The effects of artificial drainage of floodwaters from acid sulfate soil backswamps on deoxygenation in the Clarence River estuary, Australia.

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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 ground water 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.

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*. 2000), 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.* 2000). 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, 2000).

When ASS backswamps are flooded there are likely to be interactions between the decomposition of organic matter and surface accumulations of 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 a) describe temporal changes to drainage water chemistry after flooding from two drained coastal floodplain ASS backswamps, b) examine processes responsible for these changes, c) estimate the flux of oxygen depleting compounds from the two drains to the estuary, and d) estimate the contribution of artificial drainage of ASS backswamps to the observed estuarine deoxygenation event.

Material and methods

Study Areas

The Clarence River catchment (Fig. 1) has an area of 22,700 km^2 and the Clarence River estuary is a mature barrier system (Roy, 1984). The floodplain is over 2,600 km^2 and underlain by an estimated 530 km^2 of acid sulfate soils (Tulau, 1998). There are over 1700 km of floodgated drains and water courses on the Clarence River floodplain. The two study areas were Blanches and Maloneys (Fig. 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 <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 Maloneys than Blanches (Johnston *et al*. 2002), resulting in large differences in the acid flux dynamics of the respective drains. Maloneys 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 (S.G. Johnston, P.G. Slavich and P. Hirst, unpublished data).

Blanches is located on Everlasting Swamp (Fig. 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, 1999).

Maloneys is located in the lower eastern Shark Creek backswamp (Fig. 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, particularly those with high levees and few natural drainage lines such as eastern Shark Creek, this natural limit may well have been higher.

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. 1). Rainfall data used in this study is an arithmetic mean from both weather stations.

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 MacDonald *et al*. (1998) in the ASS backswamp at both sites along 400 m transects perpendicular to the piezometers (Fig. 2) four days before and three weeks after flooding.

River, drain and ground water 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). 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}.

Data collected by NSW Fisheries (Pollard, 2001) 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. 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.

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

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^{o} 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 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^{o} C, sub-samples extracted and analysed for Chemical Oxygen Demand (COD) (di-chromate digestion, colorimetric-APHA 5220-D), Total Fe and Total Al (ICPMS-APHA 3120), Dissolved Fe and Dissolved Al (0.2 µm cellulose acetate filtration, ICPMS-APHA 3120), Cl^- (FIA-AHPA 4500 Cl), SO_4^{2-} (APHA SO_4^{2-}-E), Dissolved Organic Carbon (DOC) (combination Infra-red-APHA 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).

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). 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) was derived from the sum of the hourly discharge volumes (q_h) using,

$$q_h = V_h.A_h \qquad (1)$$

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 0.05 m diameter slotted PVC pipe and surveyed to AHD.

Drain flux estimates

Daily flux estimates were made by multiplying Q_d by the daily concentration (C_d). 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. 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 µmol 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.

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 equation,

$$\theta_s = (Q_b + Q_m)/2.A \qquad (2)$$

where θ_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 Maloneys 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.

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 Maloneys. Each sample comprised of 10 small sub-samples taken from a randomly selected 2 m^2 area until a volume of about 250 cm^3 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^{o} 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 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) that are readily available for biomediated reduction (Lovley and Phillips, 1986).

Results

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. 3). The last major flood in the Clarence prior to this event was in 1996. Backswamp ground water 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. 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, Maloneys backswamp experienced relatively shallow flooding of shorter duration. At Maloneys, 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. 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.

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 (NSW Agriculture and Fisheries, 1989). Open pasture areas at both Blanches and Maloneys 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 Maloneys 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 Maloneys, however leaf litter was abundant.

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.

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.

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. 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, 2000). 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 $\mu mol\ L^{-1}$ and then underwent a gradual decline over a four day period to almost zero (Fig. 3). The DO concentrations in Blanches drain remained below 5 $\mu mol\ L^{-1}$ 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. 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 $\mu mol\ L^{-1}$) associated with the initial infilling floodwaters. A sharp drop to <15 $\mu mol\ L^{-1}$ then occurred over a 24 hr period associated with an increase in EC (Fig. 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. 4) due to dilution from river water. This river water also caused a mild recovery in drain water DO concentrations. 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 5b), but was lower at Blanches drain with minimum recorded values close to 0 mV. The initial temperature of the floodwaters was around 23 C^{o}. Water temperatures on the floodplain increased rapidly (~33 C^{o} measured in Blanches backswamp surface waters) in response to a period of high daily temperatures and drain waters remained >25 C^{o} for most of the monitoring period (Fig. 6a). The pH of Blanches drain water following flooding was generally between 6 - 7 (Fig. 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. 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. 5c and d). While drain water at both sites had similar initial DOC concentrations, a sharp increase occurred in Blanches drain whilst Maloneys drain remained relatively static. It is highly likely that these DOC trends are related to the substantial differences in ground cover loss and vegetation decomposition evident between the two sites. 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 1).

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).

At Blanches, increases in Total Fe in drain water were positively correlated ($r^2 = 0.82$, exponential regression) with increasing DOC (Fig 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 ground water are likely to have been a more important source of mobile Fe in drainage waters at this site (Johnston *et al.* 2002).

No titratable acidity to pH 5.5 was detected in any samples taken in Blanches drain following the flood. Drain water at Maloneys had low initial values of titratable acidity, followed by a sharp increase on 14 February (Fig. 6b), which was associated with large increases in dissolved Fe and dissolved Al.

