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

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

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Abstract. Surface soils from an acid sulfate soil (ASS) backswamp were inundated in a temperature controlled environment and surface-water chemistry changes monitored. The soils had contrasting in situ vegetative cover [i.e. 2 grass species, Cynodon dactylon and Pennisetum clandestinum (Poaceae), and litter from Melaleuca quinquenervia (Myrtaceae)]. The different vegetation types had similar biomass and carbon content; however, 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 sustained O\textsubscript{2} depletion and sustained low Eh (\(-9 \text{ mV}\)), high dissolved organic carbon (DOC), and moderate pH (5–6). Their soil acidity was partially neutralised, sulfaies were re-formed, and reductive dissolution of Fe(III) led to the generation of stored acidity in the water column as Fe\textsuperscript{2+} (aq). In contrast, M. quinquenervia litter was high in decay-resistant compounds. Its surface waters had lower DOC and low pH (<4) and only underwent a short period of low O\textsubscript{2}/Eh. Soluble Al caused M. quinquenervia surface waters to have higher titratable acidity and soil pH remained consistently low (~3.8–4.0). Concentrations of Cl\textsuperscript{−} and Al in surface waters were strongly correlated to initial soil contents, whereas the behaviour of Fe and SO\textsubscript{4}\textsuperscript{2−} varied according to pH and redox status. This study demonstrates that changes in vegetation communities in ASS backswamps that 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.

Additional keywords: carbon decomposition, wetland biogeochemistry, anaerobic, iron reduction, drainage.

Introduction

Large areas of acid sulfate soils (ASS) lay beneath Australia’s eastern coastal floodplains (Naylor et al. 1995). Floodplain backswamps that 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. 2000; 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\textsubscript{4}\textsuperscript{2−}, are abundant in ASS (Walker 1972; van Breejen 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 in 2 ASS backswamps after flooding was strongly influenced by coupling of Fe and SO\textsubscript{4}\textsuperscript{2−} reduction with anaerobic decay of in situ surface vegetation. Bacteria usually mediate redox transformations of these species in inundated soils and reduction reactions typically consume protons (van Breejen 1973; Stumm and Morgan 1981). Accompanying changes in soil pH and Eh influence both mineral stability and metal solubility (Satwathananont et al. 1991; Warren and Haack 2001) and have a profound influence on the chemistry of overlying waters (Ponnampenneruma 1972; van Breejen 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 Breejen 1975; Blodau and Peiffer 2003). Other factors influencing reduction processes and pathways include the species of bacteria present, soil pH (van Breejen 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 decay of organic matter 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) and by 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).

The area of different vegetation types occurring within ASS backswamps on Australia’s east coast has changed due to drainage and agriculture (Goodrick 1970; Pressey and Middleton 1982; Pressey 1989). Decreases in the natural hydroperiod (i.e. duration of inundation) of ASS backswamps (White et al. 1997) have 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 to 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 acidification and influence the chemical composition of inundating surface waters. The encroached areas of M. quinquenervia identified by Johnston et al. (2003b) had minimal understory, and surface vegetative carbon was dominated by leaf litter. Previous studies (i.e. Greenway 1994) have invoked slow decay rates to explain substantial accumulations of M. quinquenervia litter in floodplain environments.

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 (i) assess and compare the changes in surface water chemistry (both acidification and deoxygenation/reduction processes) following inundation of these soils, and (ii) relate the observed changes to initial sediment chemistry and labile organic carbon from surface vegetation.

**Materials and methods**

**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 organic-rich topsoil (~0.3 m deep) overlying highly acidic sulfatic horizons with Fe(III) minerals and jarosite mottles, which are underlain by sulfide sediments of emuwarra origin at 0.8–1 m below the ground surface (Lin and Melville 1993; Johnston et al. 2003b).

Whole blocks of surface soil (0.15–0.18 m deep by 0.48 m wide by 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/nodes 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 (see Johnston et al. 2003b) and their dominant *in situ* surface vegetative cover was the grass species C. dactylon. These blocks were collected during a prolonged dry period (January 2003) 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 (Johnston et al. 2003b). 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 from a different area of ASS on the Clarence floodplain (Albury Creek, see Tulis 1999), in accord with the methods outlined above. The *in situ* surface vegetative cover on this block consisted of improved pasture species dominated by actively growing kykyuyu (*Pennisetum clandestinum*). The surface soil at this site was less acidic and the sulfide layer was > 1.0 m from the ground surface.

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°C, standard deviation 1°C). Sufficient distilled water was prepared and allowed to equilibrate to laboratory temperature and atmospheric O2. Each tub was flooded quickly (10 min) 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 h after initial inundation and the ‘raft’ was re-submerged and weighted down. 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.

