Chemical controls on acid discharges from acid sulfate soils under sugarcane cropping in an eastern Australian estuarine floodplain

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Abstract

Chemical controls on acid discharges from acid sulfate soils (ASS) were investigated in an eastern Australian estuarine floodplain cropped with sugarcane. The results show that the acid export was controlled mainly by the combined effect of soil hydrological and chemical processes. During high evapotranspiration spells, lowering of the watertable allowed air to penetrate into the upper part of sulfidic subsoils and the oxidation products of sulfides were then transferred upwards by capillary action. Since the hydraulic gradient during these periods was from drains towards soils, the upwardly moved acid materials tended to be temporarily stored in the non-sulfidic upper soil layer (jarositic layer) in both soluble and buffered forms. During the alternating low evapotranspiration spells, the acid materials accumulated in the jarositic layer were exported from the soils to the drainage system after heavy rain events. However, the amount of acid exported into the drainage system during rainfall events appears to be limited, providing a large proportion of acidity stored in the upper soil layer was in buffered forms through ion adsorption and formation of basic Fe and Al sulfates (predominantly jarosite). Release of this buffered acidity did occur but tended to be very slow under successive water extraction in the laboratory. Field observation showed that the drianwater pH of the study site hardly dropped below 3.5. Such a pH value is greater, compared to that observed from the drains in the estuarine floodplains with limited drainage (e.g. Sammut et al., 1996. Marine Freshwater Research 47, 669–684.). Under sugarcane farming conditions in the study site, the intensive drainage has intensified soil acidification by increasing the frequency and magnitude of low watertable conditions which enhanced the oxidation of sulfides in the subsoils, but at the same time, the creation of highly oxidized conditions in the upper soil layer due to this artificial drainage also caused the accumulation of jarosite which appears to have an important effect on preventing more extreme acidification from occurring in the soil-drainage system. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Acid discharge; Acid sulphate soil; Sugarcane; Sulphides; Jarosite

1. Introduction

The postglacial marine transgression (PMT) caused the drowning of previous coastal river valleys and the formation of various estuaries around the world's coastal zones. Siltation of these estuaries has created deltaic and estuarine plains which attract economic development due to their favourable geomorphic and hydrological conditions for agriculture and, consequently, other agriculture-based economic activities. However, reclamation of these coastal lands has frequently encountered problems from acid sulfate soils (ASS; Dent, 1986). The improper use and management of ASS could result in the failure of economic investment on them and, in extreme situations, cause total degradation of estuarine ecosystems by exporting acid toxic substances from soils to their adjacent waterbodies. The total area of ASS was about 12.6 million ha (Beek et al., 1980), but this figure under-estimated the actual worldwide distribution of ASS because these problem soils were not recognized or mapped in many countries.

Traditionally, research into ASS has focussed on the improvement of its conditions for agricultural usage (e.g. Dost, 1973; Dost and van Breemen, 1982). Increased attention has now been paid to acid drainage from ASS and its environmental impacts (e.g. Callinan et al., 1993; Willett et al., 1993; Lin et al., 1995; Sammut et al., 1996). Acid sulfate discharges are complex events affected by many factors, but basically they are directly controlled by the combined effect of the chemical and hydrological behaviours of soil pore water resulting from the interaction of soil, physical setting and landuse.

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There has been limited research, however, on understanding the interaction of soil, physical setting and landuse on acid drainage from ASS (White et al., 1993). For this initiative, an experimental station was established in 1991 in a representative estuarine floodplain in eastern Australia to monitor various parameters concerning acid sulfate drainage. The hydrological processes controlling acid discharges have been discussed previously (White et al., 1993; Melville et al., 1998). We present here further results of the chemical aspects concerning acid discharges in the study site.

2. Study site and research methods

2.1. Study site

The study site is the estuarine floodplain of McLeods Creek, a tributary of the Tweed River, eastern Australia (Latitude 28° 18′ S, Longitude 153° 30′ E; Fig. 1). Almost the entire floodplain of the Tweed estuary has been mapped as containing ASS to some degree (Naylor et al., 1995). Most of these soils are used successfully for sugarcane production. Sugarcane has been grown in the floodplain bordering McLeods Creek (approximately 460 ha) for more than 40 years, following the construction of an intensive drainage system. McLeods Creek was widened and straightened to form the main drainage canal and numerous lateral drains feed into it from surrounding canefields. The drainage density of the floodplain near Mcleods Creek is now approximately 216.8 m/ha.