While both sites have shallow sulfidic soils and acidified shallow ground water with similar chemical composition (Table 2) there were marked differences in the Cl^{-}:SO_4^{2-} ratios of drainage water following inundation (Fig. 6c). Low, stable ratios at Maloneys drain indicate that the sources of drainage waters at this site, firstly, are associated with the oxidation of sulfides (Mulvey, 1993) and secondly, 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^{-}, but relatively stable SO_4^{2-} concentrations. This apparent attenuation of SO_4^{2-} relative to Cl^{-} is most likely related to SO_4^{2-} reduction and sulfide mineral reformation occurring in the Blanches backswamp during this period (see below).

Higher total and dissolved Al concentrations at Maloneys drain also suggest an increasing influence of shallow ASS ground water drainage at this site (Fig. 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^{-1}) (Table 1). However, acetate in discharge waters at the floodgates (2½ km from the backswamp) were consistently below detection limits (0.001 mmol L^{-1}) which may indicate in situ oxidation or complexation in floodwaters prior to discharge.

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 3). Significant, but much lower concentrations occur in surface sediments at Maloneys. 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 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 Maloneys site.

Drain discharge and flux estimates

Total flux estimates of oxygen depletion potential, DOC, SO_4^{2-}, Fe, Al and acidity at Blanches and Maloneys drains for 30 days after the flood are provided in Table 4. The timing of this flux is represented in Fig. 8. Drain discharge rates decreased in the latter stages of flood recession (Fig. 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. 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. 8 suggest that artificial drainage increased the DOC flux by an additional 1.4 times at both study sites.

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. 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.

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. 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. 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_2S 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_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^{2+} and 1 mol of oxygen consumed for every 4 mol of Fe^{2+} oxidised (Cook *et al*. 2000), this only accounts for a mean of about 1% of the COD at both Blanches and Maloneys.

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 (Lin *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 Maloneys 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 Maloneys 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 3), the strong positive correlation between Fe and DOC (Fig. 7), the significant concentrations of dissolved Fe in backswamp surface (Table 2) and drainage water (Fig. 5f), and the attenuation of SO_4^{2-} relative to Cl^- in drainage water (Fig. 6c).

The low pH, high titratable acidity, low $Cl^-:SO_4^{2-}$ ratios and high Al in drain waters at Maloneys suggest there was a greater input of shallow ASS ground water 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 ground water during the period of observation. These suggestions accord with other research conducted at both sites, which showed large differences in the magnitude of ASS ground water inputs to the respective drains (S.G. Johnston, P.G. Slavich and P. Hirst, unpublished data).

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 microbially mediated Fe and SO_4^{2-} reduction and catalysed by Fe (II) – Fe (III) redox cycling. Inputs of shallow ASS ground water were also important at one of the study sites. The accumulation of easily reducible Fe and 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.

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Table 1. Chemical analyses of backswamp surface waters at Blanches and Maloneys study sites following the February flood
Water depth at sampling locations was ~0.2 m. All concentrations in mmol L^{-1} except where stated.

	Blanches (19/02/01)[A]	Maloneys (21/02/01)[A]
pH	6.03	6.27
EC (dS m^{-1})	1.09	0.18
Chemical Oxygen Demand	25.6	3.4
Dissolved Organic Carbon	22.5	2.8
Total Fe	1.58	0.16
Dissolved Fe	1.10	0.02
SO_4^{2-}	1.27	0.26
Cl^-	5.63	0.95
Total Al	0.024	0.006
Acetate	2.62	0.01

[A] Date sampled.

Table 2. Chemical analyses of shallow ASS ground water at Blanches and Maloneys 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.

	Blanches (n=7)	Maloneys (n=25)
Titratable Acidity - H^+	9.1	13.9
Cl^-	52	17
SO_4^{2-}	38	19
Total Fe	3.9	2.7
Dissolved Fe	2.3	2.2
Total Al	5.2	5.0
Dissolved Al	1.2	3.8
$Cl:SO_4^{2-}$	1.4	0.8

Table 3. Iron and sulfur fractions in backswamp surface sediments at Blanches and Maloneys study sites
Sample depth 0-2 cm. Post-flood samples were collected during May 2001 while the backswamp surface was still inundated after flooding.

	Blanches	s.e.	Maloneys	s.e.
Oxalate-extractable Fe (III) [A]	1120	263	206	8
SO_4^{2-} [A]	19	6.9	1.6	0.2
Pre-flood S_{Cr} (%)	0.06	0.01	nd [B]	nd
Post-flood S_{Cr} (%)	0.74	0.12	nd	nd
Post-flood AVS (%)	2.5	0.64	nd	nd

[A] mmol kg^{-1}.
[B] nd = no data available.

Table 4. Total discharge and total flux estimates for the Blanches and Maloneys 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.

	Blanches	Maloneys
Discharge (10^3 m^3)	4900	1300
Oxygen depletion potential [A]	62	37
Dissolved Organic Carbon flux	200	87
SO_4^{2-} flux	216	332
Total Fe flux	25	29
Dissolved Fe flux	9.6	10
Total Al flux	1.0	1.5
Acidity flux [B]	0	53

[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 Methods).
[B] Based on titratable acidity to pH 5.5, expressed as $CaCO_3$ equivalent. (Note; no titratable acidity recorded at Blanches, see Fig. 6b).

