pers. comm.) and it may account for the observed Fe (III) flocs.

Figure 4.6. Changes in the pH and Eh of surface waters over time after inundation in two M. quinquenervia tubs (M1 = closed diamond, M3 = open diamond). Sampling times correspond to the linear sequence shown in Fig. 4.4. The straight line represents the theoretical boundary between the stability areas of Fe²⁺(aq) (grey area) and Fe(OH)₃ (plain area) for flooded soils (assuming an Fe²⁺(aq) activity of 1 mmol at 25 °C – after Ponnampuruma et al. 1967). Day 11 (highlighted) coincided with a large measured decrease in Fe²⁺(aq) (Fig. 4.4c) and the appearance of Fe (III) flocs in the tubs.

The sequence of O₂ depletion in the tubs showed some relation to the type of vegetation. Submersible data loggers revealed complete depletion of surface water O₂ within 12 hrs of inundation in P. clandestinum (K1), 19 hrs in C. dactylon (C1, C2) and 46 hrs in M. quinquenervia (M1, M2). This sequential pattern was confirmed by spot monitoring of DO (Fig. 4.4d). While DO remained ~0 in the tubs containing grass species for the duration of the experiment, a gradual recovery occurred in the M. quinquenervia tubs. Increases in
dissolved organic carbon (DOC) following inundation and were of greater magnitude in *P. clandestinum* > *C. dactylon* > *M. quinquenervia* respectively (Fig. 4.4e); a pattern which also accords with the differences in the biodegradability of surface vegetative carbon. There was an increasing trend in EC in all the tubs (Fig. 4.4f) and concentrations at day 8, not surprisingly, show a strong positive linear correlation (*r*² = 0.85) with initial surface soil EC.

**Figure 4.7.** Changes in mean surface water a) titratable acidity, b) dissolved Al, c) Cl⁻ and d) SO₄²⁻ over time after inundation associated with the different vegetation types. Error bars are ± the standard deviation. A = This left Y-axis relates to *M. quinquenervia* only. B = This right Y-axis relates to *C. dactylon* and *P. clandestinum* only.

Titratable acidity increased sharply over several days in the *M. quinquenervia* tubs and stabilised at a mean value ~2 mmol H⁺ L⁻¹ (Fig. 4.7a). However, titratable acidity was much lower and increased relatively slowly in the tubs containing *C. dactylon*. Titratable acidity behaved quite differently in the tub containing *P. clandestinum*, rising rapidly within the first week and then falling sharply from day 16 onward. Theoretically Fe²⁺ can generate 2 mol of H⁺ (via oxidation) and Al³⁺ can generate 3 mol (via hydrolysis) (van
Breemen 1993). These acidic metal cations can be responsible for much of the acidity in ASS drainage waters (Cook et al. 2000a). If one assumes that dissolved Al is mainly in the form of Al$^{3+}$ then combined, these cations can account for most of the titratable acidity measured in the surface waters of both the *M. quinquenervia* and *C. dactylon* tubs (Fig. 4.8). The theoretical individual contribution of Fe$^{2+}$ and dissolved Al to titratable acidity can thus be calculated. Fe$^{2+}$ clearly dominated the titratable acidity in the tubs containing grass species, whereas dissolved Al accounted uniformly for almost all the titratable acidity in the *M. quinquenervia* tubs (Fig. 4.9a and 4.9b). Neither Fe$^{2+}$ or Al$^{3+}$ can explain all the titratable acidity recorded in the *P. clandestinum* surface waters. One possible explanation may be the peroxide oxidation step used during the titratable acidity method causing the generation of acidity by oxidation of H$_2$S.

**Figure 4.8.** Linear correlation between the sum of acidic metal cations (Fe$^{2+}$ and dissolved Al) and titratable acidity in surface waters. Assumes that dissolved Al is in Al$^{3+}$ form and that 2 mol and 3 mol of H$^+$ are generated per mol of Fe$^{2+}$ and Al$^{3+}$ respectively. Data presented are mean values for each vegetation type.
Figure 4.9. The theoretical relative contributions of a) Fe$^{2+}$ and b) dissolved Al to the titratable acidity of surface waters associated with the different vegetation types. Assumes dissolved Al is in Al$^{3+}$ form and that 2 mol and 3 mol of H$^+$ are generated per mol of Fe$^{2+}$ and Al$^{3+}$ respectively. Data presented are mean values.

Dissolved Al was much higher in the *M. quinquenervia* tubs (Fig. 4.7b) which accords with the low pH and higher initial soil concentrations of soluble Al (Table 4.1). Chloride concentrations increased steadily over time in all the tubs (Fig. 4.7c) whereas SO$_4^{2-}$ decreased in the tubs with grass species (Fig. 4.7d). This decrease in SO$_4^{2-}$ is likely to be a result of reduction and sulfide formation in soils (Table 4.1). This suggestion also accords with the Eh / pH signature of surface soils which shows for much of the experiment the grass species soils were either close to or within the range theoretically occupied by sulfate reducing bacteria in natural environments (Fig. 4.10). In contrast the *M. quinquenervia* tub
soils occupied an Eh / pH range more commonly associated with Fe bacteria and *Thiobacteria* spp. (Baas Becking *et al.* 1960).

**Figure 4.10.** Surface soil pH / Eh signatures for each of the soil blocks during the experiment. The approximate areas occupied by different types of bacteria are also shown (after Baas Becking *et al.* 1960), where the grey area represents sulfate reducing bacteria, the hatched area represents iron bacteria and the plain area represents *Thiobacteria* spp..

Mean Cl\(^{-}\):SO\(_4^{2-}\) ratios remained uniformly low in the *M. quinquenervia* tubs throughout the experiment, whereas SO\(_4^{2-}\) decreased relative to Cl\(^{-}\) in the tubs with grass species (Fig. 4.11a). Figure 4.11a also includes Cl\(^{-}\):SO\(_4^{2-}\) ratios collected from two different ASS backswamp drains after flooding using data from Johnston *et al.* (2003a). One of these drains (Maloneys) was located at the Shark creek study site where about 50% of the backswamp consists of *M. quinquenervia* (Johnston *et al.* 2003b). This drain had uniformly
low Cl:\SO_{4}^{2-} ratios. The other drain (Blanches) was located in a backswamp dominated by decaying pasture species after flooding (Johnston et al. 2003a) and in contrast, this drain exhibited decreasing SO$_{4}^{2-}$ relative to Cl$. This comparison helps confirm that the associations between vegetation types and chemical processes observed in the tub waters are applicable to those occurring in surface drainage waters at a field scale.

Figure 4.11. Changes in surface water a) Cl:\SO_{4}^{2-} ratios and b) Cl: dissolved Al ratios. Data presented are mean values. Maloney's post-flood and Blanches post-flood data (including their date of inundation) derived from Johnston et al. (2003a).

In contrast to both SO$_{4}^{2-}$ and Fe$^{2+}$, the behaviour of Cl$^-$ and dissolved Al was conservative and relatively uniform over time in all of the tubs (Fig. 4.11b). Concentrations of both Cl$^-$ and dissolved Al in surface waters were strongly correlated with initial soil contents prior
to inundation (Fig. 4.12a and 4.12b). This suggests that initial soil concentrations play a primary role in determining resultant surface water concentrations of these species. There were also strong positive linear correlations between soil EC$_a$H and soluble Al (Fig. 4.13a) and soil EC$_a$H and Cl$^-$ and in the upper 2 cm of the soil (Fig. 4.13b). This data compares well with data presented in Johnston et al. (2003b) and confirms the utility of EM38 measurements as a surrogate for assessing relative concentrations of acidic and non-acidic solutes in surface soils in this particular ASS backswamp.

Figure 4.12. Positive linear correlation between initial surface soil concentrations and resultant surface water concentrations of a) Cl$^-$, and b) soluble Al. $^A$ = Surface water concentrations are from day 8 after inundation. Note: dissolved Al data from M2 is omitted due to experimental error.
Figure 4.13. Positive linear correlation between EC₄H and a) surface soil (0 - 2 cm) soluble Al and b) surface soil (0 - 2 cm) Cl⁻ concentrations. Individual *M. quinquenervia* and *C. dactylon* soil blocks are identified. Black squares are data derived from Johnston *et al.* (2003b).

Solid phase Fe (III) minerals commonly regulate Fe²⁺ activity in ASS (Satawathananont *et al.* 1991). Data in Figure 4.14 show that Fe²⁺ activities within the tub surface waters are mostly between the theoretical stability range identified for amorphous Fe(OH)₃ and goethite. Surface waters collected from the field (Table 4.2) and sulfuric horizon groundwater collected from the Shark Creek backswamp are also included in Fig. 4.14 and
lay within the same range. The theoretical stability range for schwertmannite lies between that of ferrihydrite and goethite (Bigham et al. 1996; Kawano and Tomita 2001), suggesting that this Fe(III) mineral may play an important role regulating Fe solubility in these soils.

**Figure 4.14.** Relationship between pE, Fe$^{2+}$ activities and pH for surface waters from the different tubs relative to the theoretical stability range for goethite and amorphous ferric hydroxide. Data shown for *M. quinquenervia* and *C. dactylon* are mean values. Field surface waters and sulfuric horizon groundwater from the Shark Creek backswamp are also presented. Stability constants derived from Satawathananont et al. (1991).

**4.4.4. Field surface waters**

While sample numbers were limited, the chemical composition of field surface waters from within the different vegetation zones show some similar trends to those observed in the tubs (Table 4.2). The *M. quinquenervia* samples had consistently lower pH and higher titratable acidity, dissolved Al and SO$_4^{2-}$ than samples from adjacent areas of open swamp
dominated by grass species. This is likely a reflection of the higher concentrations of acidic solutes generally present in the surface soils in the *M. quinquenervia* areas (Johnston *et al.* 2003b). However, while Eh was lower in the open swamp areas (data not shown) DO was higher. This may be a result of greater photosynthesis occurring in the open areas due to higher light conditions.

**Table 4.2. The chemical composition of field surface waters collected from areas of different vegetation types in the Shark Creek backswamp.**

Samples were collected on 19/03/2003, 7 days after rainfall caused inundation of the backswamp surface. Samples points are paired and were located 100 m either side of an encroached *M. quinquenervia* forest tree line. *Os* is open swamp dominated by *C. dactylon* and *P. distichum*. *Mq* is *M. quinquenervia* forest. All concentration units are in mmol L$^{-1}$ unless otherwise stated and the ratio is molar.

<table>
<thead>
<tr>
<th></th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>Os</em></td>
<td><em>Mq</em></td>
<td><em>Os</em></td>
</tr>
<tr>
<td>pH</td>
<td>4.54</td>
<td>4.12</td>
<td>4.15</td>
</tr>
<tr>
<td>EC (dS m$^{-1}$)</td>
<td>0.25</td>
<td>0.49</td>
<td>0.25</td>
</tr>
<tr>
<td>DO (µmol L$^{-1}$)</td>
<td>173</td>
<td>84</td>
<td>145</td>
</tr>
<tr>
<td>Titratable acidity H$^+$</td>
<td>0.20</td>
<td>0.38</td>
<td>0.23</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>0.011</td>
<td>0.052</td>
<td>0.023</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.36</td>
<td>0.82</td>
<td>0.50</td>
</tr>
<tr>
<td>Cl$^-$/SO$_4^{2-}$</td>
<td>3.71</td>
<td>3.39</td>
<td>2.71</td>
</tr>
</tbody>
</table>

**4.5. Discussion**

The physico-chemical characteristics and geochemistry of surface waters during the experiment was strongly influenced by both the biodegradability of the different vegetation
types and initial concentrations of soluble ions in surface soils.

Carbon is the main source of electron donors driving redox processes and therefore has a primary effect on the behaviour of redox sensitive species. The quantity and lability of organic carbon provides a fundamental constraint on the relative rates of Fe and SO$_4^{2-}$ reduction in sediments (Blodau and Peiffer 2003) and subsequent proton consuming processes (Ponnamperuma 1972). This is clearly evident in the contrasting surface water chemistry associated with the different vegetation types. The labile-carbon rich grass species surface waters had rapid O$_2$ consumption, a sustained lower redox status, higher pH, substantial Fe reduction and evidence of concurrent sulfate reduction in the form of sulfide formation and decreasing Cl$^-$:SO$_4^{2-}$ ratios. One mol of Fe$^{2+}_{(aq)}$ has potential to generate 2 mol of H$^+$ upon oxidation (Dent 1986). Therefore the high concentrations of Fe$^{2+}_{(aq)}$ observed in the grass species surface waters would, in a field situation, act as a highly mobile potential source of acidity, gradually released as surface waters become more oxidising.

The relative lack of labile carbon and abundance of decay resistant compounds in the M. quinquenervia litter limited the extent of Fe and SO$_4^{2-}$ reduction and associated proton consumption in surface waters and sediment. The initial release of Fe$^{2+}_{(aq)}$ into surface waters was attenuated by precipitation of Fe (III) mineral(s) triggered by a recovery in Eh and DO concentrations. Available data suggest some sulfide oxidation may have occurred in M. quinquenervia surface soils over the duration of this experiment instead of sulfide formation. The initial concentrations of redox-insensitive species (i.e. Cl$^-$ and Al) in surface soils appear to have a controlling influence on their resultant concentrations in surface water. Soluble Al in M. quinquenervia surface soil was the main contributor to the
higher titratable acidity of associated surface waters. Increases in surface soil soluble Al was one of the major effects of the *M. quinquenervia* encroachment that has occurred at the Shark Creek backswamp (Johnston et al. 2003b). This study confirms that these increases will likely contribute to enhanced acidification of surface waters following inundation. The higher acidity associated with Al$^{3+}$ species is also likely to have buffered any pH increases that might have otherwise occurred in surface soils due to any proton consuming reduction processes following the initial inundation. Given that soil pH values also exert a critical influence on redox pathways and resultant surface water chemistry in re-flooded soils containing sulfate (van Breemen 1975), the sustained low pH in *M. quinquenervia* surface soils was an important control on surface water chemistry.

The inhibition of sulfate reduction in *M. quinquenervia* soils is likely to be related to the limited nature of electron donors and higher redox potential plus the lower pH (Blodau and Peiffer 2003). Acidic conditions (pH <4), which prevailed in the *M. quinquenervia* soils, are known to thermodynamically favour Fe (III) reduction and inhibit sulfate reduction (Postma and Jakobsen 1996; Peine et al. 2000; Kusel et al. 2001). In addition, high amounts of amorphous Fe (III) oxides can inhibit sulfate reduction, allowing Fe (III) reducers able to outcompete sulfate reducing bacteria for organic substrates (Lovely and Phillips 1987; Achtenich et al. 1995; Thamdrup 2000). Fe (III) reducers also have a high degree of metabolic versatility and capable of using a wide range of organic substrates, including aromatic compounds (Thamdrup 2000). The contrasting soil Eh / pH signatures associated with the different vegetation types combined with their water chemistry data are suggestive of contrasting microbial ecology. Both Fe (III) and Al hydroxide have been reported as inhibiting litter decomposition due to either adsorption and/or toxicity effects (Miltner and Zech 1998). It is possible that the high concentrations of both Al and Fe
evident within the *M. quinquenervia* litter may have an inhibitory effect on decay rates, though this would require further study to ascertain. Several studies have also examined a possible inhibitory effect of essential oils from various *Melaleuca* spp. on litter decay rates (Boon and Johnstone 1997; Bailey *et al.* 2003).

An important consideration is how these results relate to conditions occurring in the field. Available data show some similarities between surface waters in the field and experimental data, including lower pH, higher titratable acidity, higher dissolved Al and lower Cl:\text{SO}_4^{2-}\text{-in surface waters derived from *M. quinquenervia* areas. However, the differences are not as pronounced as those observed in the laboratory experiments. This may be due to the open conditions in the field which allows mixing of waters between the vegetation zones. In the field there are also diurnal temperature fluctuations and potential for photosynthesis and release of O\textsubscript{2} into the water column, particularly in areas with partially submerged grass species. A further consideration is that the ionic strength of surface waters in the tubs are likely to represent a substantial exaggeration over actual field conditions. This is due to the contained nature of the experimental inundation. In a natural setting downward leaching of solutes would occur during initial rainfall, thus partly depleting surface soils of solutes. A further complication in the field environment is the potential for living wetland plants to exert species specific effects on rhizosphere biogeochemistry, thus affecting redox processes involving Fe and SO\textsubscript{4}^{2-} (Armstrong 1975; Chen and Barko 1988; Wright and Otte 1999).

This study has substantial implications for the quality of surface drainage waters associated with any projects which attempt to either restore, manage or modify ASS backswamp hydrology in such a way that causes subsequent changes to vegetation communities. This study also has implications for the interpretation of surface water quality draining from ASS
backswamps. For example, in a study of surface water quality after flooding, Johnston et al. (2003a) attributed the lower pH, higher titratable acidity and uniformly low Cl⁻:SO₄²⁻ ratios observed at the Shark Creek site (Maloneys) to an increasing influence of shallow groundwater from ASS. However, data from Johnston et al. (2003b) combined with results from this study, suggest that these observations may be equally explained simply by surface waters draining from the large areas of encroached *M. quinquenervia* forest located within the drains sub-catchment.

4.6. Conclusions

This study demonstrates that the biodegradability of surface vegetative carbon and the concentration of acidic solutes in surface soil can exert a controlling influence on the redox processes, the form of acidity and chemical characteristics of surface waters in ASS backswamps. Vegetation communities in Australia’s coastal floodplain ASS backswamps have undergone large changes following drainage. Given that some of these changes have demonstrably altered the lability of the vegetative carbon pool and the concentration of acidic solutes in surface soils, these findings suggest that surface drainage water quality is likely to have altered correspondingly. Future interpretations of the chemistry of surface waters in ASS backswamps should account for the effects of altered vegetation on redox and acidification processes occurring following inundation.

4.7. Acknowledgments

We thank the Shark Creek landholders for their assistance and cooperation. B. Makins contribution to many aspects of the field work is also gratefully acknowledged. This study was funded by Land and Water Australia, Acid Soil Action, Sugar Research and Development Cooperation, Acid Sulfate Soils Program and NSW Agriculture.
Chapter 5

The acid flux dynamics of two artificial drains in acid sulfate soil backswamps on the Clarence River floodplain, Australia

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Design: Johnston, Slavich

Collection of samples, laboratory analysis and interpretation of data

Collection of samples: Johnston, Hirst (60:40)

Laboratory analysis: NSW Agriculture Analytical Laboratory Wollongbar; Johnston, Hirst (titratable acidity / Fe\textsuperscript{2+}) (30:70)

Interpretation of data: Johnston, Slavich

Writing of publication

Original draft: Johnston

Proof reading and edits: Slavich, Johnston, several anonymous referees

Preparation of computer graphics: Johnston
5.1. Abstract

The export of acidity, iron, aluminium and sulfate to an estuary from two drains in acid sulfate soil backswamps was monitored over 18 months. The backswamps had similar geomorphology, stratigraphy and drainage density, and comparable soil and groundwater acidity. However, the flux rates, temporal dynamics and export pathways of acid and other sulfide oxidation products varied greatly and were controlled to first order by a) the saturated hydraulic conductivity \( K_{\text{sat}} \) of sulfuric horizons, and b) the tidally influenced groundwater gradients. The site with very high \( K_{\text{sat}} \) and large tidally influenced groundwater gradients had high acid flux rates \( (5300 \, \text{mol H}^+ . \text{ha}^{-1} . \text{year}^{-1}) \), chronic acid discharge, high drain water acid and metal concentrations and the primary flux pathway was direct groundwater seepage (interflow / bypass flow) to the drain. The site with lower \( K_{\text{sat}} \) and smaller groundwater gradients displayed low acid flux rates \( (50 \, \text{mol H}^+ . \text{ha}^{-1} . \text{year}^{-1}) \), infrequent, highly episodic discharge and the primary flux pathway was dilute surface run-off following dissolution of sulfide oxidation products accumulated on the soil surface. Importantly, the majority of acid export at both sites occurred while the backswamp groundwater level was within a very narrow elevation range.
5.2. Introduction

Holocene sulfidic sediments and acid sulfate soils (ASS) underlie large areas of coastal floodplain in eastern Australia (Naylor et al. 1995). Export of acidity from drained coastal floodplain ASS to estuaries is of major ecological concern (White et al. 1997). Identifying how sub-catchment hydrological and soil characteristics interact to affect the dynamics of acid export from drained ASS is critical for the development of effective management strategies.

The hydrology of many floodplains on the east coast of Australia has been highly modified by artificial drainage and flood mitigation works (White et al. 1997). This has reduced surface water retention times in ASS backswamps and altered the floodplain water balance (White et al. 1997). It has been demonstrated that floodplain drainage systems, particularly those in ASS backswamp landscapes, can export large amounts of acidity and other sulfide oxidation products to adjacent estuaries (Sammut et al. 1996; Wilson et al. 1999; Blunden and Indraratna 2000; Cook et al. 2000a; Johnston et al. 2003a). Many coastal floodplain ASS backswamps in New South Wales have elevations close to mean sea level and the sulfide layer is often near the ground surface (<1 m) with relatively thin fluvial capping (Walker 1972; Lin and Melville 1993). The sulfide layer is usually overlain by a pronounced sulfuric horizon and large reserves of actual acidity are often contained in the upper soil profile and shallow groundwater (Lin and Melville 1993; Sammut et al. 1996). In such landscapes even relatively shallow drains can intercept these acid soil horizons and receive groundwater that is highly acidic and rich in sulfate, iron and aluminium (Dent 1986). Exported acidity is principally in the form of ferrous iron and aluminium ions (Cook et al. 2000a). Floodplain drainage systems generally have one-way tidal floodgates near their confluence with the estuary which effectively allow drainage to mean low tide.
level and prevent tidal ingress.

Most of the high-priority ASS management areas identified by the NSW Government (Tulau 1999) are backswamps with shallow sulfidic horizons. These backswamps are major contributors of acidity and other sulfide oxidation products to coastal estuaries in eastern Australia. A clear understanding of their acid export dynamics is essential for the development of effective management strategies. Estimates of acid export from artificially drained coastal ASS backswamps in NSW, range from about 100 to 500 kg H$_2$SO$_4$.ha$^{-1}$ year$^{-1}$ (Sammut et al. 1996; Blunden et al. 1997; Wilson et al. 1999). These estimates were based on sub-catchment water balance models which require calculation over sufficiently long periods (~monthly) and consequently lack detailed temporal resolution. Studies with high resolution (hourly / daily) acid flux estimates based on direct flow measurements provide greater opportunity to identify key hydrological and soil factors governing acid export dynamics (Cook et al. 2000b) and are thus important to furthering our understanding of ASS backswamp hydrology.

This study has two aims: (1) to provide quantitative daily and hourly estimates of the flux of primary sulfide oxidation products (acidity, SO$_4^{2-}$, Fe, Al) from two drains in low elevation backswamps with shallow sulfides, and (2) compare the rates, pathways and temporal dynamics of this flux and explain observed differences by comparing site specific hydrological and soil characteristics.

5.3. Materials and methods

5.3.1. Study areas

The study areas, Blanches drain and Maloney’s drain, are located on the lower Clarence
River floodplain (29°30' S, 153°15' E) (Fig. 5.1). Both sites drain water from ASS backswamps to the estuary. The estuary is a mature barrier system (Roy 1984) with a floodplain area >2600 km$^2$ which is underlain by an estimated 530 km$^2$ of high risk acid sulfate soils (Tulau 1999). The backswamps are infilled Holocene estuarine embayments (Roy 1984; Lin and Melville 1993) with relatively flat topography and surface elevations mostly <0.2 m Australian Height Datum (AHD; 0 AHD ~mean sea level). Both backswamps are underlain by sulfidic sediment ~1 m from the ground surface (Lin and Melville 1993; Milford 1997).

**Figure 5.1.** Clarence River catchment (inset) and lower floodplain study site locations and associated ASS backswamps. ASS backswamp boundaries after Milford (1997).
Blanches drain is located on Everlasting Swamp (Fig. 5.2) and drains an ASS backswamp area of ~600 ha, plus a proportion of the substantial upland catchment. Maloneys drain is located in lower eastern Shark Creek (Fig. 5.2) and has a sub-catchment containing 208 ha of ASS backswamp and 300 ha of upland. Both drains have one way floodgates at their outlets. The main landuse at both backswamps is grazing, though there is some sugar cane on the natural levee at Maloneys.

Figure 5.2. Blanches and Maloneys study sites, showing the location of submersible data loggers / flow / drain water level monitoring stations (A - B), piezometers, drains, floodgates and ASS backswamp margin. ASS backswamp boundaries after Milford (1997).
The climate is sub-tropical and annual rainfall on the Clarence River floodplain ranges from 1100 to 1500 mm. Meteorological data was collected at both sites using automated weather stations. During the period of this study, August 2000 to December 2001, there were two major floods that caused inundation of both backswamps.