A canefield block (approximately 3 km from the junction of McLeods Creek with the Stotts Channel of the Tweed River, Fig. 1) was chosen for installation of the monitoring equipment. Three automatically recording piezometers were positioned from the middle of the block to the northern edge to monitor the groundwater dynamics. These slotted wells were inserted to a depth of 2 m into the soil. The tops of the wells project 2 m above the soil surface. This is above the height of the anticipated flood peak. Air temperature, humidity, net radiation, rainfall and wind speed were monitored above the canopy. Data from the environmental sensors were fed into a data logger and downloaded weekly via a mobile phone link to the computers at the University of New South Wales (Sydney). The system was powered by a solar panel. In addition, two submersible data loggers were placed in McLeods Creek to monitor stream pH, dissolved oxygen, electrical conductivity, temperature and water depth. Periodical monitoring of water quality was also carried out along the entire length (about 3.5 km) of McLeods Creek (White et al., 1993).
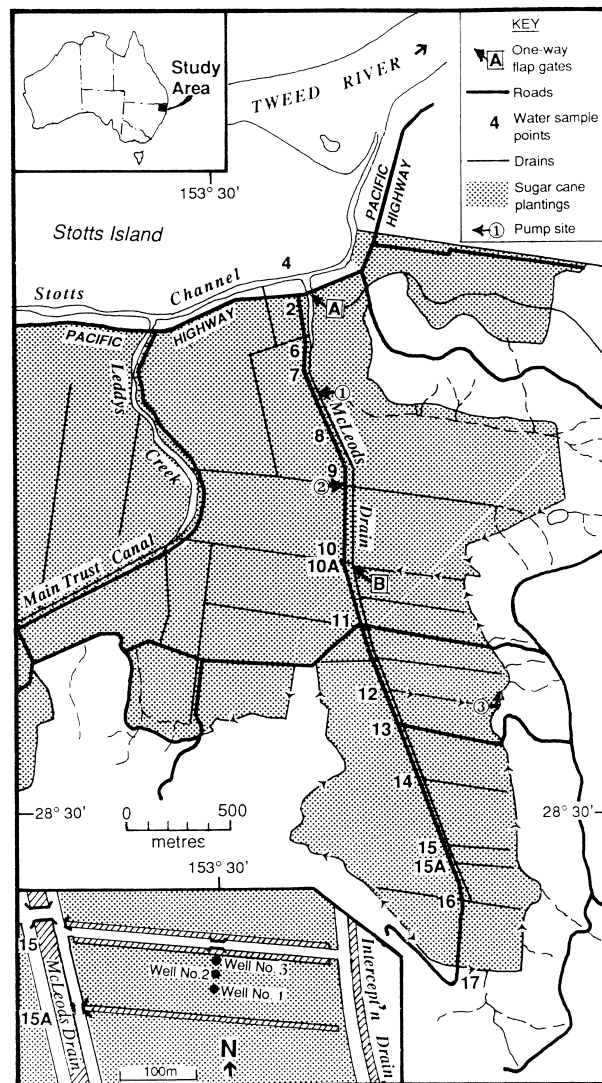

Fig. 1. Map of the investigated area showing the monitoring sites.

2.2. Soil investigation

More than 100 soil profiles have been observed and sampled to a depth > 2 m within the study area. In general, soil samples were collected using a hand auger plus a Russian D-section for materials below the water-tables. Samples were frozen in the field and oven-dried in the laboratory to minimize the oxidation of sulfides (Dent, 1986). The oven-dried samples were then hand-ground to pass a 2 mm sieve.

Particle size distribution was determined by hydrometer and sieving (Gee and Bauder, 1986). Mineral composition was determined by an X-ray diffraction (XRD) method. 1:5 (soil:water), 1:5 (soil:1 M NH_4Cl) and 1:5 (soil:1 M KCl) extracts were prepared for measurements of pH, soluble ions, exchangeable bases and exchangeable acidity. Na, K, Mg, Ca and Fe in these extracts were measured by atomic absorption spectrophotometry (Unicam 929 AA Spectrometer). pH in

water extract was measured using a MeterLab standard pH meter. Soluble SO_4 was determined turbidimetrily (Rhoades, 1982). Cl was determined using a chloride ion selective electrode (ISE), coupled with an Unicam pH/ISE meter. Al was measured by pyrocatechol violet (PCV) method (Wilson and Sergeant, 1963). Sulfur fractions of a soil sample were separated using a range of extractants: deionized water (1:5), 0.1 M EDTA solution (1:20) and 1 M HCl solution (1:25). S concentrations of a soil sample after various extractions were then measured using a Leco 2000 CNS Analyzer. According to Begheijn et al. (1978), EDTA extractable S includes soluble sulfate-S, gypsum-S and adsorbed sulfate-S, while HCl extractable S includes EDTA extractable S and jarosite-S. The sum of gypsum-S and adsorbed-S was obtained by subtracting the S concentration of a soil sample after EDTA extraction from that of a sub-sample after water extraction. Jarosite-S was obtained from the difference between S concentration of a soil sample after EDTA extraction and that of a subsample after HCl extraction. Reduced-S concentration was obtained from the S concentration of the sample after HCl extraction.