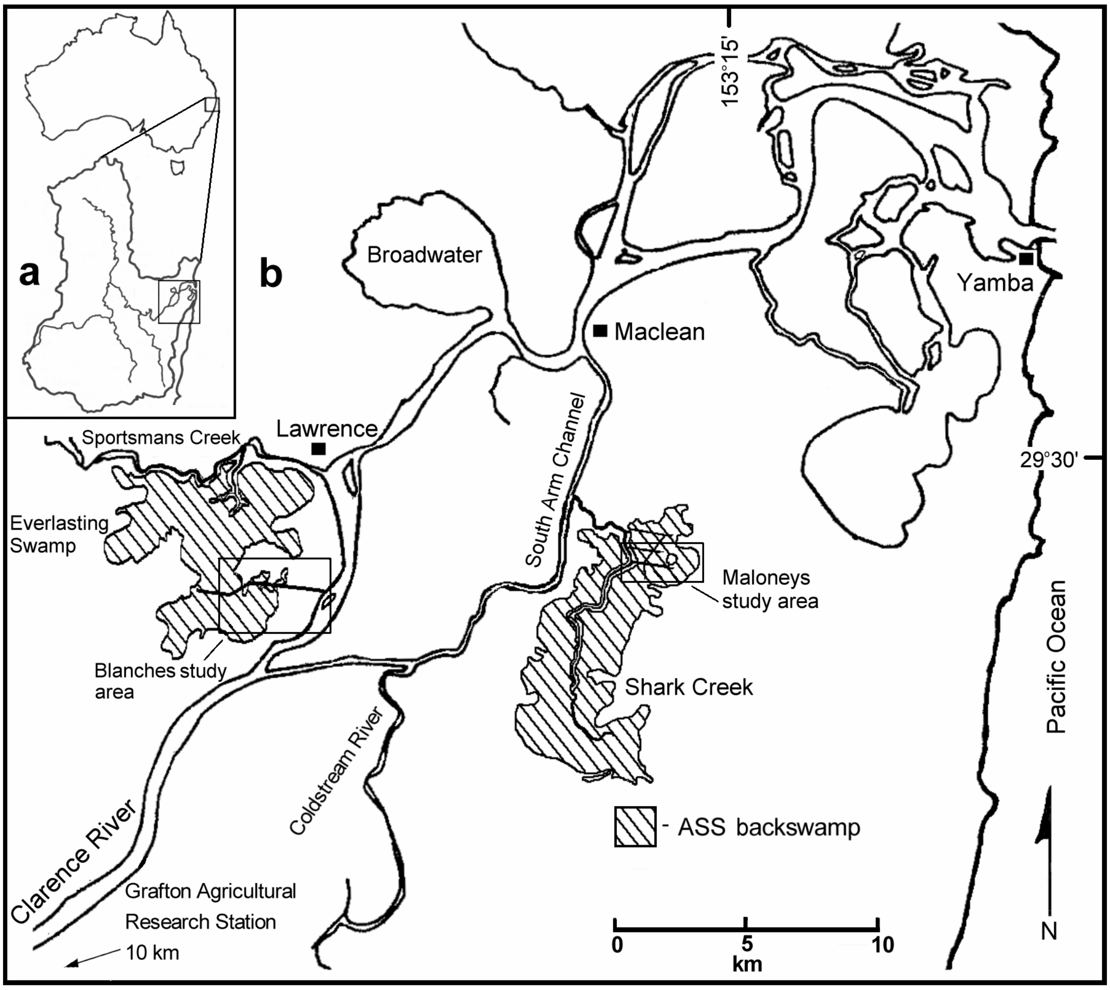

Fig. 1. a) Clarence River catchment and b) lower floodplain, study site locations and associated ASS backswamps.