5.3.2. Drain water quality

Hourly measurements of dissolved oxygen, pH, electrical conductivity (EC) and temperature were made with Greenspan CS304 submersible data loggers (SDL). Two SDLs were installed in each drain, one near the floodgates and one near the backswamp margin (Fig. 5.2). The SDLs were cleaned, maintained and calibrated every 28 - 32 days. Spot measurements of in situ drain water dissolved oxygen, pH, EC, temperature and redox potential (ORP) were recorded at the time and location of sample collection using freshly calibrated portable field equipment (TPS 90FLMV). Redox potential was measured with a platinum tipped Ag/AgCl reference electrode and all ORP values are reported as recorded without correction. Comparison of spot measurements with logged SDL values at Maloney's and Blanches floodgates show the mean difference in pH was $\pm 1.2\%$ and $\pm 1.7\%$ of scale (0 - 14), respectively. For EC the mean difference was $\pm 0.4\%$ and $\pm 0.7\%$ of scale (0 - 60 dS m$^{-1}$) at the Maloney's and Blanches sites, respectively.

5.3.3. Water levels

Five piezometer wells were installed in the backswamps at each site perpendicular to the drain (Fig. 5.2). Each piezometer consisted of a 10 cm diameter hand augured hole about 1.4 m deep, with a 5.5 cm diameter slotted and screened PVC pipe inserted. This was backfilled with clean sand and auger cuttings in the screened zone and then with bentonite to the surface. Each well was surveyed to AHD and well distances from the drain are 2, 10,
63, 335, and 410 m at Malonesys and 2, 11, 65, 173, and 318 m at Blanches. Water levels in each piezometer were logged hourly using capacitance probes (Dataflow - model 392, accuracy ± 0.01 m). Drain water levels near the backswamp margin and immediately inside and outside the floodgates were also monitored hourly with capacitance probes. All capacitance probes were cleaned and calibrated every 2 - 3 months.

5.3.4. Sample collection, treatment and analysis

Drain water samples were collected at logging stations A and B (Fig. 5.2). Sampling intensities were flow dependant, ranging from daily during high flow / flux periods, to every ~4 - 10 days during periods of low to intermediate flow / flux and none during prolonged periods of no outflow. Sampling was timed to coincide with outflow periods where possible to avoid vertical stratification of the water column and ensure accurate representation of discharge water. Water samples were collected from 0 - 0.3 m below the surface at centre channel using a clean 10 L plastic bucket thoroughly pre-rinsed with the drain water to be collected. From this a minimum of two 250 mL sub-samples were taken in clean (acid rinsed, distilled water flushed) polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times. Visible air bubbles were excluded prior to sealing the cap and samples placed in cold storage (approx. 4°C). One 250 mL sub-sample was analysed for titratable acidity to pH 5.5 on same day as sample collection (APHA (1995), 2310B - including the peroxide oxidation step). One 250 mL sub-sample per sampling day was selected for further chemical analysis and frozen within 8 h of collection to minimise chemical / biochemical changes. Samples selected for chemical analysis were transported frozen, thawed at 4°C, sub-samples immediately extracted and analysed for Total Iron and Total Aluminium (ICPAES - USEPA 6010), Dissolved Iron and Dissolved Aluminium (0.45µm cellulose acetate filtration, ICPAES - USEPA 6010), Chloride (FIA -
5.3.5. Discharge estimates

Flow velocity in the drains was measured using a Doppler sensor (Starflow - 6526-51) with a velocity range of 0.021 to 4.5 m s\(^{-1}\). The Starflow unit also measured water level using a hydrostatic pressure sensor vented to the atmosphere and was located in the floodgate culvert. The Starflow unit was positioned at centre channel (centre of one cell at Blanches), at ~0.6 channel depth relative to culvert dimensions and surveyed to AHD. Checks undertaken using a calibrated current meter in the Doppler sensor field of view, under a range of flow conditions (>1 to ~0.1 m s\(^{-1}\)), yielded flow velocities within ±10% of the Doppler sensor. Daily drain discharge \((Q_d)\) was derived from the sum of the hourly discharge volumes \((Q_h)\) using Eq. (5.1),

\[
Q_h = (V_h \cdot A_h) \quad (5.1)
\]

where \(V_h\) is the mean hourly flow velocity and \(A_h\) is the mean hourly cross-sectional area of water in culvert.

5.3.6. Flux estimates

Total flux estimates of acidity, \(\text{SO}_4^{2-}\), Total Fe, Dissolved Fe, Total Al and Dissolved Al were made using two methods. The first was a daily estimate (Eq. 5.2) and the second an hourly estimate using logger values to infer ionic concentrations in drain water (Eq. 5.3),

\[
\Sigma F_d = \Sigma (Q_d \cdot C_d) \quad (5.2)
\]

\[
\Sigma F_h = \Sigma (Q_h \cdot C_h) \quad (5.3)
\]

where \(F_d\) is the daily flux estimate and \(Q_d\) is daily discharge volume and \(C_d\) is daily concentration of the relevant parameter. For sampling days \(C_d\) was the concentration of the
parameter measured in the drain water outflow sample from logging station A. For non-
sampling days, $C_d$ was estimated by linear interpolation between adjacent sampling day
concentrations. $F_h$ is the hourly flux estimate and $Q_h$ is hourly discharge volume. $C_h$ is the
hourly concentration of the relevant parameter in drain outflow water and was calculated by
regression analysis. This regression analysis was conducted between the concentration of the
relevant parameter in drain outflow water samples and SDL values (EC or pH) at the time of
sampling. Hourly flux estimates were made only during limited periods when regression
analysis yielded a high correlation ($r^2 >0.8$) between SDL values and outflow sample ionic
concentrations. Table 5.1 compares the variability between these two methods for the
Maloneys site and shows that hourly flux estimates were consistently higher than daily. This
difference can be explained by the rapid variations in drain water chemistry that can
accompany tidally modulated outflow periods (i.e. increasing acidity during the ebb tide
cycle) and more accurate integration of the area under the velocity and concentration curves
by the hourly method.

Table 5.1. Comparing variation between the methods used to calculate flux at Maloneys; ($F_d$)
daily interpolation and ($F_h$) hourly logger inferred.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation^A (%)</th>
<th>$r^2$^B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titratable acidity</td>
<td>15.5</td>
<td>0.95</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>4.0</td>
<td>0.90</td>
</tr>
<tr>
<td>Total Fe</td>
<td>7.6</td>
<td>0.85</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>14.4</td>
<td>0.83</td>
</tr>
<tr>
<td>Total Al</td>
<td>16.5</td>
<td>0.88</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>14.4</td>
<td>0.84</td>
</tr>
</tbody>
</table>

^A Variation calculated over a period when both methods were used, from
19/04/01 to 30/07/01, see Eq. (5.2) and (5.3).

^B Correlation coefficient of the equation used to infer $C_h$ from logger EC
values.
Total flux estimates are a combination of the two approaches, giving preference to the hourly method where available. They are expressed in relation to the area of ASS backswamp in the drainage sub-catchment of each study site. Flux estimates were made for 2001, except for a period of about 100 days at Blanches (June 2001 to September 2001), when logged data and spot sample titratable acidity show there was no acidity being exported and outflow volumes were low (~2.5% total discharge volume).

5.3.7. Soils

Soil profiles were hand augured (Blanches n = 10, Maloney’s n = 13) to a depth of ~160 cm and samples collected every 10 or 20 cm for analysis. Profiles were described in accordance with McDonald et al. 1990 and samples carefully handled to avoid oxidation of sulfidic materials. Soil ripeness was estimated using the hand squeezing method outlined by Dent (1986). Samples were oven-dried at 85°C within 48 h of collection and crushed to pass a 2 mm sieve then analysed for reduced inorganic sulfur species (S_{Cr} - Sullivan et al. 2000) and total actual acidity (TAA - Ahern et al. 1998; Lin et al. 2000). The pH and EC of a 1:5 water extract was determined for each sample (Rayment and Higginson 1992) and select samples analysed for soluble chloride and sulfate (APHA 4100).

5.3.8. Hydraulic conductivity

The saturated hydraulic conductivity (K_{sat}) of the backswamp sulfuric horizons was assessed using auger hole slug tests (Bouwer and Rice 1976; Bouwer 1989) and shallow pit bailing methods (Bouwer and Rice 1983; Boast and Langebartel 1984). Auger hole slug tests were conducted in 5.5 cm diameter, slotted PVC wells that were placed in freshly hand augured, close fitting boreholes. The slotting zone was positioned within the sulfuric horizon. Care was taken during sampling design to avoid underestimates of K_{sat} that can
result from low permeability well skins (Butler 1996). A rubber collar was placed on the outside of the PVC well immediately above the slotting zone to obtain a tight seal with the bore hole and prevent downward water flow along the well sides. The slug was withdrawn by rapid hand pumping and the water level recovery rate recorded at two second intervals using a freshly calibrated 1.0 m capacitance probe (Dataflow 392). Slug test wells were randomly located in the vicinity of the piezometer transects and at least 3 replicate tests conducted in each well. $K_{sat}$ was calculated using the method of Bouwer (1989).

Shallow rectangular pits (up to 0.5 m deep and 0.5 m$^2$) were excavated in each backswamp adjacent to slug test boreholes. Pit dimensions and the equilibrium water level before bailing were recorded. The water was bailed rapidly using a 10 L bucket to remove ~50 - 90% of the total water in the pit. Water level recovery was measured every 5 seconds on a ruler with 1 mm graduations. Two tests were conducted in each pit. $K_{sat}$ was calculated according to the methods of Bouwer and Rice (1983), and Boast and Langebartel (1984), which use slightly different shape factors depending on pit geometry.

Well and pit infilling at Maloney's was dominated by rapid flow through large, mainly cylindrical, macropores. Further pits (<1 m deep) were excavated at Maloney's to specifically investigate the characteristics of the macropore system. Several large pores (>20 mm diameter) had short, tight fitting plastic tubes inserted, enabling measurement of pore water outflow rates in response to an effluent gradient that was induced by bailing water from the pit. Pore water samples were collected and analysed.
5.4. Results and discussion

5.4.1. Site characteristics

The backswamp acid sulfate soils at both sites are Sulfuric / Sulfidic Oxyaquic Hydrosols (Australian Soil Classification, Isbell 1996) (Hydraquentic Sulfaquepts - Soil Taxonomy, Soil Survey Staff 1998) with high organic matter content in the top ~20 - 30 cm. Beneath the organic rich surface layer is a sulfuric horizon with iron (III) mineral and jarosite mottles extending to a depth of ~60 - 100 cm. Immediately below this is reduced sulfidic material. Soil texture at both sites was predominantly silty clay to clay with fine sand inclusions occasionally evident. Important characteristics for the study site backswamps are listed in Table 5.2. The drainage density, depth to the sulfide layer and the reduced inorganic sulfur content of the sulfide layer are similar at both sites. There is also considerable actual acidity stored in the soil and groundwater at both sites due to oxidation of underlying sulfidic material (Table 5.2).

Table 5.2. Comparing key characteristics of the study site backswamps.

Numbers in brackets are standard errors.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Blanches</th>
<th>Maloneyys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean soil profile actual acidity(^A) (kmol H(^+) ha(^-1))</td>
<td>675 [87]</td>
<td>2047 [109]</td>
</tr>
<tr>
<td>Mean depth to sulfide layer(^B) (m)</td>
<td>0.88 [0.06]</td>
<td>0.99 [0.03]</td>
</tr>
<tr>
<td>Mean S(_{\text{Ct}}) content of sulfide layer(^C) (%)</td>
<td>1.92 [0.09]</td>
<td>2.06 [0.05]</td>
</tr>
<tr>
<td>Backswamp surface elevation (m AHD)</td>
<td>~0.1 to 0.12</td>
<td>~0 to 0.22</td>
</tr>
<tr>
<td>Drainage density (m ha(^-1))</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>Area of shallow sulfides in sub-catchment(^D) (ha)</td>
<td>600</td>
<td>208</td>
</tr>
</tbody>
</table>

\(^A\) Whole profile depth integrated means based on total actual acidity (Ahern et al. 1998; Lin et al. 2000).

\(^B\) From ground surface.

\(^C\) Upper 0.4 m of sulfide layer.

\(^D\) After Milford (1997).
However, Maloney's has a broader sulfuric horizon with higher total actual acidity concentrations, resulting in a mean soil profile acidity around three times greater than Blanches (Table 5.2). Sulfuric horizon soils at Maloney's were generally riper, had greater development of structure and displayed more abundant and prominent Fe (III) mineral / jarosite mottling than those at Blanches. Backswamp surface elevations were also slightly lower at Blanches (Table 5.2). While there are many similarities between the sites, there is a large difference in the hydraulic conductivity of the sulfuric horizons.

5.4.2. Hydraulic conductivity

There was a large difference in the $K_{\text{sat}}$ of the sulfuric horizons, with Maloney's about 10 to 14 times higher than Blanches, depending on the method used (Table 5.3). The values reported for Maloney's (~120 m day$^{-1}$ for slug tests and ~180 m day$^{-1}$ for pit bailing, Table 5.3) are substantially higher than some reported previously for drained ASS backswamps on Australia’s east coast (0.4 m day$^{-1}$, Cook and Rassam 2002; 0.74 m day$^{-1}$, White et al. 1993; <4.0 m day$^{-1}$, Blunden and Indraratna 2000).

Table 5.3. Saturated hydraulic conductivity (m/day) of the sulfuric horizons at Blanches and Maloney’s.

Measured in the sulfuric horizons (upper ~0.9 m) of the backswamp soil profile. s.d. is standard deviation.

<table>
<thead>
<tr>
<th>Site</th>
<th>Auger hole slug test $^A$</th>
<th>Shallow pit bailing $^B$</th>
<th>Shallow pit bailing $^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{\text{sat}}$</td>
<td>n</td>
<td>s.d.</td>
</tr>
<tr>
<td>Blanches</td>
<td>8.7</td>
<td>13</td>
<td>7.6</td>
</tr>
<tr>
<td>Maloney's</td>
<td>125</td>
<td>10</td>
<td>43</td>
</tr>
</tbody>
</table>


$^B$ Bouwer and Rice 1983.

$^C$ Boast and Langebartel 1984.
The spatial heterogeneity of $K_{sat}$ in shallow coastal aquifers can mean realistic field scale estimates based on small scale methods (such as augerhole slug tests) can be subject to significant errors (Millham and Howes 1995). This is particularly true if flow into an auger hole is dominated by macropores whose size and spatial variability are high relative to the size of the hole. For this reason, tests which average aquifer response over larger areas (i.e. pit bailing) are more likely to be representative of actual field $K_{sat}$ values.

The very high $K_{sat}$ at Malonesys is attributed to the presence of a dense, well developed macropore network. The $K_{sat}$ of sulfuric horizons in ASS backswamps is known to be highly variable and is strongly influenced by soil structure and the existence of macropores (Bouma et al. 1993). Extremely high sulfuric horizon permeability associated with extensive soil macropores was reported by Hamming and van den Eelaart (1993) from an ASS backswamp site in Indonesia. Other coastal ASS backswamp sites in Australia have recently been found to have very high sulfuric horizon $K_{sat}$ (>100 m day$^{-1}$) related to macropores (Johnston et al. 2003c). At Malonesys, iron coated tubular macropores larger than 20 mm in diameter were observed during pit excavations and profile descriptions. These tubular macropores may be relic root channels from previous vegetation communities present during sequential accretion of the backswamp sediments. Blunden and Indraratna (2000) recorded macropores in an Australian ASS backswamp and found the orientation was mainly vertical and thus the effect upon hydraulic conductivity was mainly in the vertical plane. The sulfuric horizon macropore network at Malonesys displays evidence of high connectivity in both the vertical and the horizontal planes (see below). This is likely due to a combination of high macropore density with varying orientations in the sulfuric horizon and, importantly, the existence of planar fissures associated with structural ripening of soil.
Large (~20 mm) pores, with both vertical and horizontal orientations, were measured discharging groundwater at ~0.03 L s\(^{-1}\) under approximately 0.1 m head pressure. The discharge rates of individual pores were maintained even after yielding many tens of litres of water during continuous pit bailing experiments. Such behaviour clearly demonstrates a high degree of pore connectivity. The geometry, volume, pore size distribution and connectivity of macropores can profoundly affect groundwater movement rates (Bevan and Germann 1982; Bouma 1991), solute flux pathways in near surface soils (Harvey and Nuttle 1995; Minh et al. 2002) and the responsiveness of unconfined aquifers to adjacent tidal forcing (Hughes et al. 1998). The existence of this macropore network and the very high \(K_{sat}\) of the sulfuric horizons at Maloneys greatly favours the lateral movement of shallow groundwater solutes to the drainage system via interflow and bypass flow.

5.4.3. Tidal influence on drain water levels and groundwater gradients

Water levels in the drains adjacent to the backswamps at both sites are influenced by tides and the magnitude of the influence is much greater at Maloneys. Drain water levels adjacent to Blanches ASS backswamp were relatively high and stable with small tidally influenced variations (Fig. 5.3a). The low variability adjacent to the backswamp at Blanches is mainly due to amplitude attenuation because of the greater distance from the estuary (>2 km). In contrast, there was a high degree of tidally influenced variation in drain water levels adjacent Maloneys backswamp, which is <0.3 km from the estuary (Fig. 5.3a). Maloneys and Blanches tidally influenced drain water level variations shown in Fig. 5.3a are significantly different at \(P > 0.001\).

This difference in tidal influence upon drain water levels adjacent to the backswamp is important because it affects the magnitude of the effluent groundwater gradients that can
Figure 5.3. Comparing a) tidally influenced daily drain water level variations adjacent each backswamp and b) mean and maximum daily groundwater gradients at Blanches and Maloney's drains. Both data sets are based on a period when the backswamp water level was below the ground surface (~0.12 m AHD Blanches; ~0.2 m AHD Maloney's) and above mean minimum low water (~0.2 m AHD). For a) drain water levels were measured at monitoring station B (see Fig. 5.2). For b) gradients were calculated by subtracting drain water levels at monitoring station B from piezometer well no. 1 (2 m from drain at both sites).
develop during the ebb tide phase (Fig. 5.3b). This data shows that effluent groundwater gradients in the backswamp ASS occur with greater frequency and have a higher maximum magnitude at Maloneys than at Blanches. This is likely to favour groundwater seepage into the drain at Maloneys. The difference between Maloneys and Blanches mean and maximum groundwater gradients as shown in Fig. 5.3b are significant at $P > 0.001$.

5.4.4. Flux rates

The first five months of the study (August 2000 to January 2001) were dry with minimal rainfall, low groundwater levels (below local low tide minima) and there was and no acid outflow from either study site. Flux was estimated to be zero for this period. In early February 2001 there was a large flood followed by prolonged discharge of water from both drainage systems. Total flux estimates of acidity and other sulfide oxidation products for 2001 are presented in Table 5.4. This data shows there was a large difference in the flux of acidity, with the export rate over 100 times higher at Maloneys drain than Blanches.

**Table 5.4. Total flux estimates of acidity and other sulfide oxidation products for Blanches and Maloneys drains during 2001.**

<table>
<thead>
<tr>
<th>Flux</th>
<th>Blanches</th>
<th>Maloneys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity $^A$</td>
<td>54</td>
<td>5250</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>700</td>
<td>1392</td>
</tr>
<tr>
<td>Total Fe</td>
<td>84</td>
<td>184</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td>Total Al</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>2</td>
<td>11</td>
</tr>
</tbody>
</table>

$^A$ Acidity expressed in mol H$^+$.ha$^{-1}$.year$^{-1}$, based on the area of ASS backswamp in each drainage sub-catchment (Table 5.2).
The rate at Maloney's is equivalent to 250 kg $\text{H}_2\text{SO}_4$ ha$^{-1}$ year$^{-1}$ which is comparable to estimates derived by other researchers (Sammut et al. 1996; Wilson et al. 1999) and represents approximately 0.3% of the storage actual soil acidity at this site. However, annual acid flux rates are likely to display a high degree of interannual variability, depending upon seasonal influences. Maloney's also had higher flux rates for other sulfide oxidation products by varying degrees (2 - 5x).

5.4.5. Flux pathways, temporal dynamics and drain water chemistry

In a relatively flat backswamp there are two main hydrological pathways via which acidic solutes and other sulfide oxidation products are transported from acidified soil and groundwater into adjacent drainage systems. The first pathway is surface run-off. This requires an accumulation of acidic solutes in surface soils and adequate rainfall to cause surface runoff (saturated overland flow / Hortonian flow). This may occur when upward flux from the capillary fringe and evapo-concentration of acidic solutes on exposed soil surfaces is followed by enough rainfall to cause dissolution and surface run-off to the drain. The extent of surficial solute accumulation is controlled primarily by the water table depth (Tuong 1993), groundwater chemistry (Walker 1972), soil micro-porosity (Harvey and Nuttle 1995) evapo-transpiration rates and cumulative evapo-transpiration (Minh et al. 1998). Solute accumulation without adequate rainfall to cause profile saturation and surface run-off may lead to downward leaching and redistribution in the profile. The second pathway is groundwater seepage, which includes interflow / bypass flow directly into the drain (Bouma 1991; Tobias et al. 2001; Minh et al. 2002). In accordance with Darcy's law, the rate of groundwater seepage per unit area of drain bank is controlled mainly by the hydraulic properties of soil and driving gradients (Boulding 1995). These two pathways (surface vs groundwater) are fundamentally different and the prevalence of...
one over another is likely to have a significant effect on acid export dynamics (Cook et al. 2000b).

Export of acidity at Blanches was highly infrequent (one event only) and of short duration with a relatively low magnitude (Fig. 5.4). This event occurred after rainfall brought the water table to the surface following a dry period favouring surficial solute accumulation. Evapo-transpiration was in excess of rainfall by 469 mm during the 14 weeks prior to the event.

**Figure 5.4.** Backswamp drain water and groundwater levels and daily acidity flux estimates during 2001 for a) Blanches and b) Maloney’s drain in relation to c) rainfall.

Drain water acidity and metal contents were relatively low during this event (Table 5.5) with very small changes in pH following sample peroxide oxidation (Table 5.6) suggesting most acidic metal cations were already in an oxidised form. There was also a significant
departure from groundwater ionic ratios (Table 5.7). While some groundwater seepage certainly occurred at this site, these data suggest dilute surface run-off was the main pathway via which acidity was transported to the drain.

Export of acidity at Blanches took place while the water level in the backswamp was within a very narrow elevation range (Fig. 5.5). A similar feature is evident at Maloney’s (Fig. 5.5). This water level elevation range is approximately defined by backswamp topography (upper levels of backswamp surface ±0.05 to 0.1 m), and tidal minima experienced in the drain adjacent to the ASS backswamp, and is referred to hereafter as the ‘acid export window’.

**Table 5.5. Comparing the chemical composition (µmol L⁻¹) of drainage outflow water at Blanches and Maloney’s during 2001.**

Data presented are flow weighted means derived from flux estimates. Peak concentrations are shown in parenthesis and are derived from actual samples.

<table>
<thead>
<tr>
<th></th>
<th>Blanches acid event A</th>
<th>Blanches post-flood B</th>
<th>Maloney’s C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titratable acidity</td>
<td>200 (430)</td>
<td>0</td>
<td>2110 (5190)</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>5420 (6560)</td>
<td>298 (570)</td>
<td>4090 (8000)</td>
</tr>
<tr>
<td>Total Fe</td>
<td>5 (11)</td>
<td>76 (460)</td>
<td>530 (1830)</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>5 (9)</td>
<td>14 (140)</td>
<td>510 (1630)</td>
</tr>
<tr>
<td>Total Al</td>
<td>35 (60)</td>
<td>8 (50)</td>
<td>220 (560)</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>34 (70)</td>
<td>4 (40)</td>
<td>190 (560)</td>
</tr>
</tbody>
</table>

A A single event between 23 November and 15 December 2001 (Fig. 5.4).
B Calculated after two major flood events when the backswamp water level was above the ground surface and discharge was dominated by surface runoff. Period of calculation accounts for 91% of Blanches drain total discharge volume for 2001.
C Calculated during periods when the backswamp water level was in the acid export window (Fig. 5.5).
Figure 5.5. Cumulative flux estimates of acidity, $\text{SO}_4^{2-}$, total Fe, dissolved Fe and dissolved Al for a) Blanches and b) Maloney’s drainage systems during 2001 in relation to mean daily backswamp water level. (See Results and discussion for an explanation of the acid export window). MLW is ~mean minimum tidally influenced low water level in drain (monitoring station B).
The existence of an acid export window can be logically inferred with reference to the main acid export pathways. Neglecting groundwater displacement via upper catchment inflow or sub-aquifer recharge (Tobias et al. 2001; Schultz and Ruppel 2002), groundwater seepage to the drains in a topographically flat ASS backswamp is likely to be highest during periods when the surface water has largely gone, through preferential drainage, and groundwater levels are above local tidally influenced minima. Surface run-off borne acidity is also likely to be most significant when the groundwater is near the surface and the soil profile saturated. Given that surface elevations of the study site backswamps are only about 0.3 - 0.4 m above local tidal minima (~-0.2 m AHD), this suggests that acid export is likely to be concentrated within a relatively narrow water level elevation range. The existence of a narrow elevation range in which acid export is concentrated is in general agreement with the findings on the Tweed River which demonstrated the importance of the antecedent water table position in determining the magnitude of acid export in a given rainfall event (Wilson et al. 1999). As the lower boundary of the acid export window is defined by local tidal minima, any changes which decrease the local tidal minima (i.e. drain vegetation cleaning or estuarine dredging / entrance modifications) may enhance acid flux by increasing the effective range over which groundwater seepage may occur.