2.3. Laboratory testing for acid release from ASS

To understand the immediate sources of acid readily released from soil matrix to water in contact with it, a soil sample collected from the lower part of the jarositic layer was successively extracted by deionized water. The sample was collected from the depth between 0.6 and 0.65 m which was at an elevation slightly higher than the bottom of the branch drains adjacent to the monitored block. This depth was, therefore, within the soil layer where the sulfide oxidation products were most frequently leached out through lateral outflows.

The procedure for sample pretreatment was the same as those described above. The sample contained 1350 mg/kg of EDTA extractable S and 2950 mg/kg of HCl extractable S. 25 ml of deionized water was added into 5 g of oven-dried sample in a centrifuge tube and then shaken in a rotary shaker. After 1 h of shaking, the sample was centrifuged and the supernatant was transferred into a clean tube. The soil was continuously treated following the same procedure until pH of the extract rose to about 5. Comparison between 1 h and 10 min of shaking for the first 15 extracts has shown that both procedures have very similar extracting effects in terms of the pH and EC (Electrical conductivity) values of the same number of the extracts. The shaking time was then reduced to 10 min in order to accelerate the extraction process. Apart from the monitoring of pH and EC of the extracts, the titratable acidity (TA) of the extracts was also determined using an autotitrator. Measurements of S, Na, K, Ca, Mg, Al and Fe in the selected extracts were also conducted using an ICP-OES (Perkin Elmer Optima 3000DV).

3. Results

3.1. Soil characteristics

The main soil properties are summarized in Table 1. Some variations in these soil parameters existed among the investigated soil profiles but, in general, the soils consisted of four major layers: (1) topsoil; (2) jarositic layer; (3) seasonally oxidized sulfidic layer; and (4) reduced sulfidic layer. The topsoil was very similar to

Table 1
Major soil characteristics relating to acid discharges of the investigated site

Parameter	Topsoil	Jarositic layer	Seasonally oxidized sulfidic layer	Reduced sulfidic layer
Depth (m)	0–0.2	0.2–0.7	0.7–1.7	> 1.7
% clay (< 0.002 mm)		46	21–46	21–47
Bulk density (g/cm³)	1.03–1.12 ($n = 5$)	0.95–1.06 ($n = 7$)	0.66–0.95 ($n = 5$)	
Organic C (%)	7.05–7.56 ($n = 2$)	1.05–1.75 ($n = 5$)	1.35–2.46 ($n = 11$)	1.60–3.55 ($n = 7$)
Electrical conductivitty (dS/m)	0.15–1.75 ($n = 20$)	0.67–2.05 ($n = 21$)	0.91–3.52 ($n = 35$)	1.06–3.67 ($n = 55$)
Σ(Na, K, Ca, Mg) (mmol$_c$/kg)	35–76 ($n = 15$)	30–105 ($n = 15$)	42–200 ($n = 35$)	115–205 ($n = 55$)
SO_4/Cl (mmol$_c$/mmol$_c$)	0.10–0.22 ($n = 10$)	0.16–0.37 ($n = 20$)	0.20–0.67 ($n = 25$)	0.35–0.61 ($n = 50$)
Pyrite	not detectable	not detectable	minor	abundant
Jarosite	trace	abundant	not detectable	not detectable
pH	3.62–4.50 ($n = 20$)	3.55–4.56 ($n = 32$)	4.52–7.05 ($n = 53$)	7.03–7.76 ($n = 50$)
Exchangeable acidity (mmol$_c$/kg)	31–65 ($n = 7$)	12–59 ($n = 15$)	0–25 ($n = 35$)	0 ($n = 20$)
Soluble Fe (mg/kg)	0–1.5 ($n = 10$)	0–3.5 ($n = 25$)	0–15 ($n = 25$)	0 ($n = 50$)
Exchangeable Fe (mg/kg)	35–60 ($n = 10$)	5–35 ($n = 25$)	5–350 ($n = 25$)	5–25 ($n = 50$)
Active Fe (mg/kg)	12 700–13 900 ($n = 2$)	7200–15 200 ($n = 5$)	8320–13 600 ($n = 10$)	6950–8260 ($n = 10$)
Soluble Al (mg/kg)	0.5–1.6 ($n = 11$)	0.2–0.6 ($n = 10$)	not detectable	not detectable
Exchangeable Al (mg/kg)	35–75 ($n = 10$)	11–72 ($n = 25$)	5–16 ($n = 5$)	0 ($n = 5$)
Active Al (mg/kg)	4100–4500 ($n = 2$)	1130–2720 ($n = 5$)	1600–3000 ($n = 10$)	2200–3200 ($n = 10$)
Adsorbed and gypsum-S (mg/kg)	290–320 ($n = 2$)	670–750 ($n = 6$)	0–550 ($n = 3$)	not detectable
Jarosite-S (mg/kg)	450–660 ($n = 2$)	3160–3760 ($n = 6$)	0–1360 ($n = 3$)	not detectable
Reduced-S (mg/kg)	1100–1700 ($n = 2$)	200–700 ($n = 5$)	8600–22 680 ($n = 7$)	16 000–25 250 ($n = 3$)