**Surface vegetation sampling and analysis**

All surface organic matter (including leaf litter and standing grass) was removed from 2 quadrats 0.1 m by 0.1 m on each soil block. Samples were placed in a fan-forced oven and dried at 60°C for 96 h.
dry weights were obtained for each quadrat, and the mean of both quadrats was used to calculate biomass. The 2 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 (ICPES—USEPA 6010), carbon (LECO), nitrogen (LECO 3336), lignin (acid detergent) (ANKOM Technology—9.89), water-soluble carbohydrate (WSC) (modification of Technicon Industrial Method 302-73A), acid detergent fibre (ADF) (ANKOM Technology—9.89), and neutral detergent fibre (NDF) (ANKOM Technology—9.89).

**Soil sampling and analysis**

Surface soils (0–2 cm, starting immediately below the litter layer) were sampled from each soil block prior to re-flooding and on days 8, 19, and 26 post-flooding. Each occasion samples were collected from 4 random locations and bulked prior to drying. Soils were oven-dried at 85°C within 48h 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 Higgins 1992). All samples were analysed for reduced inorganic sulphur species (S₀, —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 4110), and water-soluble Al (U.P.A.S.—USEPA 9060 M), and total carbon and organic carbon (Rayment and Higgins 1992).

The in situ pH and redox potential of surface soils (0–2 cm) was determined regularly by direct inserting probes at 2 random locations in each soil block using freshly calibrated equipment (TPS 90FLMV). The mean of the 2 values was used. The 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 (Penniman 1972).

**Water sampling and analysis**

The surface water pH, EC, redox potential, dissolved oxygen (DO), and temperature were measured regularly 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 CSS04 submersible data loggers. DO was measured via a diffusion rod, pH using a double junction Ag/AgCl 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 subsamples 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 3 times with the water to be sampled. From this sample a 200-mL subsample was analysed for titratable acidity to pH 5.5 (APHA 2310B—including the peroxide oxidation step) within 24h of sample collection. Another 30-mL subsample was immediately filtered (0.45 µm pore size), placed into cold storage (−4°C), and analysed for ferrous iron within several hours of collection (spectrophotometrically, phenanthroline method—HACH 8146). A further 150-mL subsample was immediately filtered (0.45 µm pore size) 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 thawed at ~0°C and analysed for Cl⁻ and SO₄²⁻ (ion chromatography—APHA 4110), dissolved Al(0.45 µm filtration, ICPES—USEPA 6010), and dissolved organic carbon (combustion infrared—APHA 4310).

Shallow surface waters were sampled from the Shark Creek backswamp after rainfall caused inundation of the surface. Six samples were collected, 3 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 were measured at the site of sample collection. Selected samples were collected in clean 250-mL polyethylene bottles and analysed according to the methods and procedures outlined above.

**Results**

**Surface vegetation cover**

The mean dry weight biomass of *in situ* surface vegetation, prior to inundation of the soil blocks, was similar for each vegetation type. The mean dry weight biomass of *C. dactylon* was 2.8 kg/m² (s.d. = ±0.7 kg), *M. quinquenervia* 3.6 kg/m² (s.d. = ±0.8 kg), and *P. clandestinum* 3.9 kg/m². This includes all standing grass and leaf litter. The *M. quinquenervia* litter accumulation is comparable to values reported previously for floodplain environments in subtropical eastern Australia (Greenway 1994).

Although the different vegetation types had similar total carbon contents (Fig. 1a) there were 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. 1b). The difference between ADF and NDF consists of plant cell wall material comprising 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* than *M. quinquenervia* (7%) (Fig. 1c). 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 the more recalcitrant, stable carbon fraction. Figure 1d shows that the mean lignin content of *M. quinquenervia* litter (~40%) is far higher than either *C. dactylon* (~15%) or *P. clandestinum* (~6%). There were no significant differences in C:N ratios for all three vegetation types, at 30, 53, and 40 for *P. clandestinum*, *C. dactylon*, and *M. quinquenervia*, respectively. However, *M. quinquenervia* had a higher total Al and Fe contents than the grass species (Fig. 1e,f).

**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. 2a). 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*, followed by *C. dactylon* then *M. quinquenervia* (Fig. 2b). This pattern accords with the observed differences in the biodegradability of vegetative carbon.