In contrast to acidity, most export of SO$_4^{2-}$, Fe and Al at Blanches occurred during high volume dilute flows dominated by anaerobic surface water with near neutral pH in the weeks immediately following flooding (Table 5.5, Table 5.6 and Fig. 5.5). Mobilisation of Fe in the post flood period at Blanches was associated with microbially catalysed reductive dissolution of poorly crystalline Fe (III) oxides in surface sediments coupled with anaerobic metabolism of backswamp organic matter (Johnston et al. 2003a).
Table 5.6. Comparing physico-chemical characteristics of drainage outflow water at Blanches and Maloney's during 2001.

All values are means based on spot measurements. Numbers in brackets are standard errors.

Periods of measurement correspond to those outlined in Table 5.5.

<table>
<thead>
<tr>
<th></th>
<th>Blanches acid event</th>
<th>Blanches post flood</th>
<th>Maloney's</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (f)</td>
<td>4.11 [0.21]</td>
<td>6.26 [0.14]</td>
<td>3.46 [0.05]</td>
</tr>
<tr>
<td>pH (f) - pH (ox)</td>
<td>0.02</td>
<td>0.14</td>
<td>0.30</td>
</tr>
</tbody>
</table>

\( \Delta \) pH (f) is *in situ* field measurement and pH (ox) is after sub-sample peroxide oxidation step [APHA 2310B (1995)].

Table 5.7. Change in drain water ionic ratios relative to groundwater during acid export events.

\( D_R \) is the mean drain water ratio and \( G_R \) is the mean groundwater ratio. Acid export events correspond to the periods outlined in Table 5.5. All ratios based on molar concentrations derived from actual samples.

<table>
<thead>
<tr>
<th>Ratio shift</th>
<th>Blanches ( (D_R/G_R) )</th>
<th>Maloney's ( (D_R/G_R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}^-:\text{SO}_4^{2-} )</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>( \text{Cl}^-:\text{Fe} )</td>
<td>52.5</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{Cl}^-:\text{Al} )</td>
<td>15.2</td>
<td>2.8</td>
</tr>
<tr>
<td>( \text{Cl}^-:\text{H}^+ )</td>
<td>6.8</td>
<td>2.3</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-}:\text{H}^+ )</td>
<td>3.5</td>
<td>1.3</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-}:\text{Fe} )</td>
<td>29.0</td>
<td>1.1</td>
</tr>
<tr>
<td>( \text{Fe}:\text{Al} )</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>( \text{H}^+:\text{Al} )</td>
<td>1.4</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Acid export at Maloney's was far more frequent with discharge episodes lasting up to several months at a time and peak acid export rates exceeding 25000 mol H\(^+\) day\(^{-1}\) (Fig. 5.4). The majority of the flux of acidity, dissolved Fe and dissolved Al occurred after surface waters had largely drained away and the backswamp water level was within the acid export window (Fig. 5.5). The large increase in acid flux around mid April is due to sharply increasing drain water concentrations of acidity, SO\(_4^{2-}\), Fe and Al, which occurred once the surface water had largely left the site (Fig. 5.4). The majority of the acid flux (~80%) was exported by a relatively small proportion of the total volume of outflow water (13%). This is in agreement with the findings of Cook et al. 2000b, who found that while direct groundwater seepage from ASS comprised a small proportion of the water balance, it made a significant contribution to acid flux due to the high concentrations of acidity and acidic metal cations. Drain water acidity and dissolved metal contents were relatively high during the acid export window period (Table 5.5). There were significant decreases in drain water pH following peroxydite oxidation (Table 5.6) most likely due to oxidation of reduced acidic metal species such as Fe\(^{2+}\) (van Breemen 1993). Ionic ratios in drainage outflow water in the acid export window were similar to groundwater ratios (Table 5.7). Combined, these data clearly demonstrate the main pathway for acid and sulfide oxidation products at Maloney's was groundwater seepage.

5.4.6. Hourly acid flux, tidal modulation and local hydrology

Hourly estimates of acid flux allow closer examination of the interrelationships between site hydrology, topography and local tidal dynamics. During Blanches acid export event, groundwater levels rose to the surface in response to rainfall early on 25 November (Fig. 5.6). Backswamp groundwater gradients were effluent for several days following, but outflow volumes and acid flux remained low. More rainfall on 27 November led to surface
overtopping and run-off and was accompanied by a rapid rise in drain water levels near the backswamp. Acid flux increased after this point, further suggesting that surface run-off was the dominant acid export pathway. Acid flux displayed strong tidal modulation with peak outflows of ~750 mol H⁺ h⁻¹.

The hourly flux of acidity at Maloneys over 10 days in early June 2001 is shown in Fig. 5.7. Surface water was largely absent from the backswamp during this time and acidity was entering the drain mainly via interflow and bypass flow. The export of acidity is highly

Figure 5.6. Hourly acidity flux estimates at Blanches drain during the sole acid export event in relation to estuary, drain and groundwater levels and rainfall.
variable over short time scales with peak discharges in excess of 4500 mol H⁺ h⁻¹. Local tidal dynamics at the point of discharge strongly modulates acid flux by a) regulating the outflow volume of acid water already stored in the drain, and by b) increasing the magnitude of effluent groundwater gradients. Conversely, moderate low tides, such as on 31 May, reduce discharge, stabilise drain water levels and limit the magnitude of the effluent gradient developing during the ebb tide phase.

**Figure 5.7.** Hourly acidity flux estimates at Maloney's drain in relation to estuary, drain and groundwater levels and rainfall. Note the strong tidal modulation of flux, large in-drain tidal amplitude and development of effluent groundwater gradients during the ebb tide phase.
A high correlation was observed between groundwater gradients and acid export rates at Malonesys while the groundwater was in the acid export window (Fig. 5.8). Acid export can be expected to occur at this site whenever the backswamp water level is within the acid export window and effluent groundwater gradients exist. This contrasts with a lack of correlation between gradients and acid export at Blanches (Fig. 5.8). The lower elevation of the backswamp surface at Blanches effectively reduces both the potential magnitude of effluent groundwater gradients and the range of the acid export window. Excluding groundwater displacement, if the backswamp surface elevation was lower than local tidal minima then acid flux via groundwater seepage would be very small due to a lack of driving gradients.

Figure 5.8. Relationship between daily acid flux and maximum daily groundwater gradients at Blanches and Malonesys. Blanches is based on the sole acid export event, between 23 November and 15 December 2001 (Fig. 5.4). Malonesys is based on a period between 26 April and 8 August 2001.
Figure 5.9 provides a schematic representation of acid flux dynamics in high $K_{\text{sat}}$ / high gradient and low $K_{\text{sat}}$ / low gradient ASS backswamps with respect to lithofacies and groundwater losses by evapotranspiration and groundwater seepage.

**Figure 5.9.** Schematic representation of acid flux dynamics in a) high $K_{\text{sat}}$ / high gradient, and b) low $K_{\text{sat}}$ / low gradient ASS backswamps, with respect to lithofacies and groundwater losses by evapotranspiration and groundwater outflow.
5.4.7. Acid flux comparison

The large difference in annual acid flux between the two sites can be attributed mainly to the difference in saturated hydraulic conductivity of the sulfuric horizons and differing local groundwater gradient dynamics. Other influencing factors include the higher levels of soil acidity at Maloney's, which is likely to have enhanced flux loads, even though overall mean concentrations of Fe and Al in shallow groundwater were similar at both sites (Johnston et al. 2003a).

Groundwater seepage was clearly a dominant acid flux pathway at the Maloney’s site. While surface runoff appears to be the dominant acid flux pathway at Blanches, some groundwater seepage is certain to occur, particularly over longer time periods. Darcy’s law provides the basis for a simple means to compare and rank the relative importance of the various factors affecting longer-term acid export via groundwater seepage at each site. Over a sufficiently long time period acid export via groundwater seepage ($A_{gw}$) can be represented by Eq. (5.4),

$$A_{gw} = C_{gw} \cdot K_{sat} \cdot H_e \cdot t_d \cdot A_s$$

(5.4)

where $C_{gw}$ is the sulfuric horizon mean groundwater acidity concentration (mol H$^+$ m$^{-1}$), $K_{sat}$ is the saturated hydraulic conductivity of the sulfuric horizon (m day$^{-1}$), $H_e$ is the mean effluent groundwater gradient towards the drain (m m$^{-1}$), $t_d$ is the duration (days) that the mean daily groundwater gradient was effluent, and $A_s$ is the area of the drain walls subject to groundwater seepage. Data from Table 5.3 and Fig. 5.3b were used to estimate $K_{sat}$, $H_e$ and $t_d$. Data from Johnston et al. (2003a) were used to estimate $C_{gw}$ and $A_s$ was based on the length of drain in each ASS backswamp. The parameter ratios between Maloney's:Blanches for $C_{gw}$, $K_{sat}$, $H_e$, $t_d$ and $A_s$ were 1.4, 10.2-14.4 (depending on the method used), 1, 4.1 and 0.4 respectively. This analysis suggests that soil hydraulic
conductivity is the dominant factor causing different acid export rates via groundwater seepage at the two sites. The effects of hydraulic conductivity become amplified in Eq. (5.4) as they are multiplied by differences in effluent gradient dynamics and groundwater acidity concentrations.

5.4.7. Groundwater responsiveness to drain water levels

The high \( K_{sat} \) and macropore connectivity in the sulfuric horizons at Maloney's results in the shallow groundwater being highly responsive to drain water levels. Water tables were generally quite flat across wells 1 to 5. During floodgate opening experiments the groundwater showed rapid responses to tidal increases in drain water levels in excess of 300 m from the drain, without overtopping of the ground surface occurring (Fig. 5.10).

![Figure 5.10](image)

Figure 5.10. Tidal forcing during a floodgate opening event at Maloney's caused rapid aquifer response over large distances from the drain due to high sulfuric horizon \( K_{sat} \).
Rapid changes in sulfuric horizon groundwater chemistry were also observed >10 m from the drain during the floodgate opening experiment shown in Fig. 5.10 (Johnston et al. 2002a). This is in contrast to other studies in ASS (White et al. 1997; Wilson et al. 1999) which suggest that drains have limited influence on water tables throughout adjacent fields, particularly during dry periods. The responsiveness of the aquifer at Maloney's to tidal forcing clearly demonstrates that in soils with these hydraulic properties the influence of drain water levels on the shallow groundwater table over significant distances (via hydraulic forcing and recharge) cannot be disregarded.

In contrast, the shallow groundwater adjacent to the drain at Blanches was relatively unresponsive to tidal forcing during floodgate opening experiments (Fig. 5.11).

**Figure 5.11.** The lower sulfuric horizon K$_{sat}$ at Blanches limits aquifer response to tidal forcing. Substantial increases in the height of the shallow groundwater in the piezometer wells occurred only after overtopping of the ground surface took place, causing infiltration down the profile.
Substantial increases in the height of the shallow groundwater in the piezometer wells occurred only after overtopping of the ground surface took place (Fig. 5.11). While this is most likely to be related to the lower $K_{\text{sat}}$ of the sulfuric horizon soils, it also points to the possible existence of a semi-confining layer near the drain bank face. This behaviour further suggests that seepage of acid groundwater to the drain at Blanches is likely to be highly attenuated relative to Maloneys.

5.5. Conclusions

The large difference in acid flux dynamics between the two sites is mainly related to (a) the hydraulic conductivity and physical properties of the sulfuric horizons, and (b) local groundwater gradient dynamics. These differences profoundly affected acid export pathways, flux rates and drain water chemistry. Local groundwater gradients in ASS backswamps can be strongly affected by tidally influenced water level variations in adjacent drains and ground surface elevations. This study emphasises the high degree of heterogeneity in sulfuric horizon hydraulic conductivity in drained coastal ASS backswamps in eastern Australia. It also highlights the importance of understanding site specific soil and hydrological factors when interpreting, predicting or managing acid export. Assumptions about acid flux dynamics and shallow aquifer responses based on one site are not necessarily transferable to other sites except in the context of a clear understanding of the governing hydrological factors. Among these governing factors sulfuric horizon $K_{\text{sat}}$ and local groundwater gradients are paramount.
5.6. Acknowledgments

We thank the Blanches and Maloney landowners for their assistance and cooperation. We thank several anonymous referees for their helpful suggestions with the manuscript. We also thank Clarence River County Council and the Department of Infrastructure, Planning and Natural Resources for assistance and access to data. This study was funded by Land and Water Australia, Acid Soil Action, Sugar Research and Development Cooperation, Acid Sulfate Soils Program and NSW Agriculture.
Chapter 6

The effects of a weir on reducing acid flux from a drained coastal acid sulfate soil backswamp

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Writing of publication

Original draft: Johnston
Proof reading and edits: Slavich, Johnston, several anonymous referees
Preparation of computer graphics: Johnston
6.1. Abstract

A trial was conducted to examine the effects of retaining drain water with a weir on reducing acid flux from a drained coastal acid sulfate soil backswamp. Prior to weir construction, groundwater seepage to the ditch drain was the main hydrological pathway for acid flux. High hydraulic conductivity (>120 m day\(^{-1}\)) in the sulfuric horizons due to extensive macropores, combined with tidal modulation of drain water levels encouraged rapid seepage of acid groundwater. Most seepage occurred while the backswamp groundwater table was in a narrow elevation range, referred to as an ‘acid export window’. The acidity of drainage water was highly sensitive to the hydraulic gradient between the groundwater table and the adjacent drain water level. Acid flux rates from groundwater seepage were strongly positively correlated to effluent groundwater hydraulic gradients. The constructed weir was designed to reduce the magnitude of effluent groundwater gradients and retain shallow groundwater by maintaining high and stable drain water levels. This reduced groundwater seepage to the drain and increased the proportion of shallow groundwater lost from the system via evapotranspiration.

The weir affected 60% of drainage network and observed and modelled data suggest acid flux from groundwater seepage was reduced by about 65 - 70%. Effluent groundwater gradients behind the weir were reduced by about 80%. The main effect of the weir was to reduce discharge volumes, although reductions in H\(^+\) and acidic metal cation concentrations were also observed. This study demonstrates that a weir can be an effective means of reducing acid flux in coastal acid sulfate soils where main hydrological pathway of acid export is groundwater seepage. However, this strategy may not prevent continued sulfide oxidation. Reduced acid export, but continued acid generation, combined with enhanced evaporative flux has the potential over the longer term to increase the net accumulation of acidic products in the backswamp soil and groundwater. Further monitoring is required to assess this possibility.
6.2. Introduction

Acid sulfate soils (ASS) underlie large areas of the coastal floodplains of eastern Australia (White et al. 1997). Acidity is derived from the oxidation of Holocene sulfidic sediments and can be particularly severe in backswamps with shallow sulfidic horizons (Dent 1986). ASS backswamps typically have high concentrations of acidity, sulfate, iron and aluminium in soil and shallow groundwater (Walker 1972). Thousands of hectares of ASS backswamps on Australia’s eastern coastal floodplains have been artificially drained for Agriculture (Tulau 1999). Artificial drainage systems export large quantities of acidity, Fe and Al from these environments into adjacent estuaries, with reported rates equivalent to 100 to 500 kg H$_2$SO$_4$.ha$^{-1}$ yr$^{-1}$ (Sammut et al. 1996; Blunden et al. 1997; Wilson et al. 1999; Johnston et al. 2004). Drainage from ASS backswamps can cause extensive acidification and deoxygenation of estuarine waters (Sammut et al. 1996; Johnston et al. 2003a) resulting in severe negative impacts upon estuarine biota and fisheries resources (Callinan et al. 1993; Sammut et al. 1993; Macbeth et al. 2002).

Reducing acid export from floodplain drains requires an understanding of the primary hydrological pathways via which acidity enters drainage systems and local groundwater hydrology. The pathways of acid flux can be broadly characterised as either a) surface runoff or b) groundwater seepage, which includes both bypass flow and interflow (Bouma 1991; Minh et al. 2002). The two main climatic drivers of the floodplain water balance which govern acid export are rainfall (P) and evapotranspiration (ET) (White et al. 1997). Floodplain water tables fluctuate seasonally and the annual ratio P:ET varies widely with cyclic El Nino Southern Oscillation fluctuations. The saturated hydraulic conductivity ($K_{sat}$) of sulfuric horizons is a critical factor governing groundwater behaviour in ASS backswamps (Bouma et al. 1993). It has a controlling influence upon lateral movement of
both acidic and non-acidic solutes, plus the behaviour of the groundwater table relative to adjacent drain water levels (Cook et al. 1999; Cook and Rassam 2002; Rassam and Cook 2002a). High $K_{sat}$ values can occur in ASS and have generally been found in association with substantial soil macropore networks (Hamming and van den Eelaart 1993; Johnston et al. 2003c; Johnston et al. 2004).

The hydrological pathway provided by groundwater seepage can be responsible for a significant fraction of acid flux even though its contribution to total drainage volumes is often low (Cook et al. 2000b). The contribution of groundwater seepage to acid flux will generally be greater at sites with higher hydraulic conductivity in the sulfuric horizon (Rassam and Cook 2002a). In accordance with Darcy’s law, rates of groundwater seepage to drains will be dependant upon the magnitude of effluent groundwater gradients, the hydraulic conductivity of acid soil horizons and the area over which seepage occurs. While reducing the seepage area is readily achieved by infilling and shallowing drains, this is an economically challenging option to apply on a broad scale (Blunden and Indraratna 2000). The magnitude of effluent groundwater gradients is relative to adjacent drain water levels (Fig. 6.1a). Drain water levels in coastal floodplain environments can fluctuate rapidly due to tidal influence. Many artificial drains have one way tidal flap gates (floodgates) located near the drains confluence with the receiving estuary. Floodgates allow draw down of drain water to minimum low tide level yet prevent ingress of tidal water.

There is a need for effective and practical strategies to reduce acid flux from artificial drains in ASS areas. Different techniques for reducing acid flux rates from artificial drains in ASS have been trialled in Australia. These include in-drain neutralisation strategies involving periodic flushing of drains with estuarine water (Indraratna et al. 2002) and more
comprehensive strategies aimed at containing acidity in the landscape (MacDonald 2002). Few trials have directly monitored changes in acid flux rates at the point of discharge into the estuary before and after implementation of the strategy.

![Diagram of effluent groundwater gradient and weir effect](image)

**Figure 6.1.** Schematic representation of a) the development of effluent groundwater gradients ($S'$) through tidal modulation of drain water levels, where $H_o$ is the equilibrium water table level in adjacent acid sulfate soils at distance (D) from the drain and $H_{min}$ is the minimum low tide water level in the drain, and b) the potential effect of a weir on reducing effluent groundwater gradients.

Blunden and Indraratna (2000) investigated the effect of using weirs in drains to maintain higher drain and groundwater levels and thus reduce sulfide oxidation. Blunden (2000) demonstrated that the use of weirs in this fashion may also reduce the hydraulic gradients driving groundwater seepage (Fig. 6.1b). However, the field effectiveness of this technique...
at slowing acid export rates was not tested. The potential for in-drain weirs to reduce acid flux via minimising groundwater seepage to artificial drains in ASS areas requires quantitative assessment. This study aims to (1) estimate the flux of acidity, sulfate, dissolved aluminium and dissolved iron from a drained ASS backswamp before and after the installation of an in-drain weir, and (2) assess the effectiveness of this strategy at reducing total acid flux and acid flux rates.

6.3. Materials and methods

6.3.1. Study site

The study site, Maloneys drain, is located in an ASS backswamp adjacent Shark Creek, a small tidal tributary of the Clarence River estuary (29°30' S, 153°15' E) (Fig. 6.2). The spring tidal range in Shark Creek is about 0.6 to -0.3 m Australian Height Datum (AHD; 0 AHD ~mean sea level). The backswamp is an infilled Holocene estuarine sub-embayment and surface elevations range from about 0.0 to 0.25 m AHD. The backswamp undergoes periodic flooding and inundation of the ground surface. A narrow distributary levee 1 to 3 m AHD in height fringes Shark Creek. An open ditch drainage network constructed in the backswamp conveys water through the distributary levee and discharges into Shark Creek via a single pipe culvert with one way floodgates (Fig. 6.3). The drain network is 5.4 km in length and the central channel is up to 8 m wide. The drain network intersects the sulfuric horizons in the backswamp and the elevation of the drain base in the central channel is approximately -1.2 m AHD. The elevation of the bottom of the culvert is about -1.0 m AHD. The drain sub-catchment contains 300 ha of upland and about 208 ha ASS backswamp. The main land use in the backswamp is cattle grazing on native pasture species while about half of the total backswamp area is *Melaleuca quinquenervia* forest (Johnston *et al.* 2003b). Sugarcane is grown on the levee and levee toe (Fig. 6.3). The
climate is sub-tropical and mean annual rainfall on the Clarence River floodplain ranges from 1100 to 1500 mm with a highly seasonal distribution and a distinct wet period from December to May.

Figure 6.2. a) Clarence River catchment and b) lower floodplain and study area location adjacent Shark Creek. Acid sulfate soil backswamp boundary after Milford (1997).

6.3.2. Meteorological monitoring

Rainfall, solar radiation, temperature, humidity, wind speed and soil temperature was recorded hourly with an EIT E-Tech weather station located near the drain (Fig. 6.3). Potential evapotranspiration (PET) was calculated using a Penman-Monteith equation.
6.3.3. Soils and hydraulic conductivity

The backswamp soils are Hydaqueptic Sulfaquepts (Soil Taxonomy, Soil Survey Staff 1998). An acidic, organic topsoil in the upper 0.3 m is underlain by a highly acidic sulfuric horizon with a silty clay texture and Fe (III) mineral and jarosite mottles (Johnston et al. 2003b). Sulfidic sediments are typically found within 0.8 to 1 m below the backswamp ground surface (Lin and Melville 1993; Johnston et al. 2003b). The sulfuric horizon soils have high hydraulic conductivity due to the existence of a dense, well developed macropore network (Johnston et al. 2002a; Johnston et al. 2004).

The $K_{sat}$ of the backswamp sulfuric horizons was assessed using auger hole slug tests (Bouwer and Rice 1976; Bouwer 1989), shallow pit bailing methods (Bouwer and Rice...
Auger hole slug tests were conducted in 5.5 cm diameter, slotted PVC wells that were placed in freshly hand augured boreholes. The slotting zone was positioned within the sulfuric horizon. Care was taken during sampling design to avoid underestimates of $K_{sat}$ that can result from low permeability well skins (Butler 1996). Water was withdrawn by rapid pumping and the recovery rate recorded at two second intervals using a freshly calibrated 1.0 m capacitance probe (Dataflow 392). Slug test wells were located in the vicinity of the piezometer transects and at least three replicate tests conducted in each well. $K_{sat}$ was calculated using the method of Bouwer (1989).

Shallow rectangular pits (up to 0.5 m deep and 0.5 m$^2$) were excavated in the backswamp adjacent the slug test boreholes. The water was bailed rapidly using a 10 L bucket to remove ~50 - 90% of the total water in the pit. Water level recovery was measured every 5 seconds on a ruler with 1 mm graduations. Two tests were conducted in each pit. $K_{sat}$ was calculated according to the methods of Bouwer and Rice (1983), and Boast and Langebartel (1984), which use slightly different shape factors depending on pit geometry.

Using the method described in Ferris (1951), $K_{sat}$ was also estimated from the damping of tidal amplitude between the drain and piezometers 10 m from the drain (wells 2 and 7), assuming a specific yield of 0.2. This analysis was applied to data from a period when the main floodgates were opened for four days which introduced a tidal signal into the drainage system.

6.3.4. Groundwater and drain water levels

Multiple piezometer wells were installed in the backswamp in two separate transects
perpendicular to the drain (Fig. 6.3). Each piezometer consisted of a 5.5 cm diameter slotted and screened PVC pipe inserted into a 10 cm diameter hand augured hole that was backfilled with clean sand and auger cuttings in the screened zone and then ~40 cm of bentonite to the surface. The elevation of each well was surveyed to AHD. Water levels in each piezometer were logged hourly using capacitance probes (Dataflow-model 392, accuracy ± 0.01 m). Water levels in Shark Creek and drain water levels immediately inside the floodgates (station A) and near the backswamp margin (station B) were also monitored hourly with capacitance probes. All capacitance probes were cleaned and calibrated every 2 - 3 months. Where used in this paper the term ‘mean daily backswamp water level’ refers to the 24 hr mean of piezometer wells 1 and 2. Similarly, the ‘maximum daily groundwater gradient’ refers to the difference between the mean daily backswamp water level and the minimum daily water level at drain station B, assuming a horizontal distance of 2 m. Groundwater in the backswamp sulfuric horizons has high concentrations of dissolved Fe and Al, and is highly acidic with a mean titratable acidity of 6 mmol L\(^{-1}\) under open pasture areas and 43 mmol L\(^{-1}\) beneath areas of encroached *Melaleuca quinquenervia* (Johnston *et al.* 2003b).