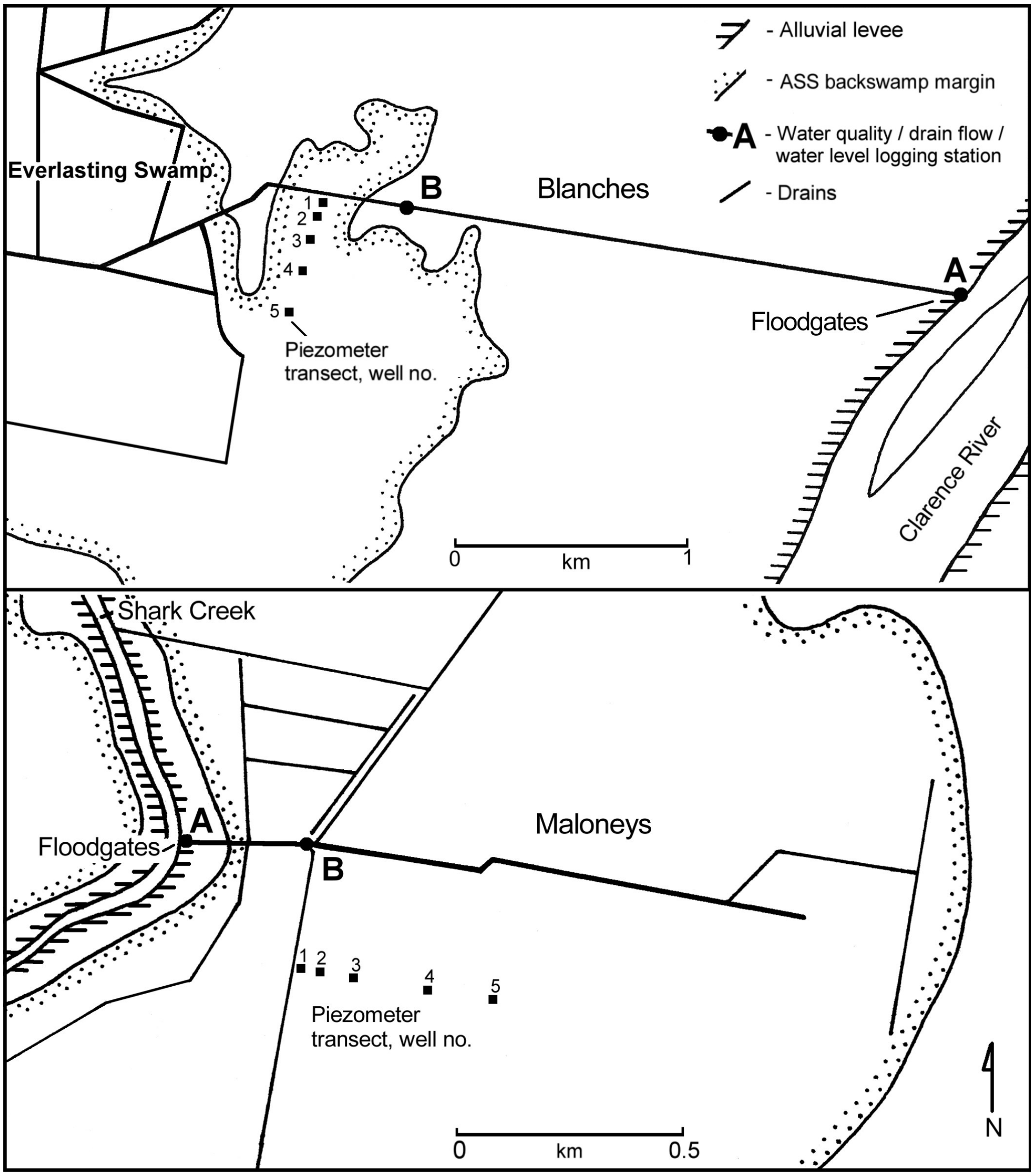

Fig. 2. Blanches and Maloneys study sites, showing the location of submersible data loggers / flow / water level monitoring stations (A-B), drains, floodgates and acid sulfate soil backswamp margin.