the jarositic layer in soil characteristics except that it contained only trace amounts of jarosite. Both layers were characterized by lower EC and pH values, compared to the sub-layers. Pyrite was not detected from both layers but abundant jarosite was present in the jarositic layer. The jarositic layer contained a large proportion of fine clay and both layers had a bulk density around 1 g/cm^3. Analysis on sulfur fractions shows that jarosite-S was the predominant species of sulfur in the jarositic layer. The layer also contained small amounts of gypsum-S and adsorbed-S. Seasonally oxidized sulfidic layer contained reduced-S but its amount was smaller, relative to the reduced sulfidic layer. Jarosite was not detected from both seasonally oxidized and reduced sulfidic layers. Both layers had greater EC and pH values than did the upper layers. These layers were also of relatively coarse texture and had a smaller bulk density compared to those in the jarositic layer.

A representative soil profile (T6A) is chosen for illustration of the vertical variations in some soil properties relating to acid discharges. Both EC value and reduced-S concentration were low in the topsoil, but significantly increase at a depth of about 0.75–0.85 m below the surface (Fig. 2). pH was also low in the topsoil and this was accompanied by the presence of both exchangeable acidity and retained sulfate-S which were not detectable at a depth below about 1 m where pH gradually rose to above 7 (Fig. 3). It can also be seen from Fig. 4 that both soluble Fe and SO$_4$/Cl ratio had a significant peak at a depth of around 0.85–1.05 m of the profile.

3.2. Soil extract chemistry

After 45 extractions of the selected soil sample, the pH of the extracts rose from 3.52 to 4.85, accompanied by a decrease in TA from 4.5 to 0.06 mmol/kg and a decrease in EC value of the extracts from 0.3215 to 0.0085 dS/m. Concentrations of Na, Ca, Mg and S all decreased sharply after first extraction. After the fifth
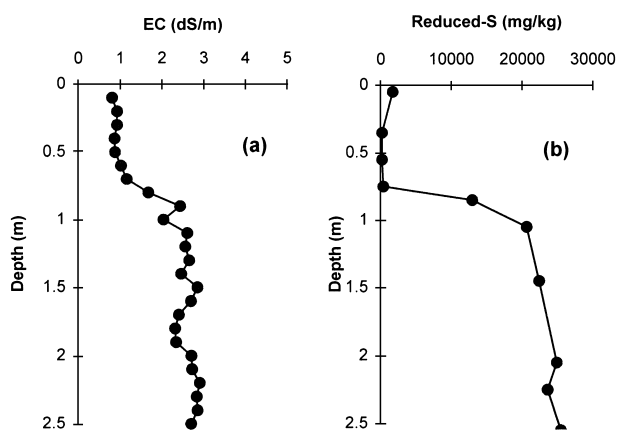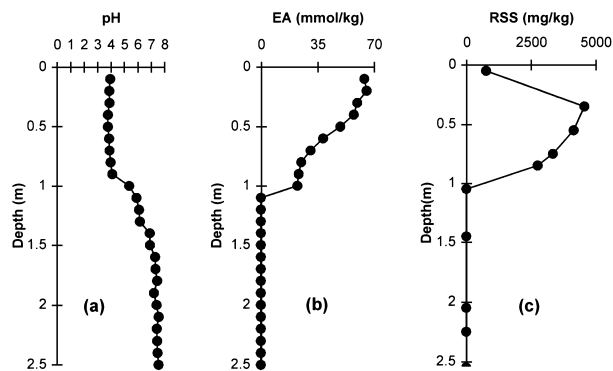