6.3.5. *Drain water quality*

Hourly measurements of drain water pH, Electrical Conductivity (EC), dissolved oxygen (DO) and temperature were made with Greenspan CS304 submersible data loggers (SDL). Two SDLs were installed in the drain, one near the floodgates (station A) and one in the backswamp (station B - Fig. 6.3). Each SDL was housed in a slotted PVC pipe that was positioned as close to centre channel as possible. DO was measured via a diffusion rod, pH using a double junction Ag/Cl electrode and EC via a toroidal sensor. The SDLs were cleaned, maintained and calibrated every 28 - 36 days. Spot measurements of *in situ* drain
water DO, pH, EC, temperature and redox potential were recorded at the time and location of sample collection using freshly calibrated portable field equipment (TPS 90FLMV). Comparison of spot measurements with logged SDL values at monitoring station A during 2003 indicate a mean difference in pH of 0.11 units ($n = 56$) and in EC of 0.17 dS m$^{-1}$.

6.3.6. Sample collection and analysis

Drain water samples were collected at stations A and B (Fig. 6.3). Sampling intensities were flow dependant, ranging from daily during high flow periods, to every ~2 - 10 days during periods of low to intermediate flow and none during prolonged periods of zero flow. Sampling was timed to coincide with outflow periods where possible to ensure accurate representation of discharge water. Water samples were collected from 0 to 0.3 m below the surface at centre channel using a clean 10 L plastic bucket thoroughly pre-rinsed with the drain water to be collected. Two 250 ml sub-samples were taken in clean (acid rinsed, distilled water flushed) polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times. Visible air bubbles were excluded prior to sealing the cap and samples placed in cold storage (approx. 4$^\circ$C). One 250 ml sub-sample was analysed for titratable acidity to pH 5.5 within 48 hours of sample collection (APHA (1995), 2310B - including the peroxide oxidation step). One 250 ml sub-sample was selected for further chemical analysis and frozen within 8 hrs of collection to minimise chemical / biochemical changes. Samples selected for chemical analysis were transported frozen, thawed at 4$^\circ$C, sub-samples immediately extracted and analysed for Total Iron and Total Aluminium (ICPAES - USEPA 6010), Dissolved Iron and Dissolved Aluminium (0.45µm cellulose acetate filtration, ICPAES - USEPA 6010), Chloride and Sulfate (Ion chromatography - APHA (1995), 4110).
6.3.7. Drain flow and flux calculations

Flow velocity in the drains was measured using Doppler sensors (Starflow - 6526-51) with a velocity range of 0.021 m s\(^{-1}\) to 4.5 m s\(^{-1}\). The scan interval was set for 30 seconds and the hourly mean, maximum and minimum logged. The Starflow units were located in the centre of the channel in the pipe culvert (station A, Fig. 6.3). A single Starflow unit was used during 2001 and a second unit added from January 2002. When data from two units were available, drain velocity was taken to be the mean of both. Velocity data from the two units had a high linear correlation \((y = 1.06x, r^2 = 0.98)\). Culvert dimensions and Starflow locations were surveyed to AHD. The Starflow units also measured drain water level using a hydrostatic pressure sensor vented to the atmosphere. Checks were undertaken using a calibrated current meter in the Doppler field of view under a range of flow conditions (>1 to ~0.1 m s\(^{-1}\)) and yielded flow velocities within ± 10% of the Doppler sensor.

Daily drain discharge \((Q_d)\) was derived from the sum of the hourly discharge volumes \((Q_h)\) using Eq. (6.1),

\[
Q_h = V_h.A_h \tag{6.1}
\]

where \(V_h\) = mean hourly flow velocity, \(A_h\) = mean hourly cross-sectional area of water in the culvert. Flux estimates were made using two methods. The first was a daily estimate using Eq. (6.2). The second was an hourly estimate using SDL values to infer ionic concentrations in drain water using Eq. (6.3).

\[
F_d = (Q_d.C_d) \tag{6.2}
\]

\[
F_h = (Q_h.C_h) \tag{6.3}
\]

Where \(F_d\) is the daily flux estimate and \(Q_d\) is daily discharge volume and \(C_d\) is daily concentration. For sampling days \(C_d\) was the chemical composition of the drain water outflow sample from station A. For non-sampling days \(C_d\) was estimated by linear
interpolation between adjacent sampling day concentrations. $F_h$ is the hourly flux estimate and $C_h$ is hourly logger inferred concentration. Hourly flux estimates were made during periods of prolonged acid outflow when there was a high correlation ($r^2 > 0.8$) between either the EC or pH values recorded by the SDL at station A and sample acidity / ionic concentrations. The hourly method is better able to account for the rapid variations in drain water chemistry that can accompany tidally modulated outflow periods (i.e. increasing acidity during the ebb tide cycle) and thus provides a more accurate integration of the area under the velocity and concentration curves. Total flux and daily flux ($f$) estimates reported in this study are a combination of the two approaches, giving preference to the hourly method where available. Daily flow weighted concentrations ($C_{fw}$) of acidity and other ionic species in drain water provide a more realistic average than spot sample concentrations and were calculated using Eq. (6.4).

$$C_{fw} = f/Q_d$$

(6.4)

6.3.8. Drain water retention

The drain was monitored from August 2000 to September 2003. A rock and concrete weir was installed in the drain in January 2002, downstream from monitoring station B (Fig. 6.3). About 60% of the total length of the drainage network was located upstream of the weir. The top of the weir was set at 0.25 m AHD, which approximately corresponds to the higher parts of the backswamp surface (Chapter 3, Figure 3.16). The weir also had two 0.4 m diameter pipe culverts with reverse facing flapgates. These flapgates could be opened to assist outflow if necessary (see Johnston et al. 2003d). When these flapgates were closed, drainage from upstream of the weir could only occur if the drain water level was over 0.25 m AHD.
6.3.9. Surface soil collection and analysis

Surface soils were collected from the backswamp using a push corer immediately adjacent piezometer wells 2, 3, 4 and 5 on four occasions (August 2001 and January, March and May 2002). Approximately ten cores 30 cm in length were taken at each location and depth increments of 0 - 5 cm, 5 - 15 cm, 15 - 25 cm and 25 - 30 cm from each core were bulked. Soil samples were oven-dried at 85°C within 48 hrs of collection and crushed to pass a 2 mm sieve. The EC and pH of a 1:5 water extract was determined for each sample (Rayment and Higginson 1992) and select samples analysed for water soluble SO$_4^{2-}$ (Ion chromatography - APHA (1995), 4110) and water soluble Al (ICPAES - USEPA 6010).

6.3.10. Water table, groundwater gradient and acid flux modelling

A simple modelling approach was adopted in order to provide a more independent analysis of the effects of the weir on the shallow groundwater table, groundwater gradients and acid flux rates. This was intended to help answer the question ‘what might acid flux have been during the post-weir period if the weir was absent?’. The modelling approach is based on data independent of the weir and draws on empirical relationships that existed between drain water levels during the pre-weir phase. The first stage was to model changes in the height of the shallow water table during the pre-weir period. The change in the height of the shallow water table in a drained backswamp can be described as a function of inputs from rainfall and outputs from evapotranspiration and lateral outflows (White et al. 1997; Cook et al. 1999). An estimate of change in the water table height over time can be derived using the following Eq. (6.5) and Eq. (6.6).

$$H_{t+1} = H_t + P - PET - D_{go} \quad \text{(6.5)}$$

$$H_{t+1} = H_t + \left(\frac{P}{S_y}\right) - \left(C_f \cdot PET / S_y\right) - D_{go} \quad \text{(6.6)}$$
Eq. (6.5) is applied when the backswamp water level is above the ground surface and Eq. (6.6) when it is below the ground surface. \( H_t \) is the mean daily backswamp water level (daily mean of piezometer wells 1 and 2) at time \( t \) expressed in mm, \( H_{t+1} \) is the mean daily backswamp water level at \( t+1 \) expressed in mm, \( P \) is rainfall (mm day\(^{-1}\) - assuming 100% infiltration), PET is potential evapotranspiration from the water table (mm day\(^{-1}\)), \( S_y \) is specific yield, \( C_f \) is a crop factor estimating vegetation water use and \( D_{go} \) is loss from the water table via lateral outflow to the drain (mm day\(^{-1}\)). A calibration and sensitivity analysis was undertaken to identify the influence of multiple values for \( S_y \) and \( C_f \) on modelled \( H_t \) in relation to observed \( H_t \) using five months of pre-weir data (Table 6.1). On this basis \( S_y \) and \( C_f \) were set at constant values of 0.2 and 0.5 respectively. These values were verified by comparing modelled \( H_t \) against 40 days of observed \( H_t \) from a period outside the calibration phase (linear regression, \( r^2 = 0.96, y = 0.951x + 0.023 \)).

### Table 6.1. Sensitivity analysis of the groundwater table model [Eq. (6.5) and Eq. (6.6)] to different values of specific yield (\( S_y \)) and a crop factor (\( C_f \)).

The equations from linear regression between observed \( H_t \) and modelled \( H_t \) are shown and are based on five months of pre-weir data (April to September 2001). Numbers in brackets are \( r^2 \).

<table>
<thead>
<tr>
<th>( S_y )</th>
<th>0.15</th>
<th>0.20</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_f )</td>
<td>[0.94]</td>
<td>[0.96]</td>
<td>[0.93]</td>
</tr>
<tr>
<td>0.4</td>
<td>( y = 0.93x + 0.01 )</td>
<td>( y = 0.93x + 0.01 )</td>
<td>( y = 0.93x + 0.003 )</td>
</tr>
<tr>
<td>0.5</td>
<td>[0.96]</td>
<td>[0.96]</td>
<td>[0.96]</td>
</tr>
<tr>
<td>0.6</td>
<td>( y = 1.04x - 0.02 )</td>
<td>( y = 1.01x - 0.02 )</td>
<td>( y = 0.99x - 0.02 )</td>
</tr>
<tr>
<td>[0.96]</td>
<td>[0.96]</td>
<td>[0.96]</td>
<td></td>
</tr>
</tbody>
</table>

It was assumed that \( D_{go} \) was directly proportional to tidal draw down in the drain at the floodgates: i.e. the difference between mean daily backswamp water levels and daily tidal
minima in the drain at station A. A lumped parameter to estimate $D_{go}$ based on the influence of tidal draw down was developed by plotting the rate of change in the water table height ($H_t - H_{t+1}$) against the difference between $H_t$ and the daily minimum low tide water level in the drain at station A, using data from the pre-weir period (linear regression, $r^2 = 0.81$). This relationship was then fitted to the model and the following Eq. (6.7) derived to estimate $D_{go}$,

$$D_{go} = (-0.0438(H_t - DW_a))$$  \hspace{1cm} (6.7)

where $DW_a$ is the daily minimum low tide water level in the drain at station A. Negative values of $D_{go}$ were given a value of zero. To model maximum groundwater gradients (the difference between $H_t$ and minimum daily drain water levels at station B) during the pre-weir period required predicting the minimum daily drain water levels at station B ($DW_b$). Correlation between minimum daily drain water levels at station A and station B (linear regression, $r^2 = 0.95$, $y = 1.065x + 0.036$) enabled use of values from station A, which is downstream of the weir, to estimate $DW_b$.

6.4. Results and discussion

6.4.1. Hydraulic properties of the sulfuric horizons

Table 6.2 summarises the results of $K_{sat}$ tests. Mean values are in excess of 120 m day$^{-1}$ and there is reasonable agreement between the different methods used. Well and pit infilling was dominated by rapid flow through large (> 5 mm diameter), mainly tubular, macropores with varying orientations. The flow characteristics of this macropore network suggest a high connectivity in both the vertical and the horizontal planes (Johnston et al. 2004). Realistic field scale estimates based on small scale methods (such as auger hole slug tests) can be subject to significant errors (Millham and Howes 1995). This is particularly true if flow into an auger hole is dominated by macropores whose size and spatial heterogeneity are high relative to the
size of the hole. For this reason, tests which average aquifer response over larger areas (i.e. pit bailing and tidal damping) are more likely to be representative of actual field $K_{sat}$ values.

Table 6.2. Saturated hydraulic conductivity ($K_{sat}$) of the sulfuric horizons at the study site backswamp.

s.e. is the standard error.

<table>
<thead>
<tr>
<th>Site</th>
<th>Auger hole slug test $^A$</th>
<th>Shallow pit bailing $^B$</th>
<th>Tidal amplitude damping $^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{sat}$ (m day$^{-1}$)</td>
<td>n</td>
<td>s.e.</td>
</tr>
<tr>
<td>Maloneys</td>
<td></td>
<td>125</td>
<td>10</td>
</tr>
</tbody>
</table>


$^B$ Bouwer and Rice 1983.

$^C$ Ferris 1951.

The geometry, volume, pore size distribution and connectivity of macropores can profoundly affect groundwater movement rates (Beven and Germann 1982; Bouma 1991) and solute flux pathways in near surface soils (Harvey and Nuttle 1995; Minh et al. 2002). The high $K_{sat}$ of the sulfuric horizons is an extremely important feature of the study site which encourages rapid lateral movement of shallow groundwater in the backswamp and high rates of acid groundwater seepage to the drain (Johnston et al. 2004). This is notably different from other some ASS sites documented in Australia (i.e. White et al. 1993; Rassam and Cook 2002b). In low $K_{sat}$ ASS, Rassam and Cook (2002b) reported substantial leaching of acidic solutes from the near drain zone and a steep groundwater gradient immediately adjacent the drain. In contrast, the high $K_{sat}$ at the study site facilitates rapid replacement of acid groundwater lost to drainage from the near drain zone, which is likely to attenuate leaching effects. Groundwater levels across the backswamp are also relatively flat and typically vary in the order of centimetres over hundreds of meters, similar to that observed by Hamming and van den Eelaart (1993) in a high $K_{sat}$ ASS in Indonesia.
6.4.2. Pre-weir acid flux dynamics

Before the weir was installed, most of the drainage flux of acidity (~80%), dissolved Al, dissolved Fe and \( \text{SO}_4^{2-} \) occurred while the backswamp water level was within a relatively narrow elevation range (about 0.25 to -0.15 m AHD - Fig. 6.4). This elevation range corresponds approximately to the upper levels of the backswamp surface and mean minimum low tide levels experienced in the drain at station B. Groundwater seepage dominates the acid flux within this range, which is henceforth referred to as the ‘acid export window’.

![Figure 6.4](image-url)  
**Figure 6.4.** Cumulative flux estimates of acidity, \( \text{SO}_4^{2-} \), dissolved Fe and dissolved Al at Maloney’s drain during 2001 (pre-weir) in relation to mean daily water levels in the acid sulfate soil backswamp. The total flux of acidity in 2001 was \( 1.07 \times 10^6 \) mol H\(^+\). Most flux occurs while the backswamp water level is within a narrow elevation range which corresponds to the shallow groundwater zone above tidally influenced low water in the drain. \(^\text{A}\) = the 24 hr mean of piezometer wells 1 and 2. \(^\text{B}\) = mean minimum tidally influenced low water level in drain at station B.
The confinement of most acid flux to this elevation range is further demonstrated by the mean daily drain pH at monitoring station A, which shows a distinct grouping of low values (<3.5) corresponding to mean drain water levels within this approximate range (Fig. 6.5).

Figure 6.5. Mean daily drain water pH values in relation to mean daily drain water levels at monitoring station A, before installation of the weir during 2001. pH values shown are the 24 hr mean from the submersible data logger at monitoring station A.

These dynamics reflect the fact that the main hydrological pathway through which acidity is transported to the drain is groundwater seepage (Johnston et al. 2004). When the water level in the backswamp is significantly above the ground surface, relatively dilute surface runoff dominates the drainage outflow (Fig. 6.5). Alternatively, when the backswamp water level falls below minimum low tide levels in the adjacent drain, no groundwater seepage to the drain occurs due to a lack of driving gradients. The extremely high
hydraulic conductivity of the sulfuric horizons facilitates rapid groundwater seepage to the drain whenever there is an effluent groundwater gradient (Fig. 6.6). Fig. 6.6 shows that seepage of groundwater acidity to the drain is extremely sensitive to small changes in the hydraulic gradient, which operates like a switch between acid containment and acid export modes.

Figure 6.6. Mean daily drain water pH values in relation to maximum daily groundwater gradients. pH values are the 24 hr mean from the submersible data logger at monitoring station A. Data shown is from periods when the mean daily groundwater level was below the surface, between December 2000 and March 2003. Influent groundwater gradients develop during dry periods. \(^\hat{A}\) = the difference between the mean daily groundwater level and the minimum daily drain water level at drain monitoring station B, assuming a horizontal distance of 2 m.

Tidal fluctuations in Shark Creek cause modulation of drain water levels in the ASS backswamp which influences the development of effluent groundwater gradients (Fig. 6.7a). This in turn plays an important role in the regulation acid flux (Fig. 6.7b). A strong
positive correlation (linear regression, $r^2 = 0.75$) was observed between the magnitude of effluent groundwater gradients and the daily acid flux rates during the pre-weir period (Fig. 6.8). Data shown in Fig. 6.8 are from periods when the groundwater is between 0.22 to -0.2 m AHD and thus acid flux is primarily from groundwater seepage. These findings broadly accord with those of Wilson et al. (1999) who showed the importance of the position of the groundwater table in regulating acid flux. This study highlights the existence of a clearly defined acid export window within which most acid flux occurs and draws attention to the role of local tidal dynamics in controlling a) the development of effluent groundwater gradients, and b) the lower boundary of the acid export window.

Figure 6.7. a) Tidal fluctuations in Shark Creek cause modulation of drain water levels at monitoring station B, influencing the development of effluent groundwater gradients in the ASS backswamp which consequently b) play an important role in regulating acid flux rates from groundwater seepage. The approximate upper levels of the backswamp ground surface are indicated by the dashed line.
Figure 6.8. Correlation between daily acid flux estimates and maximum daily groundwater gradients. Based on a period between 26th of April to 8th of August 2001 (pre-weir) when the groundwater level was between 0.22 and -0.2 m AHD. Maximum daily groundwater gradients are based on the difference between the mean daily groundwater level and the minimum daily drain water level at drain monitoring station B, assuming a horizontal distance of 2 m.

6.4.3. Post-weir acid flux

A comparison of discharge volumes, acid flux rates, flow weighted concentrations of $\text{H}^+$ and dissolved Al pre and post-weir is shown in Fig. 6.9. Fig. 6.9a shows a substantial reduction in acid flux rates in the post-weir period once mean daily backswamp water levels fall below weir height. When water levels are above the weir there is little difference in acid flux rates between the pre and post-weir periods. The main effect of the weir was to reduce drain discharge volumes by about 4 - 5 times relative to the equivalent pre-weir period, once water levels fell below the weir height and the two flapgates on the weir were closed (Fig. 6.9b). When backswamp water levels were above weir height and the flapgates on the weir were open, discharge volumes were similar to the pre-weir period.
Figure 6.9. a) Acid flux estimates, b) discharge volumes, c) flow weighted concentrations of H\(^+\) and d) flow weighted concentrations of dissolved Al in relation to mean daily backswamp water levels during the pre and post-weir periods. The post-weir period differentiates between data collected when the weir was functioning normally (post-weir, closed) and when the two flap gates on the weir were open to assist outflow (post-weir, open).

A secondary effect of the weir was a reduction in the flow weighted concentrations of H\(^+\) and acidic metal cation at the floodgate discharge point once backswamp water levels fell below weir height (Fig. 6.9c and 6.9d, Table 6.3). After the weir was installed the maximum flow weighted concentration of acidity in the drain water was about 50% lower than the pre-weir period (Fig. 6.9c). Table 6.3 shows there were significant reductions in H\(^+\) and acidic metal cations (dissolved Fe and Al) during the post-weir period compared to
the pre-weir period. However, when mean backswamp water levels were above the weir height, post-weir acidity concentrations were within the range of those observed in the pre-weir period.

Table 6.3. Mean daily flow weighted concentrations and ±standard error of titratable acidity, \( \text{SO}_4^{2-} \), dissolved Fe and dissolved Al in drainage outflow water at station A before and after the weir was installed.

Based on discharge periods when the mean daily backswamp water level elevation was <0.25 m AHD.

<table>
<thead>
<tr>
<th></th>
<th>Pre-weir (mmol L(^{-1}))</th>
<th>Post-weir (mmol L(^{-1}))</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titratable acidity</td>
<td>2.11 ±0.18</td>
<td>1.23 ±0.09</td>
<td>***</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} )</td>
<td>4.09 ±0.11</td>
<td>3.90 ±0.04</td>
<td>n.s.(^A)</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>0.51 ±0.04</td>
<td>0.15 ±0.01</td>
<td>***</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>0.19 ±0.01</td>
<td>0.12 ±0.01</td>
<td>***</td>
</tr>
</tbody>
</table>

\*P <0.05, \**P <0.01, \***P <0.001.
\(^A\) n.s. is not significant.

Analysis of paired spot water quality samples collected during 2003 upstream and downstream from the weir show significant differences between many parameters (Table 6.4). Notably, pH was significantly higher upstream from the weir. Also, while the difference in titratable acidity was not significant when the weir was open, it was significantly higher downstream from the weir when the flapgates were closed. When the flapgates on the weir were closed, preferential drainage occurred from the lateral drains downstream of the weir (Fig. 6.3). Acid groundwater seepage still occurs unimpeded from these lateral drains downstream from the weir and spot monitoring (data not shown) suggests this was mainly responsible for the apparent increase in flow weighted
concentrations of $H^+$ once the flapgates were closed (Table 6.4, Fig. 6.9c). A high positive linear correlation between titratable acidity and both dissolved Al and dissolved Fe ($r^2$ of 0.84 and 0.77 respectively) in drain water samples suggests that the dynamics observed in $H^+$ flux is also indicative of the flux of these acidic metal cations.

Table 6.4. Mean chemistry of paired spot water samples at station A (downstream from weir) and station B (upstream from weir) after weir installation.

Data shown are based on samples collected between 12th March and 21st July 2003. Results are presented according to whether the flap gates on the weir were open or closed. Concentrations are in mmol L$^{-1}$ and ratios are molar.

<table>
<thead>
<tr>
<th></th>
<th>Weir open (n = 22)</th>
<th>Weir closed (n = 40)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Station A</td>
<td>Station B</td>
</tr>
<tr>
<td>pH</td>
<td>3.97</td>
<td>4.30</td>
</tr>
<tr>
<td>EC (dS m$^{-1}$)</td>
<td>0.98</td>
<td>0.53</td>
</tr>
<tr>
<td>Titratable acidity</td>
<td>0.52</td>
<td>0.44</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>1.41</td>
<td>0.74</td>
</tr>
<tr>
<td>Dissolved Fe</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Dissolved Al</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Cl:$SO_4^{2-}$</td>
<td>3.8</td>
<td>4.9</td>
</tr>
</tbody>
</table>

$^A$ = n.s. is not significant.

$^*$ $P < 0.05$, $** P < 0.01$, $*** P < 0.001$.

6.4.4. Water table, groundwater gradient and acid flux modelling

The backswamp water levels, groundwater gradients and acid flux are dynamically altered by the weir and are also highly dependant on unique seasonal climatic and tidal influences affecting the site. The modelling conducted in this study helps account for climatic and tidal
influences and thus provides an alternative means of assessing the effectiveness of the weir beyond that of simply comparing observed flux rates / discharge volumes. Fig. 6.10a compares the observed and modelled mean daily groundwater levels during a five month pre-weir period when the backswamp water level was mostly within the acid export window. Initial water table levels were set with actual field data on the 4th April 2001, and again on the 22nd of May 2001 after the water table reached the surface following rainfall. Linear regression analysis of observed and modelled data yields a high correlation coefficient and a slope close to 1 (see Table 6.1). Fig. 6.10b provides a comparison between the observed and modelled maximum groundwater gradients during the pre-weir period, with modelled data based on modelled $H_t$ and predicted $DW_b$ (see section 6.3.10). Gradients were only calculated when $H_t$ was between 0.22 m to -0.2 AHD and negative gradients were given a value of zero. Linear regression analysis of these data yields an $r^2$ value of 0.85, $y = 0.91x$.

Observed groundwater gradients were used to predict acid flux during the pre-weir period (Fig. 6.10c) when the groundwater level was between 0.22 m to -0.2 AHD, using the linear regression relationship shown in Fig. 6.8. This simple gradient based method of modelling acid flux tends to underestimate observed flux (linear regression, $r^2 = 0.71$, $y = 0.91x$). More complex hydrological behaviour, such as displacement of acidic drain water after rainfall on May 21st 2001 (Fig. 6.10d) causing an acid flux peak, is not accounted for in this empirical model. Despite the simplistic nature of the approach used, the modelling results accord reasonably well with the observed data in the pre-weir phase. Fig. 6.10 establishes the validity of this modelling technique as a method for estimating changes in backswamp water levels, groundwater gradients and acid flux during the post-weir period, without directly relying on water level measurements from behind the weir.
Figure 6.10. A comparison of pre-weir observed and modelled data for a) mean daily backswamp water levels, b) maximum daily groundwater gradients and c) acid flux rates in relation to d) observed rainfall. Maximum daily groundwater gradients and modelled acid flux are only calculated for periods when the mean daily backswamp water level was <0.22 m AHD.

Fig. 6.11a compares observed groundwater levels from the post-weir period with groundwater levels modelled assuming the weir was absent, according to the methods outlined above. It should be noted that this approach assumes the empirical relationships used would have remained stable over the period of observation and other influencing factors, such as changes in groundwater acidity, would not have been significant.
Figure 6.11. A comparison of post-weir observed and modelled data for a) mean daily backswamp water levels, b) maximum daily groundwater gradients and c) acid flux rates in relation to d) observed rainfall. Modelled data assumes the weir was absent, using identical methods to Fig. 6.10. Periods when the two flapgates on the weir were open are also shown.