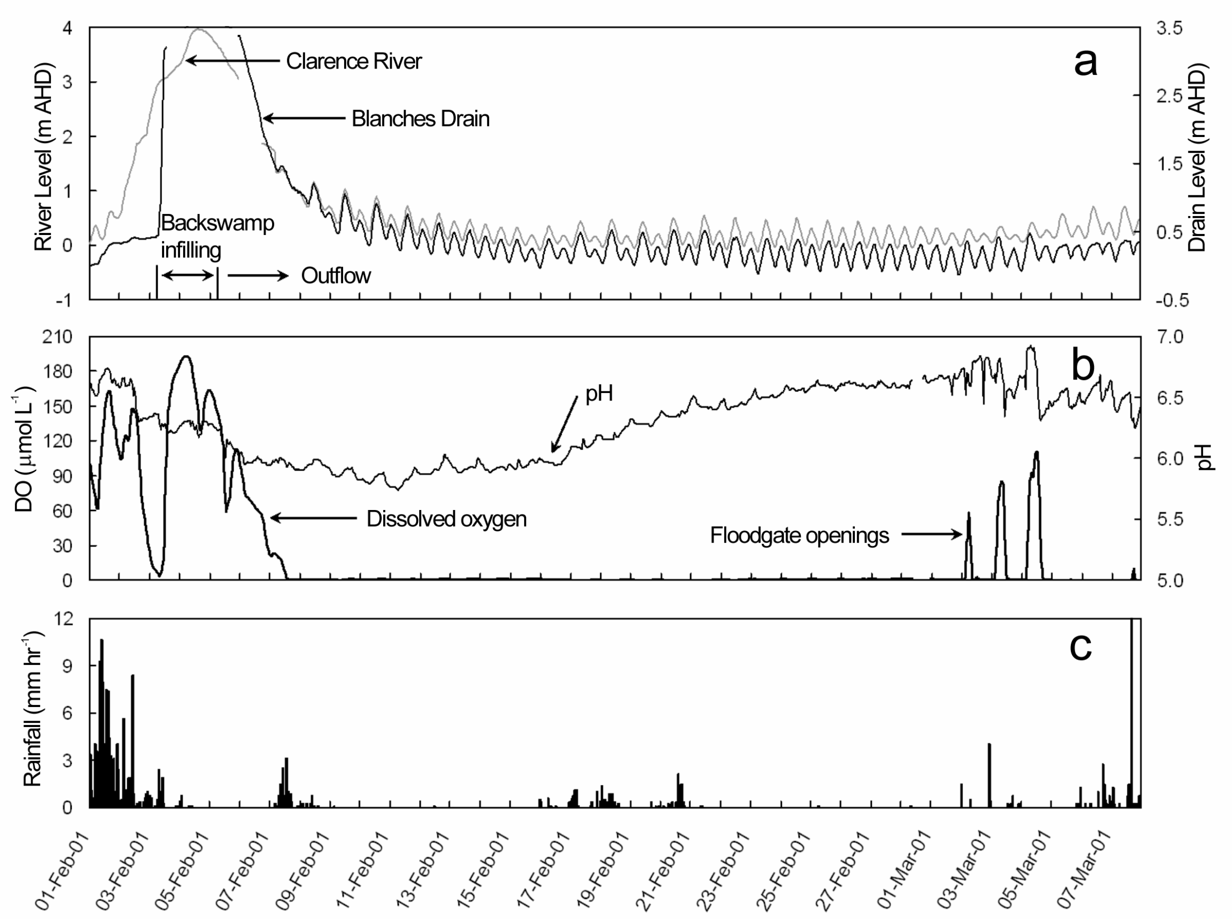

Fig. 3. a) Clarence River[A] and Blanches Drain hydrographs (note different scales), b) time series pH and DO at the floodgate SDL (monitoring station A) and c) hourly rainfall. Water level in m AHD (Australian Height Datum, 0 AHD ~ mean sea level). [A] Outside Blanches drain floodgates.

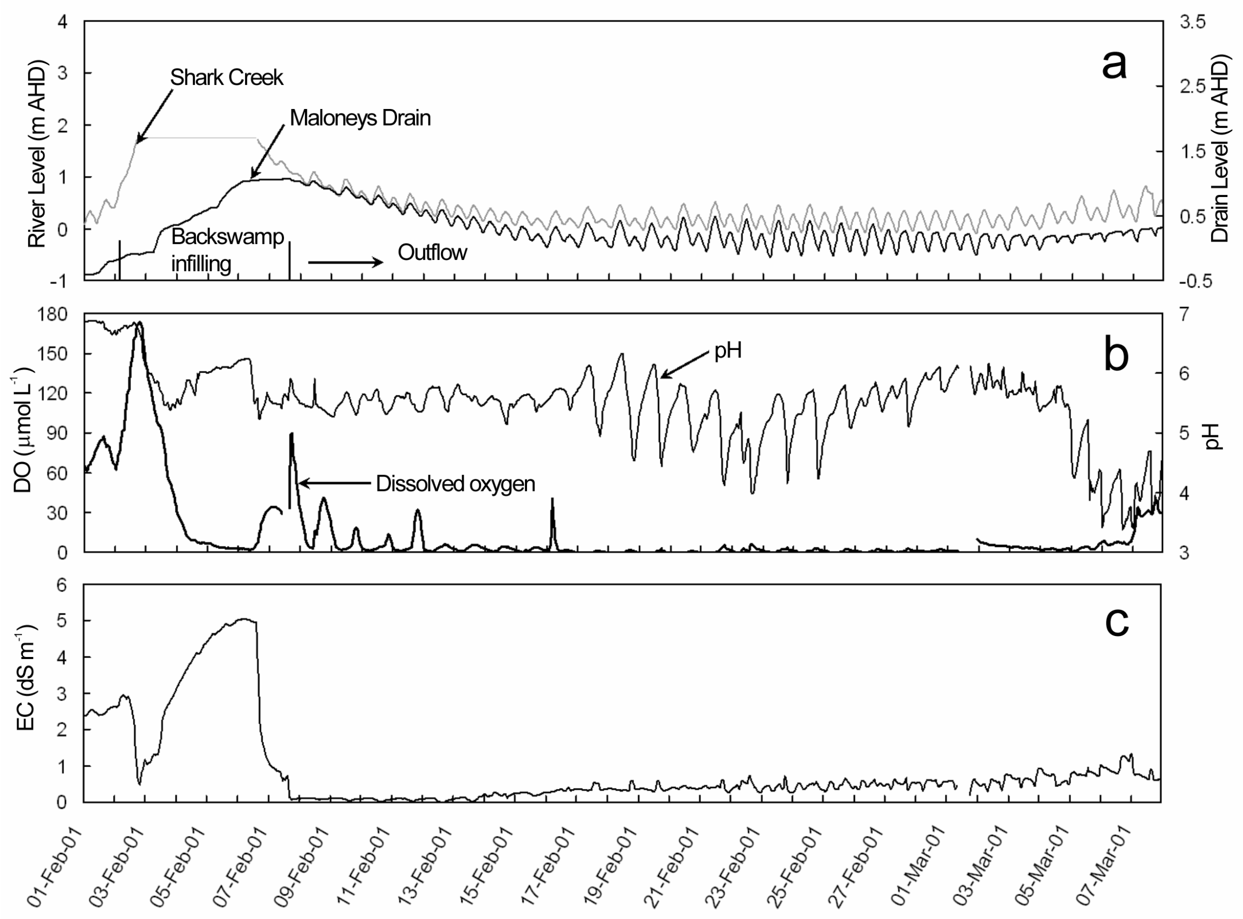

Fig. 4. a) Shark Creek [A] and Maloneys Drain hydrographs (note different scales), b) time series pH and DO at the floodgate SDL and c) time series EC at the floodgate SDL (monitoring station A). [A] Outside Maloneys drain floodgates.