The mean chemical composition of surface soils before and at day 26 of the inundation experiment is shown in Table 1. While there was little change in organic carbon, the day 26 samples display greater variability, which may reflect increasing subsample heterogeneity due to vegetation decomposition. The S(C) decreased to about half of the initial values in the *M. quinquenervia* soils, although there was a high degree of initial variability. The mean S(C) increased by about 50% of initial values of the *C. dactylon* and *P. clandestinum* soils; however, the increase was not significant and the overall amounts remained small (Table 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. While it is possible that H2S 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 SO42–) in the surface soils of the *M. quinquenervia* blocks (Table 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) of oxalate-extractable Fe (representing the poorly crystalline fraction) in surface soils (0–2 cm) from areas of open swamp.

**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*, followed by *C. dactylon* then *M. quinquenervia* (Fig. 3a). The Eh decrease was sustained for the duration of the experiment.

![Fig. 2. 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 ±1 SD.](image-url)
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. Figure 4 shows that as the ratio of lignin to WSC decreased (i.e. as carbon lability increased) the minimum Eh recorded in the surface waters increased.
of the tubs also decreased. 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. 3b). 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.

Concentrations of Fe$^{2+}$ increased rapidly in the first 10 days following inundation in all tubs (Fig. 3c). Peak values of 1 mmol/L were associated with *P. clandestinum*. While the high values remained relatively stable in tubs containing grass species, a sharp decline Fe$^{2+}$ in 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 plastic tubs. Its timing coincided with that predicted on the basis of pH/Eh data for stability of iron hydroxides in aqueous environments (Fig. 5). Schwertmannite is a poorly crystalline Fe mineral that is known to form in Fe- and SO$_4^{2−}$-rich waters with a pH range 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 personal communication) and it may account for the observed Fe(III) flocs.

The sequence of O$_2$ depletion in the tubs showed some relation to the type of vegetation. Submersible data loggers revealed complete depletion of surface water O$_2$ within 12 h of inundation in *P. clandestinum* (K1), 19 h in *C. dactylon* (C1, C2), and 46 h in *M. quinquenervia* (M1, M2). Spot monitoring of DO confirmed this sequential pattern (Fig. 3d).

While DO remained ~0 μmol/L 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*, followed by *C. dactylon* then *M. quinquenervia* (Fig. 3e), a pattern which accords with the differences in the biodegradability of surface vegetative carbon. There was an increasing trend in EC in all of the tubs (Fig. 3f), and concentrations at day 8, not surprisingly, showed a strong positive linear correlation ($r^2 = 0.85$) with initial surface soil EC.

Titratable acidity increased sharply over several days in the *M. quinquenervia* tubs and stabilised at a mean value ~2 mmol H$^+$/L (Fig. 6a). 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 by day 16 onward. Fe$^{2+}$ can generate 2 mol of H$^+$ (via oxidation) and Al$^{3+}$ can generate 3 mol (via hydrolysis). These acid metal cations can be responsible for much of the acidity in ASS drainage waters (Cook et al. 2000). 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. 7). The theoretical individual contribution of Fe$^{2+}$ and dissolved
Fig. 6. 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 ±s.d. The left y-axis relates to *M. quinquenervia* only. The right y-axis relates to *C. dactylon* and *P. clandestinum* only.

Al to titratable acidity can thus be calculated. Fe²⁺ clearly dominated in the tubs containing grass species, whereas dissolved Al accounted uniformly for almost all the titratable acidity in the *M. quinquenervia* tubs (Fig. 8a, b). Neither Fe²⁺ or Al³⁺ could explain all the titratable acidity recorded in the *P. clandestinum* surface waters. One possible explanation may be the peroxyde oxidation step used in the titratable acidity method causing generation of acidity by oxidation of H₂S.

Dissolved Al was much higher in the *M. quinquenervia* tubs (Fig. 6b), which accords with the low pH and higher initial soil concentrations (Table 1). Chloride concentrations increased steadily over time in all tubs (Fig. 6c), whereas SO₄²⁻ decreased in the tubs with grass species (Fig. 6d). This decrease in SO₄²⁻ is likely to be a result of reduction and sulfide formation in soils (Table 1). This suggestion also accords with the Eh/pH signature of surface soils, which shows that 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. 9). 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).

Mean Cl⁻:SO₄²⁻ ratios remained uniformly low in the *M. quinquenervia* tubs throughout the experiment, whereas SO₄²⁻ decreased relative to Cl⁻ in the tubs with grass species (Fig. 10a). Figure 10a also includes Cl⁻:SO₄²⁻ ratios collected from 2 different ASS backswamp drains after flooding using data from Johnston et al. (2003a). One of these drains (Maloney) was located at the Shark creek study site, where about 50% of the backswamp consists of *M. quinquenervia* (Johnston et al. 2003b).
Fig. 8. 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.

drain had uniformly low Cl$^-\colon$SO$_4^{2-}$ ratios. The other drain (Blanches) was located in a backswamp dominated by decaying pasture species after flooding (Johnston et al. 2003a). In contrast, this drain exhibited decreasing SO$_4^{2-}$-relative to Cl$^-$. This comparison merely confirms the applicability of the chemical processes and changes observed in the tub waters to those occurring in surface drainage waters at a field scale.