Initial water table levels were set with actual field data on the 7th of March 2003 and again on 15th March and 17th of May when water levels peaked above the ground surface after rainfall. This data demonstrates that the weir helped maintain higher groundwater levels during the period of observation, which is consistent with the reduction in discharge volumes evident in Fig. 6.9b. Maintenance of higher groundwater levels is also consistent
with the findings of Blunden (2000) and Joukainen and Yli-Halla (2003) who examined the role of weirs in controlling sub-surface drainage in ASS environments. A comparison of observed and modelled maximum groundwater gradients (Fig. 6.11b) suggests that the weir caused a substantial reduction, totalling about 80% over the period of measurement (calculation based on period shown when modelled $H_t$ was between 0.22 m to -0.2 AHD).

Fig. 6.11c compares observed acid flux with acid flux based on modelled groundwater gradients. This data suggests a reduction in total acid flux due to groundwater seepage of about 67% over the modelled period (observed = 3.41 x $10^5$ mol H$^+$, modelled = 1.04 x $10^6$ mol H$^+$). It also suggests a reduction in mean daily acid flux rates of about 80%, which broadly accords with the pattern observed in Fig. 6.9a.

**Figure 6.12.** Daily acid flux rates in relation to the difference between the mean daily backswamp water level and daily tidal minima in Shark Creek, comparing observed data from both the pre-weir and post-weir periods with modelled data from Fig. 6.11 for the post-weir period in 2003. Pre-weir observed and post-weir modelled data are based on periods when the mean daily groundwater level was <0.22 m AHD.
Fig. 6.12 shows the effect of the weir on the relationship between acid flux rates from groundwater seepage and the difference between mean daily groundwater levels and daily tidal minima in adjacent Shark creek. A large reduction in flux rates and shift in the relationship occurred during the post-weir phase. Modelled data in Fig. 6.12 estimating acid flux as if the weir was absent (derived from Fig. 6.11) are consistent with the relationship observed during the pre-weir period.

6.4.5. Surface sediment chemistry

In ASS areas with poor groundwater quality and a long dry season, maintaining a shallow groundwater table can increase the accumulation of acidic solutes and toxins (i.e. Al\[^{3+}\]) in the root zone through enhanced upward evaporative flux (Tuong 1993). Minh et al. (1998) showed a strong linear correlation between cumulative evaporation and the accumulation of Al\[^{3+}\] in topsoil during a drying period, which varied according to the depth at which the water table was maintained. Minh et al. (1998) also found that maintaining a surface mulch cover was an effective means of limiting this accumulation.

Analysis of surface soils collected from the study site during an extended dry period (Fig. 6.13) shows similar trends to those reported by Minh et al. (1998). Linear correlation is evident between topsoil EC, SO\[^4\]\[^2-\] and Al concentrations and cumulative PET for 180 days prior to sampling (Fig. 6.13). A decline in topsoil pH is also evident. While this data is far from conclusive, it does suggest that a factor which enhances evaporative losses from the shallow groundwater table (i.e. a weir), may encourage the accumulation of acidic solutes in surface soil over the longer term.
Figure 6.13. Correlation between cumulative PET (potential evapotranspiration) and surface soil (0 - 5 cm below ground surface) a) EC (1:5 water extract), b) pH (1:5 water extract), c) sulfate and d) aluminium (water extractable) during a prolonged dry period from August 2001 to May 2002. Error bars are standard deviation. Cumulative PET measured from 180 days prior to sampling. Numbers in brackets are the mean daily backswamp water elevation for 60 days prior to sampling.

6.5. General discussion and conclusions

This study demonstrates that an in-drain weir can be an effective strategy for reducing acid flux from groundwater seepage in drained coastal acid sulfate soils. Groundwater seepage to the drain through the highly permeable sulfuric horizons was the main hydrological pathway of acid flux at this site. Tidal modulation of drain water levels played a critical role in the development of groundwater gradients driving this seepage. Maximum
groundwater gradients behind the weir were estimated to have been reduced by about 80% and acid flux from groundwater seepage by about 65 - 70%. This is substantial given that only 60% of the total length of the drainage system is behind the weir. While the weir clearly reduced acid flux rates from groundwater seepage, it had no discernable influence on acid flux rates derived from surface runoff. Once backswamp water levels overtopped the weir there was little evidence to suggest substantial change in either discharge volumes or H⁺ concentrations. Reducing acid flux from surface runoff could still be achieved using a weir, but requires the weir be set at an elevation high enough to retain the surface water within the backswamp.

A major effect of the weir was a four to five fold decrease in the volumetric rates of water discharged from the drain when backswamp water levels fell below the weir height. The weir acts as a block to flow, slowing down tidally influenced drainage losses from the shallow groundwater table. This maintains the groundwater higher for a longer period than would otherwise be the case (Fig. 6.11a) and essentially allows more time for evapotranspiration to remove shallow groundwater from the system. Given the very high hydraulic conductivity of the sulfuric horizons, some groundwater seepage around weir is likely to have occurred. From an acid containment point of view the ideal location for the weir would be close to the levee toe downstream of all the lateral drains. However, this was not possible due to agricultural constraints. If the weir was situated so that the entire length of the drain located in the ASS backswamp was upstream from the weir, it is likely that acid flux from groundwater seepage would have been reduced to almost zero once water levels fell below weir height. However, in such a situation overtopping of the weir and displacement of acidic drain water could still occur in response to rainfall.
The weir had a secondary effect of reducing maximum flow weighted concentrations of $H^+$ and acidic metal cations at the discharge point, with post-weir flow weighted concentrations of $H^+$ about half of that observed during the pre-weir period (Fig. 6.9c, Table 6.3). This is consistent with the study of Joukainen and Yli-Halla (2003) who showed a reduction in titratable acidity and increase in the pH of drainage water from an ASS site with a weir compared to an adjacent control. At Maloney's drain this may be related to the weir reducing tidal draw down and groundwater seepage from sections of the drain network located in the *Melaleuca quinquenervia* areas of the backswamp which are known to have far higher groundwater acidity (Johnston *et al.* 2003b). The lower titratable acidity and acidic metal cation concentrations evident upstream relative to downstream from the weir during much of the outflow period may simply be a function of less groundwater seepage due to lower overall gradients. It may also be related to longer residence times and the stagnant, low flow environment behind the weir providing a greater opportunity for redox transformations of $Fe^{2+}$ and $SO_4^{2-}$ to take place in the drain, thereby consuming acidity and potentially leading to storage as monosulfidic black ooze (Sullivan *et al.* 2002).

The primary land use in the ASS backswamp at this study site is grazing on native pasture species returning relatively low gross margins per hectare. Thus a requirement of any practical acid flux reduction strategy at this, and other sites with similar low return land use, is low input costs. Landholders in this situation cannot economically justify a high cost strategy based on land reshaping, laser levelling, in-drain neutralisation of acid water and regular surface liming such as outlined by MacDonald (2002) for use in sugar cane areas. Weirs meet this criterion well as they are both cheap, depending on materials and design, and simple to construct.
The main pasture species in the backswamp include *Paspalum distichum, Pseudoraphis spinescens* and *Cynodon dactylon*. Both *P. distichum* and *P. spinescens* can thrive in wet conditions with shallow surface water (Roberts and Marston 2000) and the maintenance of higher groundwater levels by the weir is likely to favour these wetter tolerant species over *C. dactylon*. This suggestion is supported by visual observations made in wetter, more poorly drained parts of the Shark Creek ASS backswamp. Higher groundwater levels will generally not be compatible with sugar cane cropping due to cane's poor tolerance of water logging. However, the drainage outlets for the sugar cane areas at the study site were located downstream of weir and normal drainage of these areas was unimpeded.

Available evidence suggests this strategy may have potential to increase upward evaporative flux and accumulation of acidic solutes in near surface soils over time. Controlling grazing pressure to maintain a dense surface vegetative cover will reduce this risk. Downward leaching of solutes during wet periods will also attenuate this process and may be sufficient to prevent any long term accumulation trend, but further research is required. There is a need for further research to evaluate the long term impact of acid containment weirs and grazing management on the export of acidity in surface water. Further research is also required on the potential of acid containment weirs to increase the storage of soluble acidity in groundwater over the long term. This could occur after weir installation if sulfide oxidation continues at rates which are higher than the acid export rate and the rate at which acidic solutes are converted into less soluble forms.

This study highlights the importance of understanding a sites hydrological behaviour, particularly the dominant acid flux pathways and critical water table elevations over which acid flux occurs, prior to designing a management strategy. The hydraulic properties of the
sulfuric horizons along with their elevation relative to local low tide levels in adjacent drains are critical features. These features, particularly hydraulic conductivity, can be highly variable in coastal ASS in eastern Australia, which underscores the need for appropriate site assessment.

6.6. Acknowledgements

We thank the Shark Creek landholders, particularly D. Moloney and P. Moloney, for their assistance and cooperation. We also thank A. Cibilic, R. Lloyd and Clarence River County Council for assistance with developing and installing the weir. The contribution of B. Makins to many aspects of the field work is also gratefully acknowledged. This study was funded by Land and Water Australia, Acid Soil Action, Sugar Research and Development Cooperation, Acid Sulfate Soils Program and NSW Agriculture.
Chapter 7

The effects of controlled tidal exchange on improving drainage water quality in acid sulfate soil backswamps

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7.1. Abstract

Periodic opening of one-way floodgates was undertaken on two coastal flood mitigation drains to promote tidal exchange with estuarine water and improve drain water quality. The drains were located in areas with acid sulfate soils and their drainage water frequently had high acidity and low dissolved oxygen (DO). Tidal exchange via floodgate opening generally raised drain water pH levels through dilution and/or neutralisation of acidity. Increases in DO and moderation of extreme diurnal DO fluctuations were also observed. The magnitude and stability of the improved physico-chemical conditions was highly dependant on the volume and quality of tidal ingress water. Relatively rapid reversion (hours to days) in drain water pH and DO was observed once floodgates were closed again. The rate of reversion following floodgate closure was strongly related to outflow volumes, antecedent drain water quality conditions and groundwater levels. Floodgate opening caused changes in longitudinal drain water gradients and has potential to slow net drainage rates during non-flood periods. However, complex site specific interactions between drain water and adjacent groundwater can also occur. At one location, a four day floodgate opening event caused recharge of adjacent acid groundwater during the opening phase, raising the groundwater potentiometric level above local low tide minima. This was followed by tidally modulated draw down of acid groundwater and enhanced acid export in the period immediately following floodgate closure. There are also practical considerations which limit the efficacy of floodgate opening as an acid management strategy. The low elevation (close to mean sea level) of some acid sulfate soil backswamps, combined with seasonal migration of the estuarine salt wedge, means there is considerable potential for saline overtopping of what is currently agricultural land. This constrains the magnitude and duration of controlled tidal exchange. Also, it is during wet periods that acid drainage outflow to the estuary is greatest. At such times the salinity and acid buffering capacity of estuarine water is often low, thus reducing the capacity of tidal exchange waters to neutralise acidity.
7.2. Introduction

An extensive network of constructed drains and modified water courses exists on the coastal floodplains of eastern Australia. Construction of drainage schemes was intended to mitigate the negative effects of flooding on agricultural land and facilitate the expansion of agriculture on the floodplains (Pressey and Middleton 1982; Middleton et al. 1985). Drainage was designed to rapidly remove surface waters after flooding and also exclude saline, tidal estuarine waters from overtopping low lying land. Poor water quality is a common occurrence in these coastal floodplain drains, particularly during wet periods. There is substantial documentation of drainage outflow events with high levels of acidity (Sammut et al. 1996; Wilson et al. 1999; Blunden 2000; Cook et al. 2000a) and low dissolved oxygen (Pressey and Middleton 1982; NSW Agriculture and Fisheries 1989; Johnston et al. 2003a). The extensive areas of acid sulfate soils (ASS) which underlie the coastal floodplains in eastern Australia (Naylor et al. 1995) are the primary source of acidity in drainage waters (White et al. 1997).

Floodgates are a common feature on coastal floodplain drains. They usually consist of top-hinged, metal flapgates which allow one way outflow of drain water, but exclude tidal ingress. Floodgates help maintain low drain water levels, which assists in lowering regional groundwater to local low tide level (Blunden 2000) where it can then be lowered further through evapotranspiration. Floodgates can also limit small scale flooding from rises in river levels. By preventing tidal exchange, floodgates promote a stagnant, poorly flushed aquatic environment in the drain.

Floodgates are known to exacerbate poor water drain quality, particularly high acidity and low dissolved oxygen (Johnston et al. 2003d). In ASS areas, floodgates allow drains to act
as reservoir for high acidity waters which discharge during ebb tide cycles (Johnston 1995; Sammut et al. 1996). The lack of flushing and water quality conditions associated with floodgates also appear to favour the accumulation of iron monosulfides in drain basal sediments in areas with ASS (Sullivan et al. 2002). Coastal floodplain drains are typically exposed to high light levels and also flow through agricultural land, which can favour accumulation of nutrients and organic matter. These features, combined with no tidal flushing due to floodgates, can promote eutrophic conditions and episodic algal blooms which lead to wild diurnal fluctuations in DO and/or low DO accompanying decay of labile organic material (Sammut et al. 1994; Johnston et al. 2003d). There are also other ecological impacts of floodgates (Sammut et al. 1995), which include restriction of fish passage and prevention of access to upstream habitat (Pollard and Hannan 1994). The fact that floodgates allow drainage to low tide level has greatly reduced both the aerial extent and the ecological integrity of many coastal wetlands (Pressey and Middleton 1982).

Controlled tidal exchange with estuarine water by opening floodgates is being increasingly promoted and used as a means of improving water quality in drains (Haskins 1999; Indraratna et al. 2002; Johnston et al. 2003d). Sea water contains acid buffering agents, mainly bicarbonate and carbonate, and has the capacity to neutralise around 2 - 2.5 mmol H+ L⁻¹. The buffering reaction of bicarbonate with a strong acid, such as H₂SO₄ from acid sulfate soils, and formation of weak carbonic acid can be represented by Eq. (7.1).

\[
\text{HCO}_3^{-(aq)} + \text{H}^+(aq) \leftrightarrow \text{H}_2\text{CO}_3^{(aq)} \quad (7.1)
\]

The concentration of marine derived buffering agents in estuarine water is strongly related to the salinity regime in the estuary (Indraratna et al. 2002). In the Clarence River estuary the salinity regime varies greatly according to the highly seasonal freshwater inflows (Manly Hydraulics Laboratory 2000). The net acid neutralisation capacity of tidal ingress
waters entering a drain during a given flood tide cycle will be dependant on both the concentration of buffering agents within the ingress water and the ingress volume. The efficient utilisation of this acid neutralisation capacity will depend partly on adequate mixing and there is potential for slug displacement to occur within the drain.

Recent research has shown that controlled tidal exchange in drains can be a reasonably effective means of neutralising / diluting acid drain water (Indraratna et al. 2002). However, chronic discharge of highly acid groundwater following rainfall events can still overwhelm the buffering capacity of tidal ingress water (Indraratna et al. 2002). DO levels in both floodplain drains and estuaries typically display a high degree of dynamism over a variety of time scales (i.e. daily, annually, episodic flow event based). Thus the effects of controlled tidal exchange on DO concentrations in drain water are likely to be variable, depending on the timing of opening events.

Given the heterogeneity of physical and chemical properties typically associated with ASS (Dent 1986), further field investigations of controlled floodgate opening on acid buffering dynamics is required in drains from a variety ASS landscapes and hydrological contexts. There is also a need to examine the effects of controlled floodgate opening on other important water quality parameters such as DO. This study aims to (1) assess changes in drain water quality, particularly pH and dissolved oxygen, associated with controlled floodgate opening in two drains in ASS backswamps, and (2) relate these observed changes to antecedent hydrological conditions, drain flow volumes and local hydrological processes.
7.3. Materials and methods

7.3.1. Study sites

The study sites, Blanches drain and Maloney’s drain, are located on the lower Clarence River floodplain on the central east coast of Australia (29°30’ S, 153°15’ E) (Fig. 7.1). Both sites drain water from ASS backswamps to the estuary. The estuary is a mature barrier system (Roy 1984) with a floodplain area >2600 km$^2$ which is underlain by an estimated 530 km$^2$ of high risk acid sulfate soils (Tulau 1999). The backswamps are infilled Holocene estuarine embayments (Roy 1984; Lin and Melville 1993) with relatively flat topography and surface elevations mostly <0.2 m Australian Height Datum (AHD; 0 AHD ~mean sea level). Both backswamps are underlain by sulfidic sediment ~1 m from the ground surface (Lin and Melville 1993; Milford 1997).

Figure 7.1. a) Clarence River catchment and b) lower floodplain and study area locations and associated ASS backswamps. ASS backswamp boundaries after Milford (1997).
Blanches drain is located on Everlasting Swamp (Fig. 7.2) and drains an ASS backswamp area of ~600 ha, plus a proportion of an upland catchment. The main drain is over 3.5 km long and up to 10 m wide and discharges water through a two cell box culvert with outward opening floodgates. This drain was constructed through the natural levee in the 1960’s and discharges directly into the main Clarence River channel. The drain network intersects the sulfuric horizons in the backswamp and the elevation of the drain base in the central channel adjacent the backswamp is approximately -0.9 m AHD.

Maloneys drain is located in lower eastern Shark Creek, a small tidal tributary channel of the Clarence River, and has a catchment containing 208 ha of ASS backswamp and 300 ha of upland. A drainage network constructed in the backswamp conveys water through the distributary levee and discharges into Shark Creek via a single pipe culvert with one way floodgates (Fig. 7.2). The drain network is 5.4 km in length and the central channel is up to 8 m wide. The drain network intersects the sulfuric horizons in the backswamp and the elevation of the drain base in the central channel is approximately -1.2 m AHD.

The floodgates at each site can be manually raised by means of winch and pulley systems. Tidal water ingress can occur once the floodgates are raised, depending on relative water levels inside the drain and the adjacent estuary. The mechanism at Blanches drain only allowed the floodgates to be either fully open or fully closed, with no capacity for a partial opening. At Maloneys the mechanism allowed for a variable opening size. The main landuse in both backswamps areas is grazing, though there is some sugar cane on the natural levees at both sites. The climate is sub-tropical and annual rainfall on the Clarence River floodplain ranges from 1100 to 1500 mm. Monitoring was conducted at both sites from December 2000 through to October 2003.
Figure 7.2. Blanches and Maloney's study sites, showing the location of submersible data loggers / flow / drain water level monitoring stations (A - B), piezometers, drains, floodgates and ASS backswamp margin. ASS backswamp boundaries after Milford (1997).

7.3.2. Meteorological monitoring

Rainfall, solar radiation, temperature, humidity, wind speed and soil temperature was recorded hourly with an EIT E-Tech weather station located near each drain.
7.3.3. Drain water quality

Hourly measurements of DO, pH, Electrical Conductivity (EC) and temperature were made with Greenspan CS304 submersible data loggers (SDL). Two SDLs were installed in each drain, one near the floodgates and one near the backswamp margin, designated monitoring stations A and B respectively (Fig. 7.2). Each SDL was housed in a slotted 0.1 m diameter PVC pipe, positioned as close to centre channel as possible. The SDLs were cleaned, maintained and calibrated every 28 - 36 days. Spot measurements of in situ drain water DO, pH, EC, temperature and redox potential (ORP) were recorded at each SDL calibration and at the time and location of sample collection using freshly calibrated portable field equipment (TPS 90FLMV). Redox potential was measured with a platinum tipped Ag/AgCl reference electrode and values are reported as recorded without correction.

Vertical stratification of the water column is known to occur in low flow conditions in ASS drains (Sammut et al. 1994). This has significant implications for monitoring drain water quality using stationary SDLs. There are few ways to avoid this issue other than to use a nested array of SDL at multiple depths or multi-depth samplers. However, opportunistic spot monitoring (at stations A) conducted at different depths suggests that the flow associated with floodgate opening and also during discharge events causes enough velocity shear and mixing to prevent substantial stratification of drain water during these times. A comparison of spot measurements with logged SDL values at Maloney's and Blanches monitoring stations A in 2001, 2002 and 2003 is shown in Table 7.1. These suggest a relatively high degree of accuracy and precision in SDL measurements for pH and EC, but greater variability in DO measurements.

Numbers in brackets are standard errors.

<table>
<thead>
<tr>
<th></th>
<th>pH (µmol L⁻¹)</th>
<th>DO (µmol L⁻¹)</th>
<th>EC (dS m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>Blanches</td>
<td>0.05 [0.05]</td>
<td>6 [6]</td>
</tr>
<tr>
<td></td>
<td>Maloneys</td>
<td>0.11 [0.03]</td>
<td>7 [7]</td>
</tr>
<tr>
<td>2002</td>
<td>Blanches</td>
<td>-0.18 [0.09]</td>
<td>42 [18]</td>
</tr>
<tr>
<td></td>
<td>Maloneys</td>
<td>-0.13 [0.04]</td>
<td>36 [9]</td>
</tr>
<tr>
<td>2003</td>
<td>Blanches</td>
<td>0.07 [0.04]</td>
<td>24 [30]</td>
</tr>
<tr>
<td></td>
<td>Maloneys</td>
<td>0.11 [0.01]</td>
<td>34 [5]</td>
</tr>
</tbody>
</table>

7.3.4. Sample collection and analysis

Drain water samples were collected opportunistically at stations A and B. Sampling intensities were flow dependant, ranging from daily during high flow / flux periods, to every ~2 - 10 days during periods of low to intermediate flow / flux and none during prolonged periods of no outflow. Sampling was timed to coincide with outflow periods where possible to ensure accurate representation of discharge water. Water samples were collected from 0 to 0.3 m below the surface at centre channel using a clean 10 L plastic bucket thoroughly pre-rinsed with the drain water to be collected. Two 250 ml sub-samples were collected in clean (acid rinsed, distilled water flushed) polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times. Visible air bubbles were excluded prior to sealing the cap and samples placed in cold storage (approx. 4°C).

One 250 ml sub-sample was analysed for titratable acidity to pH 5.5 within 48 hours of sample collection (APHA (1995), 2310B - including the peroxide oxidation step).
Groundwater samples from the sulfuric horizons at Maloneys backswamp, which are referred to in this study, were collected and analysed according to the procedures outlined in Johnston et al. (2003b). A series of estuary water samples were collected from the Clarence River along the salinity gradient during a low flow period in January 2004. Samples were collected in clean (acid rinsed, distilled water flushed) polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times and analysed for alkalinity according to Rayment and Higginson (1992).

7.3.5. Water levels

Drain water levels were monitored hourly with capacitance probes (Dataflow - model 392, accuracy ± 0.01 m) near the backswamp margin (station B), immediately inside the floodgates (station A), and outside the floodgates in the adjacent estuary. Capacitance probes were installed in 5.5 cm diameter slotted PVC pipes and surveyed to AHD. A series of piezometer wells were also installed in the backswamps at each site perpendicular to the drain (Fig. 7.2). Each piezometer consisted of a 10 cm diameter hand augured hole about 1.4 m deep, with a 5.5 cm diameter slotted and screened PVC pipe inserted. This was backfilled with clean sand and auger cuttings in the screened zone and then with bentonite to the surface. Each well was surveyed to AHD. Water levels in each piezometer were also logged hourly using capacitance probes. All capacitance probes were cleaned and calibrated every 2 - 3 months.

7.3.6. Drain flow and flux calculations

Flow velocity in the drains was measured using Doppler sensors (Starflow - 6526-51) with a velocity range of 0.021 m s⁻¹ to 4.5 m s⁻¹. The scan interval was set for 30 seconds and the hourly mean, maximum and minimum logged. The Starflow units were located in the
centre of the channel at the floodgate culvert (centre of one culvert at Blanches). Culvert dimensions and Starflow locations were surveyed to AHD. The Starflow units also measured drain water level using a hydrostatic pressure sensor vented to the atmosphere. Checks were undertaken using a calibrated current meter in the Doppler field of view under a range of flow conditions (>1 to ~0.1 m s^{-1}) and yielded flow velocities within \( \pm 10\% \) of the Doppler sensor. Daily drain outflow and inflow volumes \( (Q_d) \) were derived from the sum of the hourly flow volumes \( (Q_h) \) using Eq. (7.2),

\[
Q_h = V_h \cdot A_h
\]  

(7.2)

where \( V_h = \) mean hourly flow velocity, \( A_h = \) mean hourly cross-sectional area of water in the culvert.

Because the drainage waters contain varying concentrations of dissolved acidic metal cations (i.e. \( Fe^{2+}, Al^{3+} \)), titratable acidity (TA) was used as the basis for acid flux calculations in this study (Cook et al. 2000a). Over short time periods there can be strong correlations between TA and pH (Fig. 7.3). The hourly acid flux estimates presented in this study were calculated using SDL values to infer ionic concentrations in drain water according to Eq. (7.3).

\[
F_h = (Q_h \cdot C_h)
\]  

(7.3)

Where \( F_h \) is the hourly flux estimate and \( C_h \) is hourly logger inferred TA. These hourly acid flux estimates were made during a short period before, during and after a single floodgate opening event at Maloney's drain where there was intensive spot monitoring/sampling and a high correlation between the pH values recorded by the SDL at station A and sample titratable acidity (Fig. 7.3). By fitting a regression equation to the data shown in Figure 7.3, the hourly pH values recorded by the SDL at station A were used to infer hourly changes
in drain water TA ($C_h$) during this event. This hourly method is better able to account for the rapid variations in drain water chemistry that can accompany tidally modulated outflow periods (i.e. increasing acidity during the ebb tide cycle) and thus provides a more accurate integration of the area under the velocity and concentration curves than daily methods. Other acid flux estimates used in this study are calculated using the methods outlined in Johnston et al. (2004).