Fig. 3. Vertical variations in (a) pH, (b) exchangeable acidity (EA) and (c) retained sulfate-S (RSS) concentration along a representative soil profile (T6A).
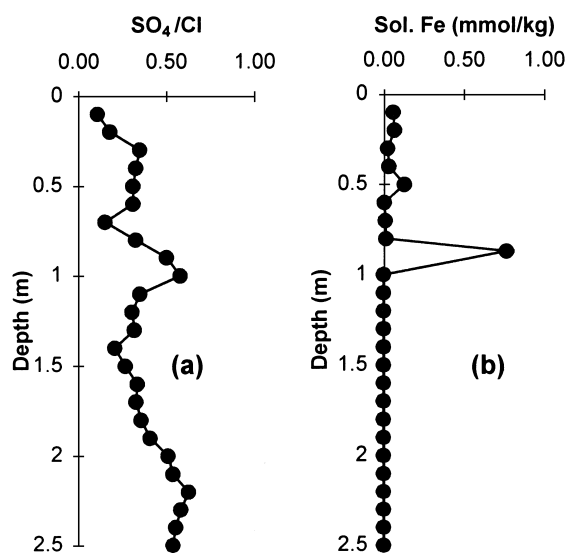

Fig. 4. Vertical variations in (a) SO$_4$/Cl ratio and (b) soluble Fe concentration along a representative soil profile (T6A).

extraction, these ions maintained at very low concentrations (frequently less than 5% of their concentrations in the first extract) until the 45th extraction. However, K had a concentration frequently more than 30% of its concentration in the first extract in all extracts obtained during the course of the successive extraction, although a sharp decrease in K concentration after first extraction can be seen. Soluble Al and Fe concentrations gradually increased after about five extractions, reached their maxima at about the 25th extraction and then gradually decreased again until the 45th extraction (Fig. 5).

3.3. Meteorological inputs, hydrological behaviour and drainwater pH

The results shown in this section have been presented in Melville et al. (in press). They are cited here to assist in illustrating the chemical controls on acid discharges

Fig. 2. Vertical variations in (a) EC value and (b) reduced-S concentration along a representative soil profile (T6A).
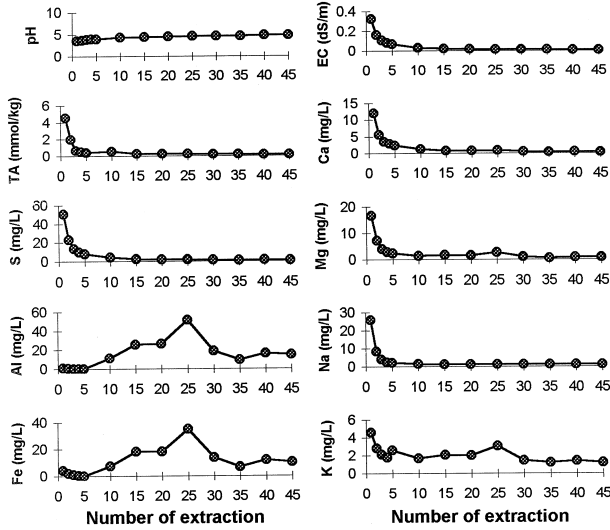
Fig. 5. Chemical changes of the monitored soil extracts from successive extraction of a jarositic soil sample with deionized water. TA, titratable acidity.

higher during the period of low ET (15 February 1992 to 8 September 1992) than during the period of high ET (7 November 1992 to 16 April 1993). This was despite the fact that the mean daily rainfall was greater during the high ET period (4.09 mm/day) than during the low ET period (3.71 mm/day). It should also be noted that the drainwater level was generally higher than the WT towards the centre of the block during the high ET period, while the converse tended to occur during the low ET period. pH of drainwater at site 10 (Fig. 1) was markedly different during these periods. Drainwater pH measured from 8 May 1992 to 14 May 1992 (low ET period) was frequently below 4 (Fig. 6(c)) when a positive watertable slope towards the drain from beneath the cane tended to occur. However, drainwater pH > 6 was recorded during the period from 28 February 1993 to 27 March 1993 (high ET period, Fig. 6(d)) when a negative water slope, away from the drain and into the cane existed.

in the study site. Fig. 6 shows the rainfall, the estimated evapotranspiration (ET) and the watertable (WT) elevations (well no. 3 is beside a branch drain and well no. 2 is about 18 m from the drain) during the period from 1 February 1992 to 3 September 1993 at the site. It is clear that the rainfall events were responsible for the sudden rise of the WT elevation recorded in most cases, but the long-term trend of the WT position was controlled by ET. The mean WT elevation in the soil was