In contrast to 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. 10b). Concentrations of both Cl$^-$ and dissolved Al in surface waters were strongly correlated with initial soil contents prior to inundation (Fig. 11a, b). This suggests that initial soil concentrations play a primary role in determining resultant surface water concentrations of these species.

Solid-phase Fe(III) minerals commonly regulate Fe$^{2+}$ activity in ASS (Satsawathananont et al. 1991). Data in Fig. 12 show that Fe$^{2+}$ activity 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 2) and sulfide-horizon groundwater

Fig. 9. 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). The grey area represents sulfate-reducing bacteria, the hatched area represents iron bacteria, and the plain area represents Thiobacillus spp.

Fig. 10. Changes in surface water (a) Cl$^-\colon$SO$_4^{2-}$ ratios and (b) Cl$^-\colon$dissolved Al ratios. Data presented are mean values. Malones post-flood and Blanches post-flood data (including their date of inundation) derived from Johnston et al. (2003a).
collected from the Shark Creek backswamp are also included in Fig. 12 and lay within the same range. The theoretical stability range for schwertmannite lies between that of ferricyanide 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.

**Field surface waters**

Although sample numbers were limited, the chemical composition of field surface waters from within the different vegetation zones showed some similar trends to those observed in the tubs (Table 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, whereas Eh was lower in the open swamp areas (data not shown), DO was higher, in contrast to the laboratory studies. This may be a result of greater photosynthesis occurring in the open areas due to higher light conditions.

**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 (Ponnampерuma 1972). This is clearly evident in the contrasting surface water chemistry associated with the different vegetation types. The surface waters associated with labile-carbon rich grass species had rapid O$_2$ consumption, a sustained lower redox status, higher pH,
Table 2. Chemical composition of field surface waters collected from areas of the different vegetation types in the Shark Creek backswamp

Samples were collected on 19 March 2003, 7 days after rainfall caused inundation of the backswamp surface to a depth of ~0.3 m. Samples were collected from inside and outside the forested area, 100 m from the forest edge. Os is open swamp dominated by C. dyctylon and P. distichum. Mq is M. quinquenervia forest. All concentration units are in mmol/L unless otherwise stated, and the ratio is molar.

<table>
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<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>

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^{3+} (aq) has potential to generate 2 mol of H^{+} upon oxidation (Dent 1986); therefore, the high concentrations of Fe^{3+} (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. In addition, receding water levels in a field situation would allow surface soils to dry, thus causing any monosulfides formed in surface sediments to subsequently oxidise and release acidity.

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^{3+} (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 that some sulfide oxidation 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 AI) in surface soils appear to have a controlling influence on their resultant concentrations in surface water. Soluble AI in M. quinquenervia surface soil was the main contributor to the higher titratable acidity of associated surface waters. Increases in surface soil soluble AI was one of the major effects of M. quinquenervia encroachment at the Shark Creek backswamp (Johnston et al. 2003b) and this study confirms that these increases are likely to be contributing to enhanced acidification of surface waters. Acidity associated with AI^{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 favours 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(II) reducers able to outcompete sulfate-reducing bacteria for organic substrates (Lovely and Phillips 1987; Achtman et al. 1995; Thamdrup 2000). Fe(II) reducers also have a high degree of metabolic versatility and are 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 (Müllner and Zeich 1998). It is possible that the high concentrations of both Al and Fe evident within the M. quinquenervia litter may also have an inhibitory effect on decay rates, although this would require further study to ascertain. Several studies have also suggested that essential oils from various Melaleuca spp. may have an inhibitory effect on litter decay rates (Boon and Johnston 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 AI, and lower Cl^{-} : SO_{4}^{2-} 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 that allow mixing of waters between...
the vegetation zones. In the field there are also diurnal temperature fluctuations and potential for photosynthesis and release of $O_2$ 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 is 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, which can affect redox processes involving Fe and $SO_4^{2-}$ (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 that attempt to 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$^-$ : $SO_4^{2-}$ ratios observed at the Shark Creek site (Maloney) 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 in the drains subcatchment.

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 biodegradability of surface carbon 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 occur with an appreciation of the dynamic links between altered vegetation and biogeochemical processes.

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