**Figure 7.3.** Correlation between drain water pH (as measured by the submersible data logger at station A) and titratable acidity at Maloney's drain two days before, during and three days after a floodgate opening event (of four days duration), which is shown in detail in Fig. 7.15.
7.4. Results and Discussion

7.4.1. Existing drain water quality conditions

Both drains experienced prolonged periods with high acid and low dissolved oxygen levels during the period of monitoring (Fig. 7.4). Maloney's drain water was more frequently and more intensely acidic than Blanches drain, and had mean daily pH values below 5.5 for about 35% of the time at monitoring station A (Fig. 7.4a). The mean daily dissolved oxygen concentration in drain water at monitoring station A was less than 60% saturation for 80% and 55% of the time at Maloney's and Blanches respectively (Fig. 7.4b).

Figure 7.4. Cumulative frequency distribution of a) mean daily drain water pH and b) mean daily dissolved oxygen at Blanches and Maloney's drains between December 2000 and October 2003. Data for both sites are based on measurements made by SDL located at monitoring stations A.
Floodgates were opened periodically during the monitoring period under a variety of hydrological conditions (high outflow / low outflow), allowing a number of individual opening events to be assessed. Most opening events were between 2 - 7 days in duration, though some prolonged (>3 weeks) partial openings occurred at Maloney's drain. Seasonal conditions had a controlling influence on drain water quality and oscillated between wet periods with substantial outflow and generally poor water quality (low pH, low DO), and dry periods with no or minimal outflow, but high pH and variable DO (Fig. 7.5).

**Figure 7.5.** An overview of seasonal hydrological conditions during the monitoring period, displaying the mean daily groundwater levels (well no. 2), mean daily drain water pH and rainfall recorded at the Maloney's study site. Distinct wet periods with low drain water pH, when groundwater levels were consistently above local low tide minima (dashed line), and dry periods with generally high drain water pH are identified.

### 7.4.2. Changes in drain water pH

The low pH which typically occurred after wet periods in both Blanches and Maloney's drains were a result of outflow of either acid groundwater or surface water from the backswamp acid sulfate soils (Johnston *et al.* 2004). When antecedent drain water pH was low and floodgates were opened, sharp increases in drain water pH were commonly observed (Fig. 7.6). Expectedly, pH values during opening periods showed a degree of
tidal modulation and there was an increasing lag in the pH response time with increasing distance from the estuary (Fig. 7.6a and 7.6b).

**Figure 7.6.** Changes in drain water pH in relation to drain water levels at Blanches drain during two separate floodgate opening events of a) 48 hrs and b) 96 hrs duration. The total volume (ML; 1 ML = m$^3$.10$^3$) of estuarine water inflow during each day of the floodgate opening event is shown in bold type.
A notable and reoccurring feature was a reversion in drain water pH once floodgates were closed (Fig. 7.6). This pattern of pH reversion was particularly apparent during a period of regular floodgate opening events at Blanches drain, where reversion began to occur almost immediately following the cessation of inflow (Fig. 7.7). The pH reversions shown in Fig. 7.7 are likely to be a result of continued inputs of acid sulfate contaminated water from the backswamp, as indicated by the sustained low volume outflow.

**Figure 7.7.** Changes in a) mean daily drain water pH at Blanches drain monitoring stations A and B in relation to b) floodgate opening events and inflow / outflow volumes.

It is logical that any increases in the pH of acidic drain water due to dilution / neutralisation with estuarine water during a given floodgate opening event are likely to be proportional to tidal inflow volumes. Detailed analysis of one individual floodgate opening event at Maloney's drain conforms to this hypothesis and shows a strong correlation between the increase in drain water pH and the cumulative inflow volume per flood tide cycle (Fig. 7.8).
Figure 7.8. Increases in drain water pH at Maloneys drain (station B) in relation to the cumulative inflow volume per flood tide cycle during a four day floodgate opening event. Both pH and inflow volume are based on hourly measurements and data points correspond to inflow periods only. All data is based on the floodgate opening event shown in Figure 7.15. The pH increase was calculated by difference from the initial drain water pH immediately prior to floodgate opening. \( r^2 \) is derived from a second order logarithmic regression.

The acid buffering / dilution capacity of tidal ingress waters within a drain can be rapidly exceeded when soluble acidity from the sulfuric horizon is transported to the drain after rainfall (Fig. 7.9). Figure 7.9 shows a period immediately before and after a rainfall event at Maloneys drain whilst the floodgates remained open. Groundwater gradients (the water level difference between well no. 2 and monitoring station B) were influent in the period immediately before and during the initial part of floodgate opening. Both pH and DO levels showed some increase and stabilisation during this initial opening period. A rainfall event on 2 June caused a rise in the backswamp groundwater levels and the development of effluent
Figure 7.9. a) Drain and groundwater levels, b) drain water pH and c) dissolved oxygen in relation to d) rainfall at Maloney's study site during a period before, during and after a floodgate opening event.

groundwater gradients adjacent to the drain in the ASS backswamp. Despite the floodgates remaining open for several days after the rainfall event, pH levels experienced a sharp decline at both monitoring stations. DO levels at monitoring station B also decreased
markedly. While the closure of floodgates on 5 June may have exaggerated or accelerated
the observed decreases, they were clearly well underway before floodgate closure.

The titratable acidity of sulfuric horizon groundwater at Maloneys can exceed 50 mmol L⁻¹
(Johnston et al. 2003b) which is about 25x the acid buffering capacity of pure seawater.
Therefore, even small volumes of groundwater seepage can have a large impact upon drain
water pH, and also potentially DO due to oxidation of Fe²⁺. The sulfuric horizons at
Maloneys backswamp have very high hydraulic conductivity (Johnston et al. 2004) which
makes this drain prone to very rapid changes in water quality conditions in response to
changing groundwater gradients, regardless of whether floodgates are open or not.

There are several possible explanations for the increase in pH recorded at the monitoring
stations during the floodgate openings. These include a) dilution with tidal ingress water,
b) neutralisation by acid buffering agents within tidal ingress water, c) displacement of
drain water as a poorly mixed ‘slug’ by tidal ingress water, or any combination of the
above. The sulfuric horizon groundwater in the study site backswamps has a distinctive
EC:H⁺ signature, which is very different from that of Clarence River estuarine water (Fig.
7.10). The EC:H⁺ signature of drainage water immediately before and during three separate
floodgate opening events is also depicted in Fig. 7.10. A clear shift in EC:H⁺
characteristics from a signature resembling that of sulfuric horizon groundwater towards
that of estuarine water occurred during these floodgate openings (Fig. 7.10). The observed
direction of response during floodgate opening conforms only partially with the theoretical
slope of acid neutralisation by 1:1 addition of estuarine water. This suggests that
substantial dilution of drain water also took place during these events and may be
indicative of displacement type flow.
Figure 7.10. Changes in drain water H$^+$ concentrations in relation to EC, before and during three individual floodgate opening events. Short arrows indicate the direction of change during the floodgate opening phase. The EC:H$^+$ signature of sulfuric horizon groundwater (from the Maloney's site), and non-acid estuary water (measured during a dry period) are also shown. Dashed lines represent the theoretical change in H$^+$ that would occur in relation to EC due to neutralisation of acidity by 1:1 addition of estuary water (based on alkalinity and EC data presented in Figure 7.17). The H$^+$ concentration of drain and estuary waters is based on pH and the sulfuric horizon groundwater is derived from titratable acidity.

7.4.3. Changes in drain water DO

Drain water dissolved oxygen at both study sites often displayed large diurnal fluctuations associated with photosynthesis / respiration cycles, particularly during warmer months (Fig. 7.11). Such behaviour is fairly typical of poorly flushed eutrophic systems. Influx of estuarine water with floodgate opening exhibits some potential to moderate extreme
diurnal fluctuations in DO, as evident during the opening event shown in Figure 7.11.

![Figure 7.11](image)

**Figure 7.11.** Drain water levels and moderation of diurnal fluctuations in dissolved oxygen saturation during a floodgate opening event at Blanches drain, in relation to solar radiation.

Sustained low DO was observed in both drains during a wet period following flooding (Johnston et al. 2003a). During this post-flood period (~February to May 2001) there were a series of floodgate opening events at Blanches drain. Examples of these events are shown in Figure 7.12. Rapid, tidally modulated increases in DO are evident during the floodgate opening phase, with the peak of the increase during a given day approximately proportional to the estuarine water influx volume (Fig. 7.12). Equally rapid declines in DO were observed on these occasions immediately following floodgate closure. The rapid declines were related to the cessation of tidal ingress and the sustained outflow of water with very low DO from the backswamp during this period. At Blanches drain a positive
linear correlation \((r^2 = 0.74)\) was observed between the mean daily drain water DO and the daily inflow:outflow volume ratio over a two month period (Fig. 7.13).

**Figure 7.12.** Changes in drain water DO in relation to drain water levels at Blanches drain during two separate floodgate opening events of a) 72 hrs and b) 114 hrs duration. The total volume (ML; 1 ML = \(\text{m}^3.10^3\)) of estuarine water inflow during each day of the floodgate opening event is shown in bold type.
The DO of eutrophic aquatic environments is highly variable and is influenced by a wide range of biotic and abiotic factors (Stumm and Morgan 1981). There were a number of occasions when the changes and trends in DO occurring during floodgate opening were relatively minor and difficult to distinguish from the high levels of background variability (data not shown).

Figure 7.13. Positive linear correlation between mean daily drain water dissolved oxygen levels at Blanches drain (station A) and the daily inflow:outflow volume ratio. Note that inflow only occurred during floodgate opening events. Based on measurements between 15/3/01 to 19/5/01. Flow volumes measured at station A.

7.4.4. Flow volumes

Opening floodgates has potential to reduce the net drainage rates and cause net influx of estuarine water by reducing and potentially reversing the mean longitudinal drain water gradient. This was demonstrated by data from Blanches drain (Fig. 7.14) which shows large openings clearly capable of causing significant net influx and alteration of the mean
longitudinal drain water gradient. Slower drainage rates will enhance the retention time of water in floodplain storage basins, increasing the potential for evaporative efflux. However, this effect will largely be confined to the floodgate opening period.

Figure 7.14. Net drain discharge volume in relation to the mean daily longitudinal drain water gradient at Blanches drain. Net inflows associated with floodgate opening are indicated by the arrows.

7.4.5. Interactions with acid groundwater

Detailed monitoring at Maloney’s drain during a floodgate opening event demonstrated that under certain circumstances a short duration floodgate opening has potential to enhance the export of acidity from the drainage system (Fig. 7.15). The following points outline the sequence of events and key features associated with this opening enhanced acid export. Figures in brackets are derived directly from the Maloney’s system.

- Before floodgate opening the groundwater in the backswamp ASS was close to the minimum ebb tide influenced drain water level [approximately -0.2 m AHD]. There was no effluent groundwater gradient and minimal seepage of groundwater to
drainage system (Fig. 7.15a). Drain water at station B was still acidic from previous outflow (Fig. 7.15b).

- The upper sulfuric horizons in the backswamp have very high $K_{sat}$ [~120 m day$^{-1}$ - Johnston et al. 2004]. The shallow groundwater in the backswamp is highly acidic and rich in sulfide oxidation products (Johnston et al. 2003b).

- Floodgates are opened and an influent groundwater gradient develops during the flood tide cycles of the opening phase (Fig. 7.15a). Recharge of the groundwater potentiometric level occurs in the near drain zone over four days [by ~0.12 m at 10 m from the drain] to a point above the minimum ebb tide drain water level (Fig. 7.15a). Dilution of shallow groundwater with estuarine influx water occurs in the first few meters adjacent to the drain, altering the shallow groundwater chemistry (Fig. 7.16).

- Floodgates are closed and effluent groundwater gradients develop during subsequent ebb tide cycles, promoting groundwater seepage into the drainage system. Acidity is transported to the drain with this seepage water, enhancing acid export during the period immediately following floodgate closure (Fig. 7.15b, 7.5c and 7.15d). Partial reversion of the near drain shallow groundwater chemistry occurs within several days after floodgate closure (Fig. 7.16).

During this opening event there was a net influx of estuarine water and groundwater levels responded to tidal forcing across the backswamp over 300 m from the drain (Johnston et al. 2004). The changes in shallow groundwater chemistry following floodgate opening (Fig. 7.16) clearly demonstrates there was appreciable dilution of shallow groundwater with estuarine influx water in at least the first few meters adjacent to the drain.
Figure 7.15. Changes in a) drain and groundwater levels, b) drain water pH, c) drain outflow volumes and d) acid flux rates before, during and after a four day floodgate opening event at Maloney's drain. Negative values for outflow volume represent tidal ingress.

While the total amounts of acidic products exported following this opening event were quite small (maximum ~770 mol H⁺ day⁻¹), it demonstrates the principle of near drain zone recharge followed by seepage of ASS groundwater back into the drainage system following a short duration floodgate opening event. The potential for such an interaction to
occur in any given drainage system will be related to a number of factors including:

a) The hydraulic conductivity of the adjacent ASS soils.

b) The chemistry of both shallow groundwater and estuarine influx water.

c) The development of effluent groundwater gradients following floodgate closure. This will be related to the degree of near drain groundwater recharge and the low tide minima occurring immediately after the event.

Figure 7.16. Sulfuric horizon groundwater a) titratable acidity, b) Cl, c) dissolved Fe and d) ORP in relation to distance from the drain before, during and after the floodgate opening event shown in Figure 7.15. Samples collected from a transect parallel to the piezometer transect shown in Figure 7.2.

An identical opening event at a similar site, but one with low hydraulic conductivity ASS, and/or a relatively high and stable drain water level with low tidal amplitude after the floodgate closure, would likely result in far less acid groundwater seepage into the drainage system.
7.4.6. Estuary water acid neutralisation capacity

Alkalinity in the Clarence River estuary is strongly correlated with the salinity regime (Fig. 7.17) in a similar manner to that reported in other Australian estuaries (Indraratna et al. 2002). While there is substantial buffering capacity at EC values approaching that of seawater (equivalent to \( \approx 2.3 \) mmol H\(^+\) L\(^{-1}\)), this decreases to less than 0.8 mmol H\(^+\) L\(^{-1}\) once the EC reaches 10 dS m\(^{-1}\). The EC at monitoring station A at both Blanches and Maloneys drains was above 10 dS m\(^{-1}\) for about 50% of the time during the study period (Fig. 7.18a). Higher EC values corresponded with dry periods and small volumes of estuary water leaking into the drain near the floodgates. However, over 95% of both the cumulative acid export and total outflow volumes recorded from both sites took place during wet periods when the mean daily drain water EC was <5 dS m\(^{-1}\) (Fig. 7.18b and 7.18c). Hence, the periods when marine derived tidal buffering capacity is most required for acid neutralisation corresponds with periods when it is least likely to be available.

![Correlation between Clarence River estuary water EC and alkalinity (expressed as bicarbonate equivalent).](image)

**Figure 7.17.** Correlation between Clarence River estuary water EC and alkalinity (expressed as bicarbonate equivalent). Samples collected during a low flow period in January 2004.
Figure 7.18. Cumulative frequency distribution of a) mean daily drain water EC, b) acid flux in relation to mean daily drain water EC and c) flow volumes in relation to mean daily drain water EC at Blanches and Maloney's drains. EC data for both sites is based on measurements from monitoring station A.
7.4.7. Overtopping of low lying land

Low elevation ASS backswamps such as Blanches and Maloney’s are about 0.6 m below the maximum high tide recorded at their floodgates (Table 7.2). Estuarian water with high marine salt concentrations is relatively common at both study sites (Fig. 7.18a). A key impediment to maintaining a higher frequency, magnitude and duration of floodgate opening events is the risk of saline overtopping adjacent land which is currently used for agriculture. This situation is relevant to a number of ASS backswamps on NSW coastal floodplains which are situated in similar relative topographic / tidal maxima contexts. Tidal forecast charts are one of the main management tools currently used by landholders to manage the risk of overtopping i.e. by opening floodgates during neap tide phases only. However, tidal anomalies occur on the NSW coastline and can lead to ocean tides in excess of 0.5 m above predicted levels. This combination of features places significant restrictions upon floodgate management in drains bisecting low elevation backswamps.

Table 7.2. Approximate backswamp surface elevation ranges at Blanches and Maloney’s in relation to the maximum recorded spring tides in the adjacent estuary during 2001 - 2003.

<table>
<thead>
<tr>
<th>ASS Backswamp surface elevation range (m AHD)</th>
<th>Maximum recorded spring tide (m AHD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanches -0.1 to 0.15</td>
<td>0.73</td>
</tr>
<tr>
<td>Maloney’s 0.0 to 0.25</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Higher frequency and duration of floodgate opening is only likely to be undertaken by landholders when there is a reliable capacity to control drain water levels and prevent overtopping of land. Manual winch gates provide relatively poor control of drain water levels and are subject to operator failure. Other types of floodgate opening devices, such as automatic mini-tidal floodgates, provide automatic closure and far greater drain water level
control (Johnston et al. 2003d). Such devices may help overcome the limitations to floodgate opening frequency associated with manually operated systems.

### 7.5. General discussion and conclusions

Floodgate opening can improve in-drain water quality, decreasing acidity, raising DO and moderating diurnal DO fluctuations. Induced changes in drain water quality occur within the context of a highly dynamic and variable aquatic environment over which antecedent seasonal conditions exert a primary influence. The extent and stability of any improvement appears to be largely dependant upon the frequency, magnitude and duration of floodgate opening and the relative interaction between both the volume and quality of drainage outflow water and in-flowing estuarine water. There are also substantial limitations and complexities, particularly in relation to short duration opening events. Improvements can often be followed by relatively rapid reversion to pre-opening conditions upon floodgate closure, depending on antecedent conditions. Prolonged, frequent tidal exchange (i.e. each tidal cycle) is likely to help minimise such reversions and help promote more stable improvements in drain water quality.

This study demonstrated the potential for a short duration floodgate opening event to increase acid export by causing recharge of groundwater levels near the drain during the opening phase and enhanced seepage of acidic groundwater back into the drainage system after floodgate closure. This is most likely to be an issue in ASS soils with very high $K_{\text{sat}}$ and very poor groundwater quality and highlights the importance of appropriate site assessment prior to the adoption floodgate opening strategies.

Floodgate opening can reduce net drainage rates by altering longitudinal drain water
gradients and may cause significant net inflow during dry periods. While overtopping of saline tidal water in low elevation ASS backswamps represents a major impediment to controlled floodgate opening, this has the potential to be overcome using automated water exchange device designs that provide a high degree of drain water level control.

5. Acknowledgements

We thank the Blanches and Maloneys landowners for their assistance and cooperation. The contribution of B. Makins to many aspects of the field work is also gratefully acknowledged. We also thank Clarence River County Council and the Department of Infrastructure, Planning and Natural Resources for assistance and access to data. This study was funded by Land and Water Australia, Acid Soil Action, Sugar Research and Development Cooperation, Acid Sulfate Soils Program and NSW Agriculture.
Chapter 8

Opening floodgates in coastal floodplain drains: effects on tidal forcing and lateral transport of solutes in adjacent groundwater

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8.1. Abstract

The effects of opening tidal barriers (floodgates) upon tidal forcing and lateral transport of solutes in shallow groundwater adjacent drains was investigated at two sites on a coastal floodplain. The sites had contrasting geomorphology, soil texture and sediment hydraulic properties. The site with lower hydraulic conductivity (0.3 - 0.9 m day\(^{-1}\)) soils (Romiaka) also had a higher elevation and effluent trending potentiometric gradients. While floodgate opening at Romiaka enhanced the amplitude of pre-existing tidal forcing in adjacent shallow groundwater, altering potentiometric gradients and causing some salt seepage, lateral solute movement from the drain was highly attenuated (<10 m). The site with very high hydraulic conductivity soils (Shark Creek; >125 m day\(^{-1}\)) had a lower elevation and seasonally fluctuating potentiometric gradients. The introduction of a tidal signal through floodgate opening at Shark Creek caused tidal forcing of groundwater over 300 m from the drain. Floodgate opening at this site also caused changes in groundwater potentiometric gradients and led to the incursion of saline drain water into shallow groundwater over 80 m from the drain. Lateral movement of solutes was relatively rapid, due to macropore flow in oxidised acid sulfate soil horizons, and caused substantial changes to the chemical composition of shallow groundwater. Conversely, when groundwater potentiometric gradients were effluent at this site there was substantial lateral outflow of acid groundwater into drains. This study highlights the importance of assessing the hydraulic properties of soils next to drains on coastal floodplains prior to opening floodgates, particularly in acid sulfate soil backswamps, in order to prevent unintended saline intrusion into shallow groundwater.
8.2. Introduction

Thousands of kilometres of artificial drains have been constructed on the coastal floodplains of eastern Australia for agricultural and flood mitigation purposes. The coastal floodplains of eastern Australia are underlain by large areas of acid sulfate soils (Naylor et al. 1995) which substantially influence drain discharge water quality (White et al. 1997). Many drains have episodic poor water quality and seasonally discharge water with low dissolved oxygen, high acidity and acidic metals cations, into adjacent estuaries (Sammut et al. 1996; White et al. 1997; Wilson et al. 1999; Blunden et al. 2000; Cook et al. 2000a; Johnston et al. 2003a).

Most coastal floodplain drains also have one way tidal flapgates (floodgates) near the discharge point. These floodgates allow drainage outflow, but prevent tidal water ingress. This compounds the accumulation poor quality water in the drain (Indraratna et al. 2002) and can help lower adjacent groundwater to low tide level. Opening floodgates to allow tidal exchange with estuarine water during non-flood periods has been promoted as a means of improving drain water quality (Haskins 1999; Blunden 2000; Indraratna et al. 2002). Opening floodgates may also increase the lateral seepage of saline tidal water into shallow groundwater adjacent the drain (Johnston et al. 2003d). This is a concern to floodplain agricultural industries with salt sensitive crops such as sugar cane.

On coastal floodplains there is typically a transition zone within the aquifer adjacent to tidal channels where mixing between low salinity groundwater and saline tidal water occurs (Reilly and Goodman 1985). Exchange of solutes between natural tidal channels and adjacent groundwater and sediment has been examined in a number of studies (Harvey et al. 1987; Harvey and Odum 1990; Harvey and Nuttle 1995; Hughes et al. 1998; Tobias
et al. 2001). Lateral transport and exchange of solutes in these transition zones is typically in a highly dynamic state of quasi-equilibrium and is influenced by factors such as sediment hydraulic properties, potentiometric gradients, regional groundwater inputs, precipitation, evapotranspiration, elevation and tidal infiltration. Altering the balance of shallow groundwater inputs or outputs will cause an equilibrium shift, resulting in expansion, contraction and/or displacement of the freshwater - saltwater transition zone (Reilly and Goodman 1985). For example, in a wetland fringing a tidal creek Tobias et al. (2001) documented substantial changes in sediment salinity in response to seasonal variation in regional groundwater inputs. Excessive groundwater extraction can also cause extensive lateral seepage of salt into shallow aquifers on coastal floodplains (Howard and Mullings 1996; Mas-Pla et al. 1999).

Tidal forcing of adjacent groundwater is a common feature in coastal environments and can be an important mechanism of porewater movement in saturated and intertidal zones (Hughes et al. 1998). In shallow unconfined aquifers, tidal forcing can enhance the extent of saltwater ingress and can also alter the configuration of solute concentration contours, particularly near the top of the water table (Ataie-Ashtiani et al. 1999). Predictive modelling of saline seepage into unconfined coastal aquifers via tidal forcing is relatively complex. There are a number of potential sources of error, including heterogeneity in sediment hydraulic properties (Beven and Germann 1982; Schultz and Ruppel 2002) and failure to adequately integrate the effects of tidal fluctuations on hydraulic gradients (Serfes 1992). As result, tidally driven subsurface fluxes of groundwater are often ignored in groundwater flux estimates (Tobias et al. 2001).

With the exception of Indraratna et al. (2002), there have been few published studies
examining lateral solute movement and tidal forcing adjacent artificial drains which become newly subjected to tidal influences through floodgate opening. This paper aims to characterise and document the effects of floodgate opening on the extent of tidal forcing and lateral solute transport in shallow groundwater adjacent to several tidal drains with contrasting geomorphology and sediment hydraulic properties. This information will be used to identify some key factors which ideally should be assessed as part of any risk management strategy employed by floodgate managers prior to opening floodgates.

8.3. Materials and methods

8.3.1. Site description

The study sites, Romiaka and Shark Creek, are located on the Clarence River coastal floodplain (Fig. 8.1). The large coastal floodplain (2600 km$^2$) is situated in an infilled river valley on the east coast of Australia (29°30' S, 153°15' E) and the estuary is regarded as a mature barrier system (Roy 1984). Infilling and formation of the floodplain during the Holocene postglacial marine transgression was characterised by bi-directional sedimentation, with terrestrial sediments accreting in a seaward direction in a low energy basin behind an expanding sand barrier of marine origin at the estuary mouth (Roy 1984). Both study sites consist of unconsolidated Holocene sediments and the aquifers examined in this study are unconfined and located within 1.5 m of the ground surface.