4. Discussion

The shallow strata of the sand barrier estuarine floodplain in southeastern Australia are characterized by thin fresh riverine sediments overlying the saline estuarine sediments frequently containing sulfides (Lin et al., 1995). The lower sediments with a relatively higher EC value and reduced-S concentration in the investigated site are of estuarine sources while the
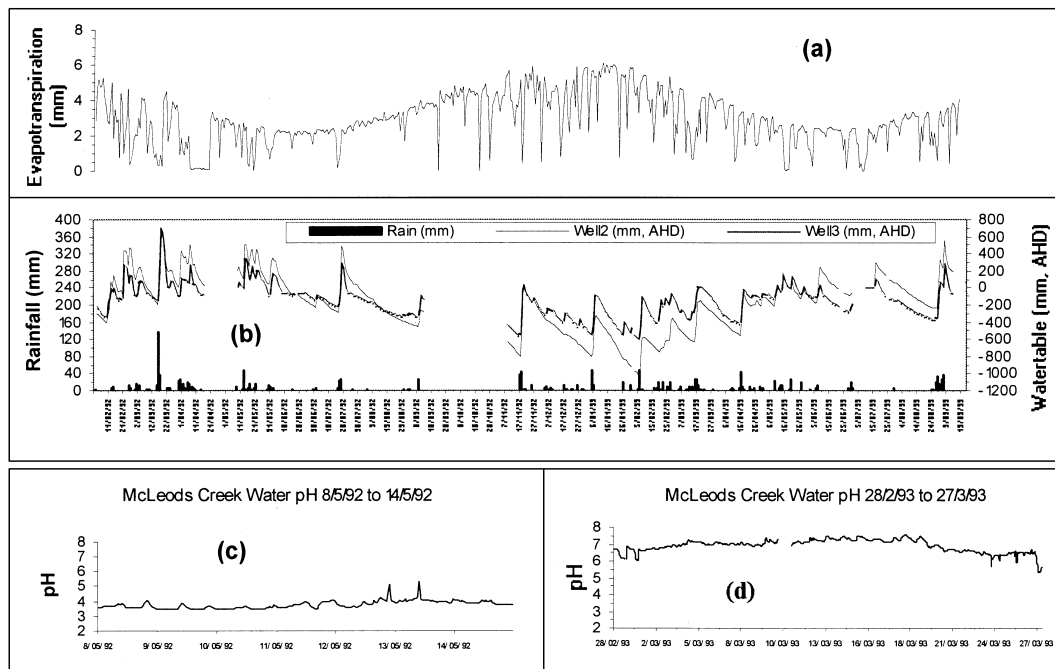

Fig. 6. Changes in (a) evapotranspiration and (b) rainfall and watertables during the period 1 February 1992 to 3 September 1993; and drainwater pH during periods (c) 8 May 1992 to 14 May 1992 and (d) 28 February 1993 to 27 March 1993 (after Melville et al., in press). AHD in (b): Australian Height Datum.

topsoils have evolved from the fresh riverine sediments. It is difficult to determine the boundary of these two layers because sulfide oxidation has occurred during the low watertable periods since the formation of the floodplain and soluble salts in the upper part of the estuarine sediments might have been removed through lateral leaching since the construction of the drainage system.

The magnitude of acid export from ASS to drainage systems is related to the rate of acid production and the proportion of total acid products being carried by the outflowing soil water. The first process is, in many cases, controlled by the elevation of the water-table relative to the depth at which the sulfidic sediments occur because negligible sulfide oxidation, leading to soil acidification, occurs under water-saturated conditions. At the study site, the current sulfidic layer normally occurs below 0.75–0.85 m from the ground surface, and the watertable elevation below this depth could be reached frequently during the high ET periods which represents the major periods for sulfide-derived acid production in the site (Fig. 6). The depth where the peaks of SO_4/Cl ratio and soluble Fe occur represents the active sulfide oxidation zone at the sampling time. However, it is likely that the oxidation of sulfides (mainly pyrite) in the seasonally oxidized sulfidic layer was incomplete, given limited penetration of air. Since the field pH of the layer was normally above 6.5 the Fe must, therefore, have been in ferrous form. The pyrite oxidation in this layer tended to follow the chemical reaction:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \qquad (1)$$

As this layer was generally below the bottom of the field drains and it is, therefore, not possible for the pyrite oxidation products to be laterally leached out except those adjacent to the main drain which had a deeper bottom. As shown in Fig. 6, during dry periods when the watertable was brought down to the sulfidic layer, the hydraulic gradient was from drain towards the soils and, therefore, there was no outflow of soil water. It is likely that most of the pyrite oxidation products tended to be transferred upwards by capillary action and this is confirmed by the fact that the topsoils had pH < 4 and contained large amounts of oxidized-S (Fig. 3).