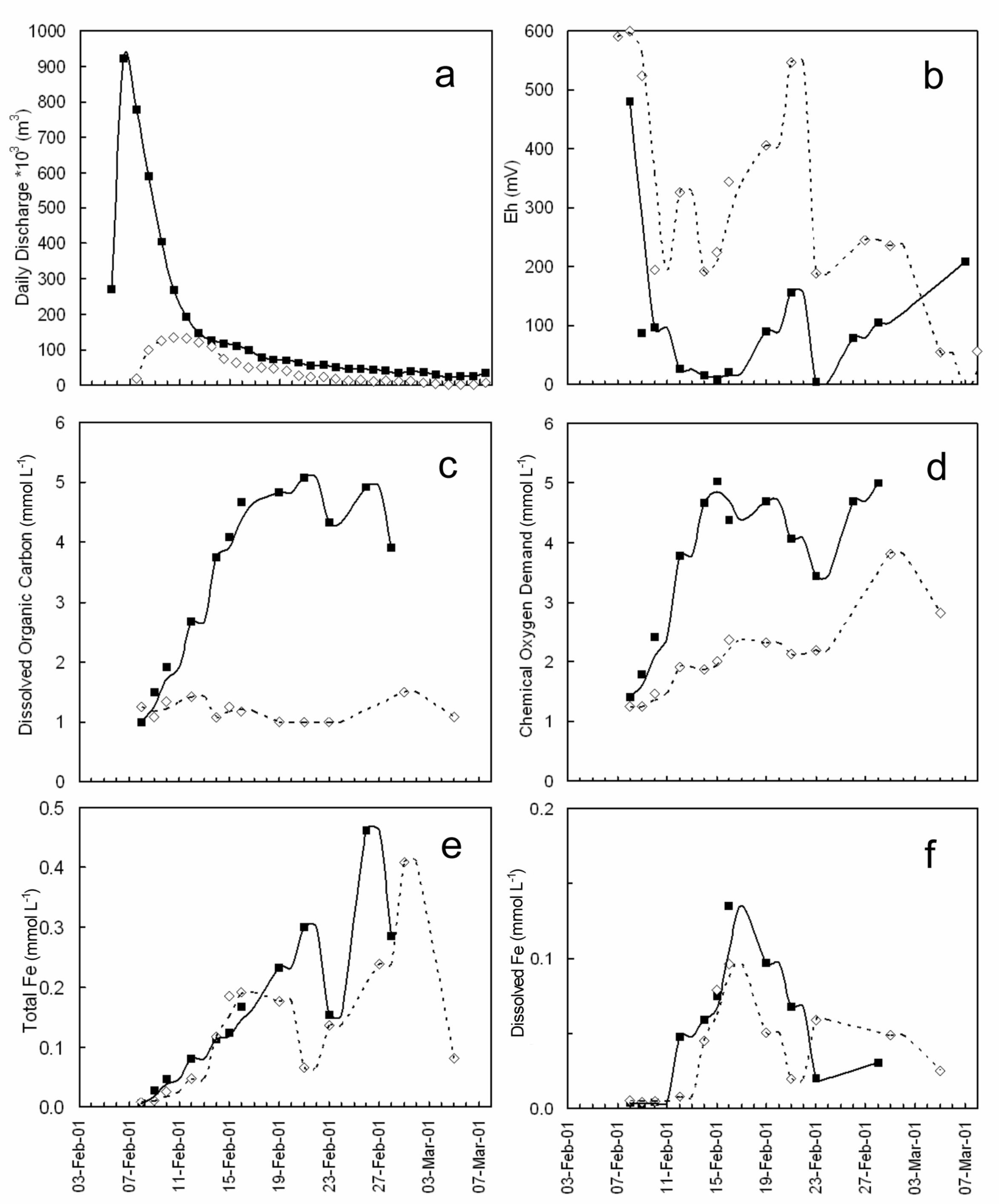

Fig. 5. Post-flood changes in Blanches and Maloneys drainage water a) discharge volumes, b) Eh, c) dissolved organic carbon, d) chemical oxygen demand, e) total Fe and f) dissolved Fe. All concentration data based on samples taken at the floodgates (monitoring station A). ■ = Blanches, ◇ = Maloneys.