The Romiaka site is located on an alluvial plain on the south-eastern prograding edge of a deltaic island in the lower estuary, and is adjacent to a large tidal channel (Fig. 8.1c). The site is close to the ocean (~6 km) and subject to strong marine influences during its geomorphic evolution, with high tidal energy and inputs of marine sediments from the coastal barrier. Fluvial sediments have been deposited during flood periods on top of
Figure 8.1. a) Location of Clarence River catchment, b) the lower Clarence River floodplain - showing unconsolidated Quaternary sediments and upland areas, c) Romiaka and d) Shark Creek study sites.

largely sandy sub-sediments and the surface elevation of most of the site is 1 - 2 m Australian Height Datum (AHD; 0 AHD ~mean sea level). The adjacent Romiaka channel is generally saline (>30 dS m\(^{-1}\)) depending on seasonal flow conditions, and experiences semi-diurnal tides up to 1.4 m in range during spring cycles. Vegetation at the site is mostly sugar cane with fringing bands of salt marsh and mangroves adjacent Romiaka
Channel. There are two main drains at the study site. The first drain (Tidal drain 1 - Fig. 8.1c), located between the sugar cane and fringing salt marsh, is connected to Romiaka channel and has been subject to tidal influence since it’s initial construction (~pre 1980). The second drain is also connected to Romiaka channel and consists of three sections. The lower section is open to the main channel and subject to continual tidal influence (Tidal drain 2). The mid-section is located behind a set of one way tidal floodgates that prevent tidal influence, but which were opened periodically during this study (Transition drain). An upper section is located behind a second set of one way floodgates which remained closed during this study and was not subject to any direct tidal influence (Non-tidal drain).

The Shark Creek site is located in an acid sulfate soil (ASS) backswamp adjacent Shark Creek, a small tidal tributary on the Clarence River floodplain (Fig. 8.1d). The backswamp is isolated from Shark Creek by a narrow, fringing distributary levee (1 to 3 m AHD). The backswamp is an infilled estuarine sub-embayment with low surface elevations (<0.2 m AHD). The sub-embayment is bounded by sandstone upland to the east and west and is further from the ocean (>30 km) and was subject to less marine influence during infilling than the Romiaka site. A lower energy environment prevailed during infilling stages and backswamp sediments are mostly fine grained (Lin and Melville 1993). Backswamp soil texture in the sulfuric and upper sulfidic horizons is predominantly silty clay to clay, with cumulative particle size analysis showing over 92% (by mass) was smaller than 60 µm (Lin and Melville 1993). The backswamp soils are Hydraquentic Sulfaquepts (Soil Taxonomy, Soil Survey Staff 1998). Sulfidic sediments are typically found within 0.8 to 1 m below the ground surface in the backswamp (Lin and Melville 1993; Johnston et al. 2003b) and are overlain by a highly acidic sulfuric horizon with Fe (III) mineral and jarosite mottles. According to Lin and Melville (1993) infilling at this site occurred in three
stages, firstly a saline, tidal stage in which a layer of pyrite rich sediments were deposited, followed by a brackish lagoonal phase and finally overbank fluvial deposition of freshwater sediments which formed the distributary levee. The formation of the distributary levee fringing Shark Creek by overbank deposition is an important feature because it effectively isolated the backswamp from direct tidal influence, even though the backswamp elevation is now ~0.3 - 0.4 m below local mean high water in the adjacent creek. The tidal range in Shark Creek is about 0.7 to 0.9 m during spring tide cycles and the salinity is often less than 10 dS m\(^{-1}\), though it can reach 20 - 30 dS m\(^{-1}\) during low flow conditions. A large network of artificial drains has been constructed in the backswamp. The main drain was excavated through the distributary levee and discharges into Shark Creek via a culvert with floodgates.

8.3.2. Meteorological monitoring

At each site temperature and rainfall were recorded hourly or every 30 minutes with an EIT E-Tech automatic weather station (Fig. 8.1c and Fig. 8.1d). The mean annual ratio of rainfall (P) to evapotranspiration (ET) by the coast at Yamba is 1.19 (30 year mean - assuming ET = 0.8 x pan-evaporation, Australian Bureau of Meteorology, unpublished data). Annual rainfall on the lower Clarence floodplain tends to decrease with increasing distance inland. At Grafton (approximately 40 km inland from the coast) the ratio of P to ET is 0.81.

8.3.3. Groundwater and drain water monitoring

A series of 5.5 cm diameter, partially screened PVC piezometer wells were installed at each site perpendicular to the drains. Well location, spacing and screen intervals are provided in Table 8.1. Water level measurements were recorded in each well every 30 minutes or hour using a Dataflow capacitance probe and 392 logger (precision ± 0.001 m;
accuracy ± 0.01 m). Dataflow capacitance probes were surveyed to AHD, freshly calibrated prior to installation and cleaned / re-calibrated every 60 - 90 days. Groundwater electrical conductivity (EC), temperature and water level were also logged at hourly or 30 minute intervals in selected wells using a Greenspan CTDP300 submersible data logger (SDL). The wells housing each CTDP300 were made of 10 cm diameter PVC with a screened interval bracketing the zone in which the greatest water level fluctuations were deemed likely to occur (Table 8.1).

**Table 8.1. Piezometer well identification, horizontal spacing and slotting screen intervals.**

<table>
<thead>
<tr>
<th>Location / transect no.</th>
<th>Well no.</th>
<th>Distance A (m)</th>
<th>Screen interval (m AHD)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Romiaka site</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>R1-1</td>
<td>0.5</td>
<td>0.58 to -0.98</td>
</tr>
<tr>
<td></td>
<td>R1-2</td>
<td>1.5</td>
<td>0.44 to -0.84</td>
</tr>
<tr>
<td></td>
<td>R1-3</td>
<td>2.5</td>
<td>0.42 to -0.82</td>
</tr>
<tr>
<td></td>
<td>R1-4</td>
<td>4.0</td>
<td>0.45 to -0.85</td>
</tr>
<tr>
<td></td>
<td>R1-5</td>
<td>6.0</td>
<td>0.47 to -0.87</td>
</tr>
<tr>
<td></td>
<td>R1-6</td>
<td>10.0</td>
<td>0.39 to -0.79</td>
</tr>
<tr>
<td>R2</td>
<td>R2-1</td>
<td>0.5</td>
<td>0.16 to -0.25</td>
</tr>
<tr>
<td></td>
<td>R2-2</td>
<td>2.5</td>
<td>0.03 to -0.43</td>
</tr>
<tr>
<td></td>
<td>R2-3</td>
<td>4.0</td>
<td>0.05 to -0.35</td>
</tr>
<tr>
<td></td>
<td>R2-3WQ</td>
<td>4.0</td>
<td>0.66 to -0.14</td>
</tr>
<tr>
<td></td>
<td>R2-4</td>
<td>10.0</td>
<td>0.34 to -0.06</td>
</tr>
<tr>
<td><strong>Shark Creek site</strong></td>
<td></td>
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<td></td>
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<tr>
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<td>M1-1</td>
<td>2.0</td>
<td>0.40 to -1.20</td>
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<td>M1-2</td>
<td>10.0</td>
<td>0.36 to -1.16</td>
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<td></td>
<td>M1-3</td>
<td>63.0</td>
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<td></td>
<td>M1-4</td>
<td>335</td>
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<td></td>
<td>M1-5</td>
<td>410</td>
<td>0.10 to -0.90</td>
</tr>
<tr>
<td>M2</td>
<td>M2-6</td>
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<td>0.10 to -0.80</td>
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<tr>
<td></td>
<td>M2-7WQ</td>
<td>10.0</td>
<td>0.12 to -0.58</td>
</tr>
<tr>
<td></td>
<td>M2-8WQ</td>
<td>25.0</td>
<td>0.08 to -0.62</td>
</tr>
</tbody>
</table>

A All distances relative to the edge of adjacent drain bank.

B Groundwater water quality and water level monitoring well.
Drain water levels were recorded at drain monitoring stations (Fig. 8.1c and Fig. 8.1d) using a Dataflow capacitance probe and 392 logger housed in a slotted PVC pipe surveyed to AHD. Hourly measurements of drain water EC, pH, dissolved oxygen (DO) and temperature were made at each drain monitoring station with a Greenspan CS304 SDL. Each CS304 was housed in a slotted 10 cm diameter PVC pipe and positioned as close to centre channel as possible. EC was measured via a toroidal sensor, pH using a double junction Ag/Cl electrode and DO via a diffusion rod. The SDLs were cleaned, maintained and calibrated every 28 - 36 days.

8.3.4. Groundwater field measurements, sample collection and analysis

Groundwater EC and pH was measured *in situ* in the piezometer wells at the Romiaka site on a regular basis using freshly calibrated portable field equipment (TPS 90FLMV). At the Shark Creek site, groundwater samples were extracted periodically from the sulfuric horizons in freshly excavated 5 cm diameter unlined wells using a hand pump. Groundwater in each well was pumped continuously for several minutes immediately after excavation until largely free of suspended sediment. The pH, EC, redox potential and temperature were immediately measured using freshly calibrated portable field equipment (TPS 90FLMV). A minimum of two 250 ml sub-samples were collected in clean polyethylene bottles thoroughly pre-rinsed with the sample water a minimum of 4 times. Visible air bubbles were excluded prior to sealing the cap and samples placed in cold storage (~4°C). One 250 ml sub-sample was analysed for titratable acidity to pH 5.5 (APHA (1995), 2310B - including the peroxide oxidation step) within 24 hrs of sample collection. One 250 ml sub-sample was selected for further chemical analysis, and analysed for total Fe and total Al (ICP AES - USEPA 6010), dissolved Fe and dissolved Al (0.45 µm filtration, ICP AES - USEPA 6010), Cl⁻ and SO₄²⁻ (Ion chromatography - AHPA (1995), 4110).
8.3.5. Soils and hydraulic conductivity

Soil cores were collected at Romiaka adjacent to the piezometer transects using a hand auger. Cores were spaced at 0.5, 1.5, 2.5, 4, 6 and 10 m from the drain, profiles described according to McDonald et al. (1990) and the soil surface surveyed to AHD. Soil samples were collected at 0.05 m, 0.2 m and every 0.2 m thereafter to a depth of ~1.5 m. Select cores were also sampled at Shark Creek. Soil samples were oven-dried at 85°C within 48 hrs of collection and crushed to pass a 2 mm sieve. The EC of a 1:5 water extract was determined for each sample (Rayment and Higginson 1992). Particle size analysis was conducted on select samples from the Romiaka site using the method of Lewis and McConchie (1994).

The saturated hydraulic conductivity ($K_{\text{sat}}$) was assessed using auger hole slug tests (Bouwer and Rice 1976; Bouwer 1989). Tests were conducted in the piezometer wells at Romiaka. At Shark Creek slug tests were conducted in 5.5 cm diameter PVC wells that were placed in freshly hand augured, close fitting boreholes. A rubber collar was placed on the outside of the PVC well immediately above the slotting zone to obtain a tight seal with the bore hole and prevent preferential downward water flow along the well sides. The slotting zone was positioned within the sulfuric horizons. The slug was withdrawn by rapid hand pumping and the water level recovery rate recorded at two second intervals using a freshly calibrated 1.0 m capacitance probe (Dataflow 392). At least three replicate tests conducted in each well and $K_{\text{sat}}$ was calculated using the method of Bouwer (1989).

At Shark Creek the saturated hydraulic conductivity of the upper sulfuric horizons was also assessed using shallow pit bailing methods (Bouwer and Rice 1983). Shallow rectangular pits (about 0.5 m deep and 0.5 m$^2$) were excavated in the backswamp adjacent to slug test
8.3.6. EM38 surveying

A number of studies have successfully used EM38 measurements to determine rootzone salinity in areas with shallow saline water tables (Slavich and Peterson 1990; Bennett and George 1995). An EM38 can be used to obtain data over broad areas relatively rapidly. Line transect surveys were conducted perpendicular to the drains using a Geonics EM38 electromagnetic induction soil conductivity meter, which was operated in accordance with the manufacturers instructions (McNeill 1986). The EM38 has a coil spacing of 1 m and measures apparent soil electrical conductivity (EC\textsubscript{a}) in mS m\textsuperscript{-1} in either a vertical (EC\textsubscript{aV}) or horizontal (EC\textsubscript{aH}) dipole orientation. The mean of the EC\textsubscript{aV} and EC\textsubscript{aH} readings was calculated to provide a more uniform integration of soil profile EC\textsubscript{a} variation (Slavich 1990).

8.4. Results and discussion

8.4.1. Romiaka tidal drain 1

The stratigraphy and soil salinity at the piezometer transect adjacent Romiaka tidal drain 1 (R1) are shown in Fig. 8.2. Soil texture varied substantially down the profile (Fig. 8.2a). The sandy sub-soils were relatively uniform across the transect and had an average of 71\% by mass (s.e. = 0.2\%, n = 12) in the fine to medium-sand size classes (125 - 500 µm).
Figure 8.2. Romiaka transect R1 a) stratigraphy, piezometer well locations and piezometer slotting zone, b) soil EC (1:5 extract) and c) mean EC in relation to distance from the drain. Soil EC contours based on linear interpolation (n = 48).
However, they still contained a substantial fraction (23%) of finer material (<60 µm). The sandy sub-soils had an apedal massive structure with no visible macropores. The hydraulic conductivity of the sub-soils at transect R1 was relatively low given the texture (Table 8.2), which may be a result of fines blocking pore spaces around sand grains and the lack of structure.

Table 8.2. Mean saturated hydraulic conductivity values at the study sites.

See Materials and methods for details regarding the soil horizons these data apply to.

<table>
<thead>
<tr>
<th>Location</th>
<th>Mean K$_{sat}$ (m day$^{-1}$)</th>
<th>s.e.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Romiaka - R1</td>
<td>0.36</td>
<td>0.08</td>
<td>13</td>
</tr>
<tr>
<td>Romiaka - R2</td>
<td>0.89</td>
<td>0.18</td>
<td>16</td>
</tr>
<tr>
<td>Shark Creek</td>
<td>125</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>Shark Creek</td>
<td>184</td>
<td>37</td>
<td>7</td>
</tr>
</tbody>
</table>


$^B$ Bouwer and Rice 1983.

There was high soil salinity within about 4 m of the drain, particularly in the elevation range of 0.4 to 0.0 AHD, which corresponds with the inter-tidal range and the light clay and peat layer (Fig. 8.2b). It is possible that this light clay and peat layer may represent a buried salt marsh surface. Soil salinity decreased rapidly between 6 to 10 m from the drain. Spring tides in Tidal drain 1 can exceed 0.8 m AHD, leading to infrequent overtopping and infiltration of saline water within 4 - 6 m of the drain. Maximum soil EC$_e$ values at this transect (estimated using the method of Slavich and Peterson 1993) are in excess of 35 dS m$^{-1}$. There was a good agreement between soil EC (Fig. 8.2b) and the mean EC$_a$ determined from EM38 measurements (Fig. 8.2c). This was consistent at all the Romiaka site locations for which paired soil and EM38 sampling was conducted, with a strong positive linear correlation ($r^2 = 0.90$, n = 18) observed between mean soil EC (1:5 extract) in the upper 1 m of the profile and mean EC$_a$. 
Tidal forcing of the shallow groundwater was observed to a distance of at least 10 m in response to the tidal signal in the adjacent drain (Fig. 8.3). The tidal signal was not sinusoidal due to mud flats at an elevation of about 0.1 m AHD located near the drains outflow point. The groundwater level was highly responsive, with fluctuations in excess of 0.3 m per tidal cycle. The amplitude of forcing was attenuated with increasing distance from drain (Fig. 8.3). Mean potentiometric gradients were effluent during the period of observation (Fig. 8.4). This is an important feature which effectively limited the extent of salt seepage.
Figure 8.4. Water level dynamics in Tidal drain 1 and piezometers at transect R1 over a 30 day period from 1 to 30 June 2000.

8.4.2. Romiaka transition drain

The stratigraphy and soil salinity adjacent Romiaka Transition drain (transect R2) are shown in Fig. 8.5. The elevation of this transect was higher and it had a thicker alluvial topsoil than transect R1 (Fig. 8.5a). There was also increasing sand content with depth, though the sandy sub-soils were generally coarser near the drain bank (Fig. 5a). Particle size analysis on the sandy sub-soils within 4 m of the drain bank showed an average of 87% by mass (s.e. = 0.3%, n = 9) in the fine to medium-sand size classes (125 - 500 μm), but finer fractions (<60 μm) were still present and accounted for a mean of 9%. The sub-soils were apedal with a massive structure. The higher hydraulic conductivity at transect R2 compared to transect R1 accords with the slightly coarser nature of the sub-soils (Table 8.2).
Figure 8.5. Romiaka transect R2 a) Stratigraphy, piezometer well locations and piezometer slotting zone and b) soil EC (1:5 extract) in relation to distance from the drain. Soil EC contours based on linear interpolation \((n = 48)\) of sampling undertaken before floodgate opening.

Soil EC at transect R2 was highest within about 4 m of the drain (Fig. 8.5b) and was substantially lower than at transect R1. Fig. 8.5b is based on soil sampling undertaken before floodgate opening. The decline in soil EC between 6 to 10 m from the drain was similar to that observed at transect R1. The elevation of the saline-fresh transition zone at
transect R2 approximately corresponds to the local intertidal range and may reflect long term low volume seepage of salt water from the transition drain due to leakage though the floodgates.

Figure 8.6. a) Tidal forcing in shallow groundwater over an 11 day period at transect R2 immediately before and during floodgate opening. b) changes in groundwater gradients at 4 and 10 m from the drain, c) changes in drain water groundwater EC and d) rainfall.

Floodgates were opened for total of 57 days over a 71 day period, allowing tidal water into the transition drain. Groundwater levels were monitored from about three weeks prior to
the first opening. Tidal forcing was evident in groundwater up to 10 m from the drain before the floodgates were opened (Fig. 8.6a), though the closest possible tidal signal during this time was over 30 m away in Tidal drain 2. This suggests that tidal forcing may be a widespread feature in sandy sub-soils across this site. The amplitude of tidal forcing clearly increased immediately following floodgate opening and was attenuated with increasing distance from the drain (Fig. 8.6a). Floodgate opening also caused rapid, dynamic changes in groundwater gradients near the drain (Fig. 8.6b). While the drain water salinity increased from 15 dS m\(^{-1}\) to over 40 dS m\(^{-1}\) immediately after floodgate opening, there was very little change detected in groundwater EC at 4 m within the first few days of opening (Fig. 8.6c).

![Graph showing water level dynamics in the Transition drain and transect R2 piezometers during a) periods of floodgate closure (n = 22 days) and b) periods of floodgate opening (n = 57 days).](image)

**Figure 8.7.** Water level dynamics in the Transition drain and transect R2 piezometers during a) periods of floodgate closure (n = 22 days) and b) periods of floodgate opening (n = 57 days).
Mean potentiometric gradients at transect R2 were effluent during monitoring periods while the floodgates were closed (Fig. 8.7a). However, floodgate opening caused a substantial change in mean potentiometric gradients, particularly near the drain, leading to influent conditions in the first few meters of the drain bank (Fig. 8.7b).

**Figure 8.8.** Correlation between EC\textsubscript{a}V and groundwater EC adjacent the Transition drain, before and during floodgate opening.

Direct monitoring of groundwater EC adjacent to the Transition drain was confined to the piezometer wells at transect R2 and another adjacent, but unreported piezometer transect. Indirect monitoring of groundwater EC was undertaken using the EM38. A strong positive correlation was observed between paired groundwater EC and EC\textsubscript{a}V measurements (Fig. 8.8). The regression equation accompanying Fig. 8.8 enabled the use of data from multiple EM38 transects to infer groundwater EC changes in response to floodgate opening / closure adjacent to the Non-tidal drain, Transition drain and Tidal drain 2 (Fig. 8.9). While there was a clear increase in groundwater EC over time in response to floodgate opening,
Figure 8.9. Changes in groundwater EC adjacent Romiaka Non-tidal drain, Transition drain and Tidal drain 2 a) before floodgate opening, b) after 16 days of floodgate opening, c) after 57 days of floodgate opening, and d) 60 days after floodgates were closed following flooding. The groundwater EC is inferred using EM38 measurements (see Fig. 8.8). Linear interpolation between points (n = 77). See Fig. 8.1c for location of x and y.

increases were mainly confined to the first 4 m of the drain by 57 days (Fig. 8.9c). It is likely that if the floodgates had been left permanently open, the groundwater EC contours adjacent to the Transition drain would end up with a configuration akin to that observed in Tidal drain 2, which is exposed to, and presumably in dynamic equilibrium with, a continual tidal signal. Minimal change occurred in groundwater EC in either the Non-tidal
drain or Tidal drain 2 during the opening period (Fig. 8.9). Once floodgates were closed again, for about 60 days during a period of flooding, much of the groundwater salts that had accumulated adjacent to the transition drain were leached from the profile (Fig. 8.9d).

8.4.3. Shark Creek

The stratigraphy at this site was relatively uniform with distance from the drain. While the backswamp soils were fine textured compared to Romiaka (Fig. 8.10a), there was very high hydraulic conductivity in sulfuric horizons (Table 8.2) due to flow through large, tubular macropores (Johnston et al. 2004).

Figure 8.10. a) Stratigraphy at Shark Creek transect M1 and b) mean EC$_a$ at transect M3 before and after floodgate periods of opening, in relation to distance from the drain. The floodgate opening size was restricted to prevent any overtopping of the backswamp surface, thus the increases in EC$_a$ are due to sub-surface flow of saline drain water into the aquifer (see Fig. 8.13).
The sulfuric horizons had moderate pedality (angular blocky) with fine, planar fissures evident. Many, medium to coarse tubular macropores with variable orientations were observed, and these were invariably lined with Fe (III) minerals or jarosite. Rapid, sustained inflow of groundwater was observed via these tubular macropores during repeat pit bailing experiments.

**Figure 8.11.** Changes in soil EC (1:5 extract) with depth at profiles M1-1, M1-4 and M1-5. Sampled prior to floodgate opening.

Soil EC increased down the profile into sulfidic horizon (Fig. 8.11). EM38 surveying at transect M3 showed substantial increases in ECa at distances greater than 50 m from drain after periods of floodgate opening (Fig. 8.10b).
Figure 8.12. a) Tidal forcing of shallow groundwater at Shark Creek during a four day floodgate opening event and b) tidally modulated changes in drain water and groundwater EC (10 m from the drain).

The shallow groundwater was highly responsive to tidal increases in drain water levels, with forcing evident over 300 m from the drain during a four day floodgate opening event (Fig. 8.12a). During this floodgate opening event there were rapid, tidally modulated increases in shallow groundwater EC at a piezometer 10 m from the drain (Fig. 8.12b). Tidal ingress water was about 5 dS m$^{-1}$ during this event and at 10 m from the drain the shallow groundwater EC increased from 1.6 to about 2.6 dS m$^{-1}$ over the four days. Tidal ingress water was confined to the drain during this opening event and no surface overtopping occurred. This fast response in groundwater EC to sub-surface tidal infiltration is in marked contrast to that evident at Romiaka in Fig. 8.6. Shallow groundwater levels
across this site are generally quite flat (Fig. 8.13a), which is partly a function of the high hydraulic conductivity of the sulfuric horizons. However, the floodgate opening event shown in Figure 8.12 altered potentiometric gradients, creating influent conditions during the opening phase (Fig. 8.13b) and slightly effluent conditions during the four days immediately after (Fig. 8.13c).

Figure 8.13. Drain and groundwater level dynamics at Shark Creek a) four days before floodgate opening, b) during floodgate opening and c) four days immediately after floodgate opening. Based on the floodgate opening event shown in Fig. 8.12.
Floodgates were then opened for a longer period (58 days), but with a restricted opening size which limited the in-drain tidal amplitude to prevent overtopping of the low lying backswamp. Tidal ingress water was approximately 10 dS m$^{-1}$ during this time. Large changes in shallow groundwater chemistry accompanied this longer period of opening. Increases in the Cl:SO$_4^{2-}$ ratio over 80 m from the drain indicates there was substantial infiltration of marine derived Cl$^-$ from drain water into the adjacent shallow aquifer (Fig. 8.14). There was also an increase in groundwater EC and decreases in both SO$_4^{2-}$ and dissolved Fe (Fig. 8.14).

![Graphs showing changes in chemical composition of shallow groundwater](image)

**Figure 8.14.** Changes in the chemical composition of shallow groundwater at Shark Creek backswamp in relation to distance from the drain, before and after periods of floodgate opening. Ratios are based on molar concentrations. Note: the floodgate opening size was restricted and no overtopping of the backswamp surface occurred during the opening periods.
In macropore dominated systems, individual pore velocities and solute transport can very rapid and extremely difficult to predict (Bouma 1991). Preferential flow via macropores and a degree of segregation in solute transport processes between matrix and macropore domains is also known to occur (Bouma 1991; Harvey and Nuttle 1995). Repeat soil sampling was not undertaken at this location after the longer floodgate opening event. Given that the groundwater sampling strategy employed in this study is likely to have preferentially drawn water from the macropore network, it is uncertain to what extent the changes in shallow groundwater chemistry were mirrored within the soil matrix itself.