Under more oxidized conditions of the upper soil layers, the upward transferred $FeSO_4$ tended to oxidize further to form jarosite:

$$3FeSO_4 + O_2 + 4H_2O + K^+ \rightarrow KFe_3(OH)_6(SO_4)_2 \\ +H_2SO_4 \qquad (2)$$
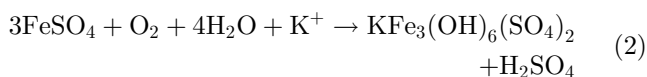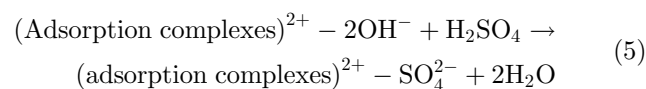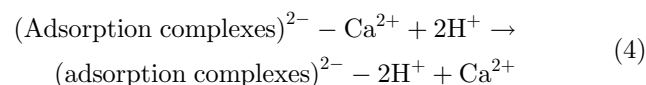
Formation of other basic sulfates of Fe and Al might also be involved, but XRD analysis suggested that jarosite was the predominant form of the oxidized-S

species in the soil. Jarosite formation, therefore, represents a major acid-buffering process which prevented extremely low pH from occurring in the soils. It is not clear whether jarosite could be formed through the reaction of H_2SO_4 with $Fe(OH)_3$ present in the upper soils in the site:

$$3Fe(OH)_3 + 2H_2SO_4 + K^+ \rightarrow KFe_3(OH)_6(SO_4)_2 \\ +3H_2O + H^+ \qquad (3)$$
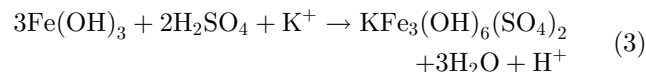
but it is certain that part of the acid transferred upwards must have been buffered through cation and anion adsorption, e.g.:

$$(Adsorption\ complexes)^{2-} - Ca^{2+} + 2H^+ \rightarrow \\ (adsorption\ complexes)^{2-} - 2H^+ + Ca^{2+} \qquad (4)$$

$$(Adsorption\ complexes)^{2+} - 2OH^- + H_2SO_4 \rightarrow \\ (adsorption\ complexes)^{2+} - SO_4^{2-} + 2H_2O \qquad (5)$$

and this is confirmed by the presence of certain amounts of adsorbed-S and great exchangeable acidity (Table 1).

Water extraction of the jarositic soil showed that 5 g of soil generated a total volume of 1.125 litres of acid water with pH values ranging from 3.52 to 4.85. The minimum pH value here was very similar to that of the drainwater observed in the field during the dry periods (Fig. 6). The amount of acid being released under the experimental conditions was about 10 mmol/kg which is a much smaller value relative to the expected total acidity, including soluble acidity and buffered acidity in the forms of exchangeable acidity and sulfate retention (sulfate adsorption and basic sulfates of Al and Fe). Clearly the acid extracted by this successive water extraction procedure mainly consisted of the originally soluble acid materials, but it is possible that part of the acidity was derived from the desorption of sulfate and dissolution of basic sulfates, especially with increasing number of extraction. The rapid extraction of soluble materials from the soil can be seen from the sharp decrease in EC value after first extraction. After the fifth extraction, EC maintained at a very low value throughout the course of the extraction. The maintenance of soluble K concentration at a relatively high percentage of its concentration in the first extract throughout the entire extraction course was in contrast with soluble Na, Ca and Mg which had the same trend as EC, indicating that sources rather than soluble forms must have been present to supply additional K^+ for its entry into the extracts. Possible candidates of such sources may include jarosite and its Al analogue, alunite (R stands for Fe or Al in the following equation) which produce H^+ upon their hydrolyses:

$$KR_3(OH)_6(SO_4)_2 + 3H_2O \rightarrow 3R(OH)_3 + K^+ \\ +3H^+ + 2SO_4^{2-} \tag{6}$$
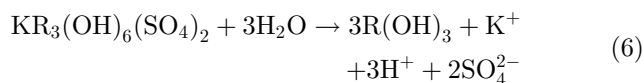
Since alunite was not detected from the investigated soils, it is assumed that the release of acidity through the above reactions was mainly from jarosite.

Adsorption complexes holding exchangeable K^+ may also release K^+ if other stronger competitors for exchange sites exist to replace K^+ adsorbed on it, e.g.:

$$(\text{Adsorption complexes})^- - 2K^+ + Ca^{2+} \rightarrow \\ (\text{adsorption complexes})^- - Ca^{2+} + 2K^+ \tag{7}$$
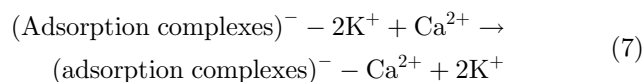
Under the extraction conditions, however, various soluble cations were rapidly removed from the soil sample during the first several extractions and, therefore, it is unlikely that there were sufficient stronger competitors present in the following extracts for the exchange sites occupied by K^+. Therefore, hydrolysis (or dissolution) of jarosite probably played a major role in this process. This also explains the supplement of additional acidity into soil extracts since one mole of jarosite can produce three moles of H^+ upon its hydrolysis (Eq. (6)). The stability field of pH for jarosite has been stated between 2–4 (van Breemen, 1973). The pH of the extracting deionized water was about 5.7, which should be able to initiate the hydrolysis of jarosite. However, the rate of this hydrolysis tended to be very slow under the experimental conditions because the pH of the extracts kept rising regardless of the reserve of large amounts of jarosite in the soil. Such a kinetic limitation of jarosite hydrolysis has been recognized by other researchers (e.g. Carson and Dixon, 1983; Shamshuddin et al., 1986). Clearly, the shaking procedure under the experimental conditions was not able to bring the reaction to equilibrium. In the field conditions, the contact between soil matrix and soil water is expected to be much weaker than in the experimental conditions. Therefore, if there are no other catalysts present to accelerate the reaction, the dissolution of jarosite should be at an even slower rate in actual field situations than in the experimental conditions. The significant accumulation of jarosite in the jarositic layer of the study site appears to provide proof of a more rapid formation rate of jarosite, relative to its dissolution. This point is meaningful because through jarosite formation, large amounts of acid can be tightly locked up in the soils with only a very small outlet for its release into environments. Such a situation may be better than that of half-drained ASS where the relatively low redox potential of the soils prevents jarosite from forming and the incomplete sulfide oxidation products, such as $FeSO_4$, are directly exported from soils into drains to cause severe acidification of drainwater (e.g. Melville et al., in press).

It is interesting to note that the changes in soluble Al and Fe concentrations of the soil extracts during the extraction course were extremely different from other cations. They started increasing after the fifth extraction and reached their maxima at the 25th extraction. This was not accompanied by corresponding increases in either EC value or TA, indicating that these soluble Al and Fe must have been at forms with very low charges. If the TA completely consists of Al^{3+} and Fe^{3+}, then the molar ratio of TA to R (the sum of Al and Fe) in an extract should be 3; if TA is completely composed of $Al(OH)^-$ and $Fe(OH)^-$, the TA/R should be 1; TA/R > 3 indicates the presence of H^+; TA/R between 1 and 3 signifies a mixed state of various Al and Fe hydroxy species; and TA/R < 1 suggests the existence of polynuclear Al and Fe species. Calculations show that the first five extracts had TA/R ratios ranging from 6.7 to 13.2, indicating that H^+ prevailed in these extracts. The extracts after the fifth extraction had TA/R ratios less than 0.1, indicative of the presence of polynuclear Al and Fe species or even suspended forms of colloidal Al and Fe hydroxides; it is not clear why this occurred. Maybe the entry of these low charged Al and Fe species into the extracts was caused, accompanied by the desorption of sulfate originally adsorbed on them; further studies are needed in order to understand the mechanism. However, the phenomenon, if also occurring in the field conditions during rainfall events, may be important since the export of these low charged Al- and Fe-bound materials, either in soluble or suspended forms, may be precipitated on the drain bottoms. Their settlement in the drainage systems would provide immediate sources for the release of toxic Al and Fe species upon subsequent acidification of drainwater.

5. Conclusion and recommendations

In the study site, sulfide in the subsoils was oxidized during dry periods when the watertable dropped. The acidic oxidation products were then transferred upwards by capillary action and gradually accumulated in the upper soil layer because it is unlikely that leaching of acid materials occurred during this period. Part of the acidity was buffered through sulfate retention (mainly through jarosite formation) and cation exchange. These enabled the temporary storage of acidity in the upper soil layer. During each rainfall event, soluble acid is firstly discharged into drains with lateral outflows due to the rising of soil watertable. The export of acid may continue with the supplement of additional acid from the hydrolysis of jarosite and sulfate desorption during prolonged rainfall events. However, it appears that the dissolution rate of jarosite through hydrolysis is very slow under pH 5.5. The significant accumulation of jarosite in the upper soil layer of the study site suggests

that the formation rate of jarosite was much more rapid, relative to its dissolution rate. This has implication on preventing more extreme acidification from occurring in the soil-drainage system. Therefore sulfide-derived acidification in the site appears to not represent a severe threat to the growth of the acid-tolerant sugarcane. This explains the sustainability of the sugarcane production in many coastal acid sulfate lands such as in Australia. As there are large amounts of buffered acid present in the soils, direct application of lime to the soils is not practical because it requires large quantities of lime. Alternatively, drain liming may be more effective given only relatively small amount of acidity contained in the drainwater and, therefore, it has economical practicability.

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