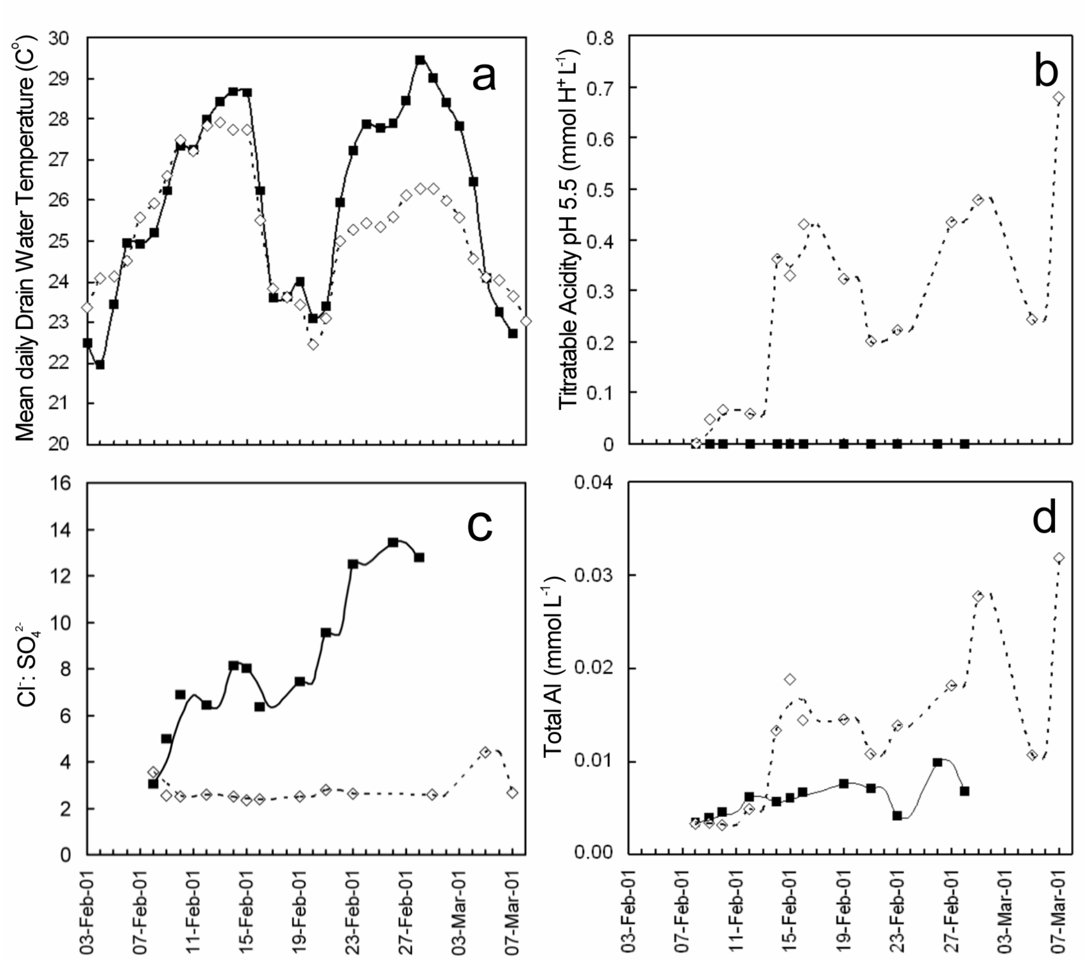

Fig. 6. Post-flood changes in Blanches and Maloneys drainage water a) mean daily temperature at the floodgate SDL, b) titratable acidity (to pH 5.5), c) $Cl^-:SO_4^{2-}$ ratios (molar) and d) total Al. All concentration data based on samples taken at the floodgates (monitoring station A). ■ = Blanches, ◇ = Maloneys.

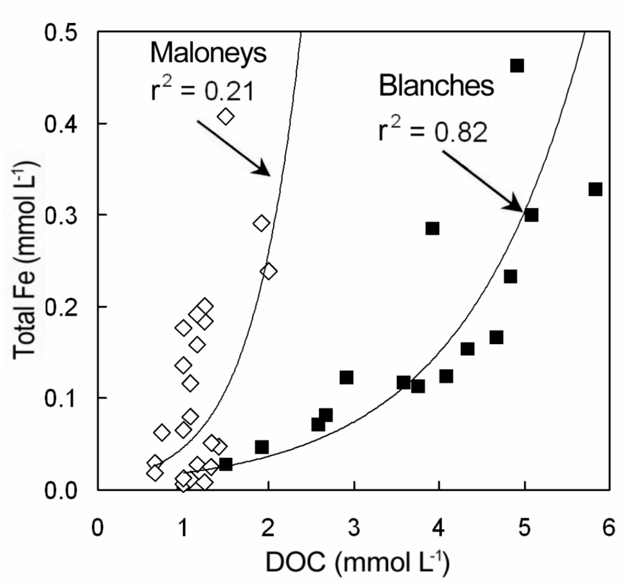

Fig. 7. Relationship between DOC and total Fe in drainage waters at the Blanches and Maloneys sites. Strong positive correlation[A] at Blanches (combined with surficial sediment chemistry data) suggests reductive dissolution of Fe associated with anaerobic decomposition of organic matter was an important process mobilising surface Fe into drainage waters at this site. [A] Exponential regression.