**Figure 8.15.** Mean daily drain water pH values in relation to maximum daily groundwater gradients. pH values are the 24 hr mean from the SDL at monitoring station A. Data shown is from periods when the mean daily groundwater level (mean of M1-1 and M1-2) was below the ground surface, between December 2000 and March 2003. Influent groundwater gradients develop during dry periods. \( \Delta \) = the difference between the mean daily groundwater level and the minimum daily water level at drain monitoring station B, assuming a horizontal distance of 2 m.

Longer term monitoring at this site showed that drain water chemistry was strongly influenced by the seasonally variable groundwater potentiometric gradients. During wet
periods, when maximum daily groundwater gradients were effluent, there was substantial outflow of acid groundwater to the drain resulting in low drain water pH values (Fig. 8.15). In contrast, influent groundwater gradients which developed during dryer periods were accompanied by circumneutral drain water pH values.

8.5. General discussion and conclusions

The difference in the extent of lateral solute transport between the two sites is largely a function of very different sediment hydraulic properties and also the potentiometric gradients that developed in response to floodgate opening. The contrasting soil physical properties between the sites was a very important feature, which in turn was closely related to their different geomorphic history.

Romiaka displayed significant tidal forcing, but limited lateral transport of salt water from the drain. Potentiometric gradients indicate regional groundwater was mostly discharging during the period of monitoring which limited the ingress of saline drain water. The higher elevation of this site (above local high tide) and the fact that long term rainfall is in excess of evapotranspiration, both encourage a higher water table and thus effluent trending gradients. While the higher energy deposition environment at this site associated with proximity to the coastal barrier led to the sub-sediments being coarse textured, the lack of structure and presence of some fines resulted in relatively low - moderate \( K_{sat} \) values, further limiting saltwater ingress. A further significant feature of this site is its proximity and exposure to an ongoing tidal signal from the nearby tidal channel. The shallow groundwater at this site was already being influenced by a tidal signal prior to floodgate opening and thus was more likely to be in a state of partial dynamic equilibrium with tidal influences.
In contrast, floodgate opening at Shark Creek backswamp caused extensive and rapid lateral transport of solutes from the drain, as well as substantial tidal forcing across the aquifer. While the ASS are fine textured, the sulfuric horizon exhibited a higher degree of structure than the sub-sediments found at Romiaka and also contained an extensive macropore network. This resulted in extremely high $K_{sat}$ values, which according to a theoretical comparison solely on the basis of texture, are approximately equivalent to what might be expected from very coarse, well sorted clean sand or even gravels (Boulding 1995). The lower elevation of the backswamp surface at Shark Creek (below local high tide) and the fact that long term rainfall decreases with distance from the coast, both encourage a lower water table relative to local tides, and thus a greater probability of influent trending groundwater gradients being creating during floodgate opening. The Shark Creek backswamp was also cut-off from tidal action by the formation of the natural distributary levee at some point after sea level stabilisation following the last post-glacial marine transgression (Lin and Melville 1993). Despite the high hydraulic conductivity of the backswamp sulfuric horizons, no tidal forcing is evident in the shallow groundwater solely in response to the tidal signal in Shark Creek (i.e. independent of the floodgate opening events). This behaviour points to the possible existence of semi-confining layers with lower hydraulic conductivity existing between Shark Creek and the backswamp, perhaps beneath the natural levee. Therefore, the re-introduction of a tidal signal into this backswamp via artificial drains represents a significant change in the balance of groundwater inputs, as this site is not in dynamic equilibrium with tidal influences.

8.5.1. Practical implications for opening floodgates

This study highlights the importance of adequate site assessment, particularly of soil hydraulic properties, prior to opening floodgates. This is particularly relevant to ASS
backswamps where differences in soil hydraulic properties can be extreme. The hydraulic conductivity of sulfuric horizons is known to be highly variable, owing to the unique chemical and physical ripening processes that accompany drying and oxidation of sulfide minerals, and the potential existence of macropores (Bouma et al. 1993). A compilation of recent investigations in a variety of ASS backswamps on coastal floodplains in eastern Australia confirms this variability, with values ranging over three orders of magnitude (Table 8.3).

Table 8.3. Comparing the saturated hydraulic conductivity of the sulfuric horizons in some ASS backswamps located in coastal floodplain environments in eastern Australia.

<table>
<thead>
<tr>
<th>Site / Coastal River</th>
<th>$K_{sat}$ range (m day$^{-1}$)</th>
<th>Test method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pimpama / Pimpama</td>
<td>~0.4</td>
<td>Constant head</td>
<td>(Rassam et al. 2002)</td>
</tr>
<tr>
<td>McLeods Creek / Tweed</td>
<td>~0.8</td>
<td>Auger hole</td>
<td>(White and Melville 1993)</td>
</tr>
<tr>
<td>Broughton Creek / Shoalhaven</td>
<td>~1 - 8</td>
<td>Falling head</td>
<td>(Blunden 2000)</td>
</tr>
<tr>
<td>Clybucca / Macleay</td>
<td>13 - 22</td>
<td>Pit bailing</td>
<td>(Morris unpublished data)</td>
</tr>
<tr>
<td>Rossglen / Hastings</td>
<td>~14</td>
<td>Pit bailing</td>
<td>(Aasø unpublished data)</td>
</tr>
<tr>
<td>Everlasting Swamp / Clarence</td>
<td>9 - 17</td>
<td>Pit bailing$^B$ / auger hole$^C$</td>
<td>(Johnston et al. 2004)</td>
</tr>
<tr>
<td>Tuckean Swamp / Richmond</td>
<td>52 - 178</td>
<td>Auger hole$^C$</td>
<td>(Johnston unpublished data)</td>
</tr>
<tr>
<td>Partridge Creek / Hastings</td>
<td>82 - 272</td>
<td>Pit bailing$^B$ / auger hole$^C$</td>
<td>(Johnston et al. 2003c)</td>
</tr>
</tbody>
</table>

$^A$ Note: This data is provided to demonstrate the variability range of $K_{sat}$ values encountered in coastal ASS in eastern Australia. Caution should be applied when interpreting or extrapolating this data due to the different methods used, different sampling intensities and the high degree of spatial heterogeneity in hydraulic conductivity.

$^B$ Bouwer and Rice 1983.

$^C$ Bouwer and Rice 1976.

In unconsolidated floodplain sediments estimates of $K_{sat}$ based on soil texture alone may be
highly misleading, as this does not account for variations in soil structure or the existence of macropores. The vertical variation in soil hydraulic properties down the profile relative to the local tidal range is also an important consideration. Previous work has demonstrated the attenuating influence that semi-confining layers can have upon groundwater flux and solute transport (Schultz and Ruppel 2002). The potential existence and effects of such layers at the drain bank face, due to chemical (i.e. Fe III clogging) or physical (smearing, detrital accumulation) processes, requires further attention.

In theory it would be ideal to conduct sophisticated modelling prior to opening floodgates at each site in order to predict the likely extent of tidal forcing and lateral solute movement in adjacent shallow groundwater. However, given the complexity of inputs required, the costs associated with obtaining reliable data and the difficulties of accurately modelling solute transport in macropore dominated systems, this is not likely to be a practical broad scale solution. There are many thousands of kilometres of drains with floodgates on coastal floodplains in eastern Australia and floodgate opening is becoming increasingly promoted and used as a water quality management strategy (Johnston et al. 2003d). An alternative to predictive modelling may be a simple hazard ranking process. This could be based on information that is either already available or relatively easy to obtain including,

- field based assessment of sediment physical and hydraulic properties
- land surface elevations relative to local tidal range
- local groundwater table ranges
- local climatic data (P, ET)
- before and after EM38 monitoring.

Such information, when combined with a cautionary, adaptive management approach, may prove to be a simple and cost effective means of managing risks of saline seepage
associated with floodgate opening.

Acknowledgments

We thank the landholders on the Clarence River floodplain for their assistance and cooperation, particularly A. Lawrence and D. Moloney. The contribution of B. Makins to many aspects of the field work is gratefully acknowledged. This study was funded by Land and Water Australia, Acid Soil Action, Sugar Research and Development Cooperation, Acid Sulfate Soils Program and NSW Agriculture.
Chapter 9

Conclusions

9.1. Summary

This research highlights some of the complex interrelationships that exist between hydrology, vegetation, soil and water quality in drained ASS backswamps. The findings emphasise how alteration of one fundamental feature (i.e. hydrology) has initiated a ripple effect of interconnected changes with far reaching implications for the internal biogeochemical processes and off-site water quality impacts of ASS backswamps.

This research provides some assessment of previously unquantified processes (i.e. the contribution of constructed drainage to an estuarine deoxygenation event), and also identified some hitherto unreported phenomena (i.e. alteration of groundwater and sediment geochemistry associated with M. quinquenervia encroachment). The discovery of sulfuric horizons with hydraulic conductivities much higher than any previously reported for coastal ASS backswamps in eastern Australia was an important finding with substantial implications for both acid export and subsequent management. The main findings of the research are summarised below.

9.1.1. Interactions between hydrology, vegetation, soils and water quality

The dominant processes affecting surface water quality in ASS backswamps (i.e. deoxygenation, redox transformations and acidification) are strongly influenced by interactions between hydrology, soils and vegetation. This research demonstrated that artificial drainage from ASS backswamps after major flooding made a substantial contribution to the magnitude of a deoxygenation event in the Clarence River estuary. The
Figure 9.1. A schematic representation of a hydrograph showing the approximate timing and sequence of events occurring after deep flooding of an ASS backswamp in relation to changes in drainage water quality. The precise timing of changes and the actual elevations (i.e. natural levee heights, backswamp surface levels and local low tide) will vary between sites (after Johnston et al. 2003d).

Flux of deoxygenating compounds from coastal ASS backswamps to adjacent estuaries after flooding had not been quantified before in eastern Australia. Anaerobic decomposition of flood intolerant pasture species coupled with Fe and S redox processes was a dominant process affecting the chemistry of backswamp surface waters. Constructed drainage facilitated the rapid and sustained removal of anoxic surface waters from floodplain ASS backswamps, well beyond what would have occurred naturally. Instead of anoxic water remaining impounded behind the natural levee system, where carbon mineralisation processes could be completed, artificial drainage bypassed this process and effectively ‘transferred’ it to the estuary. A schematic representation of the sequence of events and changes occurring in drainage water quality after deep flooding of an ASS backswamp is provided in Fig. 9.1.
The research suggests that without significant changes to the modified hydrology of floodplain ASS backswamps, similar drainage enhanced estuarine deoxygenation events are likely to occur episodically in the future. This study also suggests if the last ~0.5 m of surface water had been retained in the ASS backswamps after flooding, thus mimicking a more natural hydrology, the anthropogenic component of estuarine deoxygenation would have been greatly reduced. However, this would require substantial modification of existing drainage infrastructure and land use.

Analysis of time series aerial photography and original portion maps revealed that extensive encroachment of *M. quinquenervia* has occurred in the eastern Shark Creek ASS backswamp since European occupation and drainage. Data show that the soil and groundwater acidity is much higher beneath encroached areas. Intense, localised differences in groundwater and soil geochemistry are evident at both individual tree and whole forest scales. Data suggest upward redistribution and accumulation of acidity and soluble aluminium in surface soils is occurring in encroached areas. There are a range of possible mechanisms which may explain these differences, particularly enhanced water use by *M. quinquenervia*. However, further research is required to identify precise causal mechanisms and rank their relative importance. This is a completely new finding with serious implications for the longer term management of vegetation and acid export in ASS backswamps where this phenomenon has occurred. It is likely that such a process will contribute to drainage acid flux loads (see below). This research also demonstrated that an EM38 can be a useful surrogate for assessing spatial variation in the concentration of soil and groundwater acidic solutes in ASS backswamps.

The inundation of surface soils from an acid sulfate soil backswamp with contrasting vegetative cover (i.e. grass species and *M. quinquenervia* litter) demonstrated that labile
vegetative carbon and surface soil chemistry have a dominant influence on decay / redox processes and the chemical composition surface waters. Reductive dissolution of Fe (III) minerals appears to be an important chemical process in labile carbon rich ASS backswamp surface waters and can lead to the generation of stored acidity in the water column as Fe$^{2+}$$_{(aq)}$. Concentrations of redox insensitive ions (i.e. Cl$^-$ and Al) in surface waters were strongly correlated to initial soil contents. The higher concentrations of acidity and soluble Al in surface soil in encroached *M. quinquenervia* forests thus have potential to cause higher titratable acidities in shallow surface waters following inundation. This research demonstrates that changes to vegetation communities in ASS backswamps which substantially alter either (a) the pool of labile vegetative organic carbon or (b) the concentration of acidic solutes in surface soil, have a major influence on the chemical processes occurring in backswamp surface waters. This has implications for any projects which attempt to restore / manage or modify ASS backswamp hydrology in such a way that causes subsequent changes to vegetation communities.

**9.1.2. Acid flux dynamics**

The acid flux of drained sulfidic backswamps is highly dynamic over short time scales due to varying tidal influences and flux rates are strongly influenced by sulfuric horizon hydraulic properties. This research demonstrated the existence of sulfuric horizons with very high $K_{sat}$ (>100 m day$^{-1}$) in some ASS backswamps. Such high values had not been reported previously in coastal ASS in eastern Australia and have substantial implications for backswamp hydrology and acid flux. These high values are due to the existence of extensive soil macropore networks. However, it is clear that this phenomenon does not occur in all ASS backswamps and further research is warranted to examine the pedogenesis of these macropore networks.
This research also highlighted the importance of differentiating between surface and groundwater acid flux pathways and how outwardly similar ASS backswamps may have very different dominant pathways and resultant acid flux dynamics. The $K_{\text{sat}}$ and elevation of sulfuric horizons in relation to the local tidal minima in bisecting drains are identified as important site specific characteristics that influence whether the acid flux of a given site is likely to be dominated by one hydrological pathway or the other. A conceptual model of the respective acid flux dynamics associated with each pathway was developed (Fig. 5.9).

This research led to the development of a new concept - i.e. the ‘acid export window’. This refers to the ASS backswamp water level elevation range within which most acid export takes place. At both the Blanches and Maloney's study sites this elevation range corresponded approximately to the upper levels of the ASS backswamp surface and low tide minima in adjacent drains (Fig. 9.2). About 80% of the acid flux recorded at Blanches and Maloney's (pre-weir) occurred while the backswamp water level was within this range. Fig. 9.2 shows the location of the acid export window at Maloney's site in relation to soil stratigraphy and mean daily drain water pH. This conceptually identifies three hydrological zones which correspond to distinct backswamp water level elevation ranges. When backswamp water levels are above the upper levels of the backswamp surface (Zone 1), surface run-off is likely to be the dominant flux pathway and while discharge volumes are high, drain water acidity tends to be relatively low due to dilution (Fig. 9.2b). Zone 2 corresponds to the acid export window - when backswamp water levels are between the upper levels of the backswamp surface and low tide levels in adjacent drains. Groundwater seepage is likely to be the dominant flux pathway in this zone, along with some residual surface run-off, and while drain discharge volumes are low to moderate, drain water acidity can be very high (Fig. 9.2b). Note that the boundary between Zone 1 and 2 may be
more diffuse at some sites than is indicated in Fig. 9.2b (see below for further discussion). While the acid export window shown in Fig. 9.2 is quite narrow, groundwater seepage could potentially occur across the entire sulfuric horizon face (intersected by the main drain) whenever groundwater gradients are effluent. No acid export is likely to occur in Zone 3 as groundwater levels are below local low tide.

Figure 9.2. Maloney's ASS backswamp a) stratigraphy and surface elevation ranges, and b) mean daily drain water pH in relation to mean daily backswamp water levels. The approximate water level elevation ranges of three distinct hydrological zones are indicated (dashed lines) along with the dominant acid flux pathways, discharge volumes and drain water pH associated with each zone. MLW is the mean tidally influenced low water level in the bisecting drain. Soil stratigraphy and surface elevations are based on data from chapter 3. Drain water pH based on data collected in chapters 5 and 6.
While the broad principles represented in the conceptualisation of these three zones are likely to apply to other ASS backswamps, further comparison with other systems is warranted. In particular, there are a number of outstanding issues related to the upper boundary of the acid export window, between Zones 1 and 2. While the boundary between Zone 1 and 2 is defined here as the ‘approximate upper levels of the ASS backswamp surface’ (on the basis of field data from Blanches and Maloney's sites), accurately defining this level in some cases may prove problematic. Firstly, defining what constitutes an ‘ASS backswamp surface’ in an essentially gradational topographic sequence from the plain to a levee toe is required. While at the Blanches and Maloney's study sites this essentially refers to the area mapped as an ASS backswamp landscape (Milford 1997; Morand 1997), in which sulfuric soil conditions occur up to the soil surface, a key question is - can this be applied to other ASS backswamps? In addition, there are other factors that are likely to influence the precise elevation and characteristics of this boundary (i.e. sharp or diffuse). For example, a sharp boundary may be more likely in an ASS backswamp with a flat surface topography and narrow surface elevation range and a more diffuse boundary in one with more varied topography and a relatively wide surface elevation range. The depth of an individual inundation event may also influence the elevation of this boundary. For example, deep flooding (i.e. >2 m) which promotes extensive vegetation decay and reduction processes (thereby consuming protons) may effectively lower this boundary, as residual surface waters are more likely to be anoxic, diluted and less acidic. Whereas, shallow inundation (i.e. 0.2 m) after a dry period will cause less dilution of accumulated surface acid solutes and is less likely to promote vegetation decay and reduction processes - thereby promoting more acidic surface water and potentially raising the elevation of this boundary. The applicability of the acid export window concept to other sites and assessment of the elevation of the upper boundary of this window is an area worthy of further research and investigation.
For a given drainage system depth / density, the sulfuric horizon hydraulic conductivity and groundwater gradients are key factors controlling acid groundwater seepage. Local low tide levels in bisecting drains play a vital role in regulating the rates of acid flux via groundwater seepage by (a) controlling the magnitude of effluent groundwater gradients, and (b) determining the lower boundary of the acid export window (Fig. 9.2). Therefore any management changes which decrease the local tidal minima at high $K_{sat}$ sites (i.e. drain vegetation cleaning or estuarine dredging / entrance modifications) are likely to enhance acid flux. A conceptual model of the potential influence of $K_{sat}$ and the elevation of sulfuric horizons relative to local tidal minima in bisecting drains upon acid flux pathways and rates is provided in Fig. 9.3. This conceptual model was evaluated by comparing existing acid flux estimates from several drained ASS backswamps (Fig. 9.4). Note that this comparison is highly simplified and while it appears to conform to the general principles outlined in Fig. 9.3, it does not take into account site variations in drainage density, drain depth or differences in the acidity of sulfuric horizon groundwater.

**Figure 9.3.** A conceptual model of the influence of sulfuric horizon $K_{sat}$ and the elevation difference between sulfuric horizons and the local tidal minima in bisecting drains upon acid flux pathways and rates, for a given drainage depth / density. MLW is the mean tidally influenced low water level in the bisecting drain.
Figure 9.4. A comparison of estimated acid flux rates (no. in brackets, as kg $\text{H}_2\text{SO}_4$ ha yr$^{-1}$) of several drained sulfidic backswamps, in relation to the $K_{\text{sat}}$ of their sulfuric horizons and the elevation difference between the sulfuric horizons and local tidal minima. MLW is ~mean tidally influenced low water level in the bisecting drains. Measurements of $K_{\text{sat}}$ and upper sulfuric - local MLW are based on available data which use varying sampling methodologies and sampling intensities. Source data: Maloney’s Drain - (Johnston et al. 2004), Blanches Drain - (Johnston et al. 2004; Johnston unpub. data), Partridge Ck - (White 1998; Aaso 2001; Johnston et al. 2003c), McLeod’s Ck - (White et al. 1993; Wilson et al. 1999; Cibilic 2003), Tuckean - (Sammut et al. 1996; Johnston unpub. data).

9.1.3. Changes to drainage system management

This research demonstrates that tangible improvements in drainage water quality can be achieved by making informed changes to the current hydrological management of drains in ASS backswamps. However, some limitations and complexities exist, particularly for strategies involving floodgate opening and tidal exchange with estuarine water.

A trial was conducted to reduce acid export by containing acid groundwater within an ASS
backswamp, at a site where the main acid flux pathway was groundwater seepage. The method of achieving containment was to reduce the gradients that drive groundwater seepage by keeping the drain water level high and stable using an in-drain weir - specifically targeting the ‘acid export window’. Data showed that this was an effective means of reducing acid groundwater seepage to the drain. The weir affected 60% of drainage network and effluent groundwater gradients behind the weir were reduced by about 80%. Observed and modelled data suggest acid flux from groundwater seepage was reduced by about 65 - 70%. The main effect of the weir was to reduce discharge volumes, although reductions in $H^+$ and acidic metal cation concentrations were also observed.

Floodgate opening trials suggest that the effectiveness of floodgate opening at improving in-drain water quality is largely dependant upon the frequency, magnitude and duration of opening. Short duration floodgate openings often caused limited, short term water quality improvements. Rapid reversions (hrs / days) in drain water quality were repeatedly observed after floodgate closure. Floodgate opening also caused changes in longitudinal drain water gradients and has potential to slow net drainage rates during non-flood periods. However, this research demonstrated that complex site specific interactions can occur between drain water and adjacent groundwater. At one location, a four day floodgate opening event actually enhanced acid export in the period immediately following floodgate closure. Substantial practical limitations constrain the efficacy of floodgate opening as a stand alone acid management strategy. The very low elevation (close to mean sea level) of some acid sulfate soil backswamps on the Clarence floodplain combined with seasonal migration of the estuarine salt wedge means there is considerable potential for saline overtopping of what is currently agricultural land. Also, it is during wet periods when acid flux to the estuary is greatest. At such times the salinity and acid buffering capacity of
estuarine water is usually low, thereby reducing the capacity of tidal exchange waters to neutralise acidity.

The potential for floodgate opening to cause salt seepage into adjacent groundwater was investigated. This research demonstrated that in circumstances where the sulfuric horizon soils have very high $K_{\text{sat}} (>100 \text{ m day}^{-1})$, floodgate opening can cause tidal forcing of groundwater over very large distances from the drain (>300 m). In such high $K_{\text{sat}}$ soils, floodgate opening can also cause rapid lateral seepage of marine solutes from drain water into shallow groundwater >80 m from the drain.

9.2. Further research

Further research is required to address a number of issues related to *M. quinquenervia* encroachment including;

- Examine the extent of *M. quinquenervia* encroachment in other coastal sulfidic backswamps.
- Determine whether similar changes in geochemistry are evident beneath other tree species that have encroached in ASS backswamps (i.e. *Casuarina glauca*).
- Identify and quantify the processes involved in the enhancement of soil and groundwater acidity and rank their relative importance.
- Definitively determine if enhanced sulfide oxidation is occurring beneath encroached *M. quinquenervia* and identify the mechanism(s).
- Definitively establish the mechanism for the near surface accumulation of ions.

The magnitude of the change in the lability of vegetative carbon pools in ASS backswamps due to constructed drainage initiating shifts in vegetation communities is largely
Further research is required to determine the magnitude of this change and the effects of constructed drainage on carbon sequestration in sulfidic backswamps. The substantial peat layers that once existed in many sulfidic backswamps prior to drainage / burning suggests they once functioned as net carbon sinks. Determining whether sulfidic backswamps currently function as net sinks or sources of carbon may prove to be an important link in understanding their ecological function and contribution to estuarine productivity.

Further assessment of the acid export window concept is required. There is a need to test this concept at other ASS backswamps and to refine the identification and definition of the three hydrological zones, particularly the upper boundary of the acid export window, as they relate to backswamp water level elevation ranges.

Investigation of macropore pedogenesis and in ASS backswamps is warranted, particularly in high K$_{sat}$ soils. Identifying the dominant processes responsible for the development of dense macropore networks may yield insights useful for managing acid export at high K$_{sat}$ sites. There are likely to be relationships with historic and contemporary vegetation, the duration of drainage / frequency of profile drying, and perhaps clay mineralogy and soil chemistry. The potential for blocking macropores or breaking their continuity via physical (i.e. deep ripping) or chemical flocculation (i.e. alkaline rich water) techniques may be worthy of investigation.

While this research demonstrated some limitations associated with short duration floodgate opening, the effectiveness of longer duration floodgate opening at reducing effluent groundwater gradients and thereby acid flux requires further assessment via field research.
The potential for a weir to increase the upward evaporative flux and surface accumulation of acidic solutes over time requires further investigation. The effects of grazing pressure and fire regimes on the processes of surface accumulation of acidic solutes also require attention. Whilst the retention of shallow groundwater in Zone 2 (see Fig. 9.2a) at the Maloney’s site has reduced acid export, the amount of water retained is only a fraction of annual evapotranspiration (~1/5th). This is unlikely to be sufficient to prevent continued sulfide oxidation and acid generation during dry periods. Continued acid generation combined with reduced acid export may have potential to enhance the net accumulation of acidity in soil and groundwater over the longer term. This also requires further assessment.
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