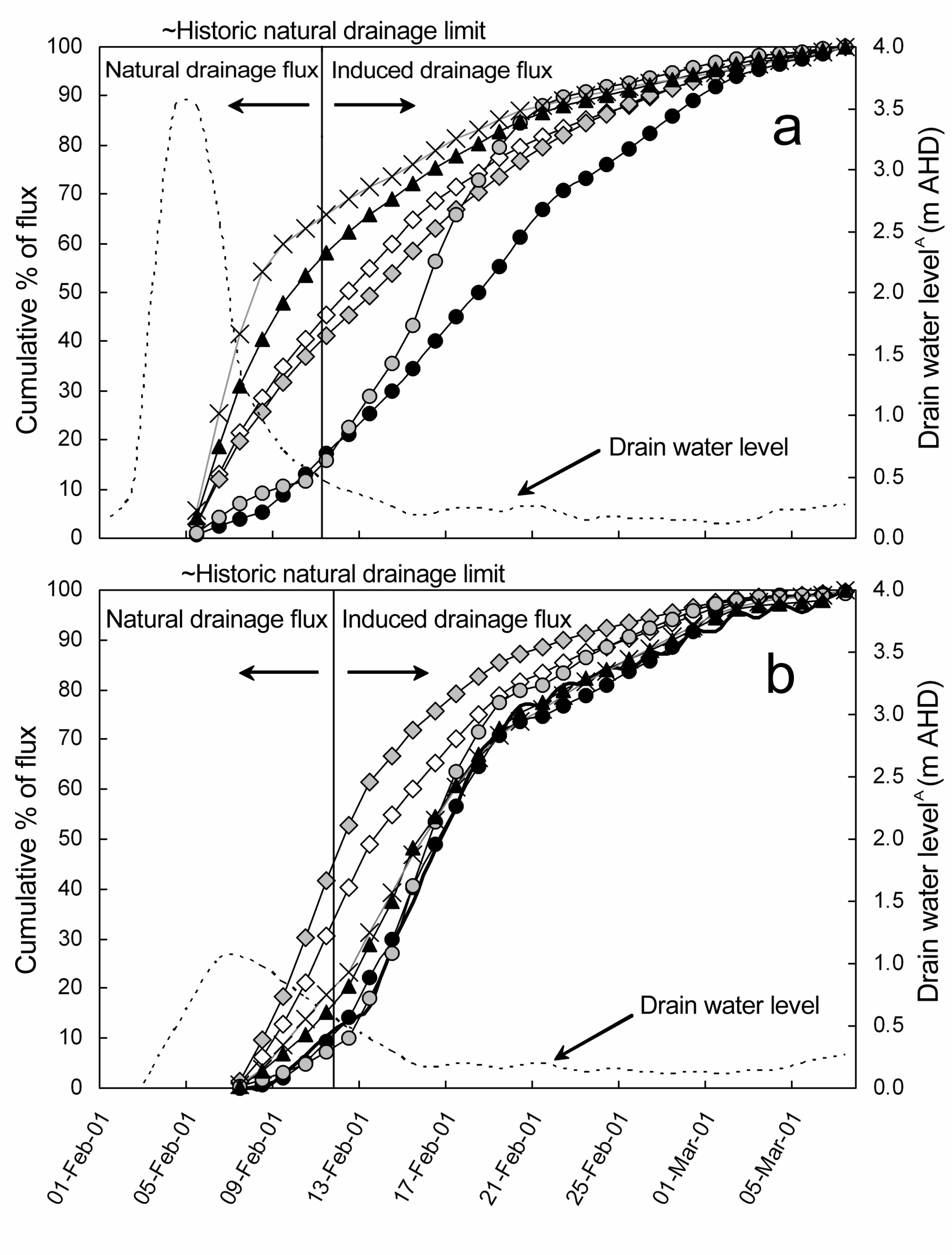

Fig. 8. Cumulative daily flux estimates for a) Blanches and b) Maloneys drainage systems for 30 days following the February 2001 flood. Historic limit to natural drainage based on 0.5 m AHD. ^A = based on 24 hr mean at floodgates. × = SO_4^{2-}, ▲ = total Al, ◇ = chemical oxygen demand, ◆ = dissolved organic carbon, ● = dissolved Fe, ● = total Fe, bold line = acidity. (Note; no titratable acidity recorded at Blanches, see Fig 6b).

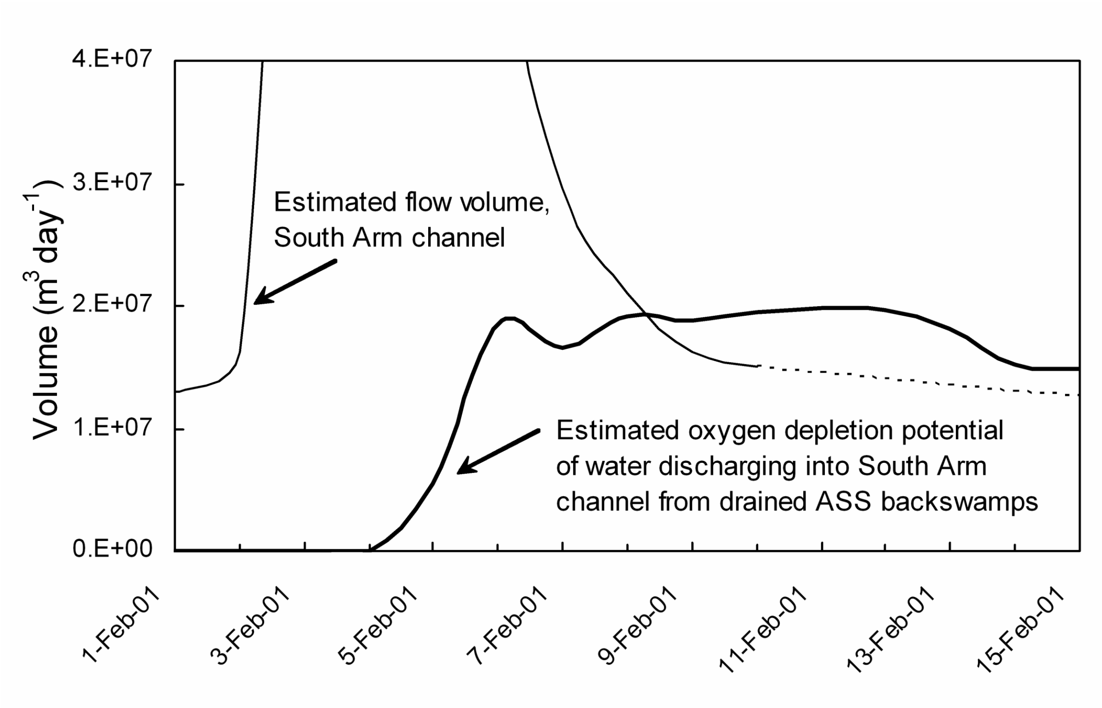

Fig. 9. The estimated oxygen depletion potential of the water discharging from drained ASS backswamps into the South Arm channel and the flow volume of the South Arm channel for ~11 days after the flood peak. (Note: dashed line indicates greater uncertainty in upper catchment flow data due to increasing tidal influence. See Methods section for details on calculations used to estimate the oxygen depletion potential of drainage waters).