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Acid Sulfate Soils (ASS): Their Impacts on Water Quality and Estuarine Aquatic Organisms with Special Reference to East Australia and South China Coasts

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Abstract

Acid export from acid sulfate soils into aquatic ecosystems were examined in three sites: (1) a well-drained sugar cane block on the Tweed River estuarine floodplain; (2) a relatively poorly-drained pasture swamp; and (3) an empoldered paddy rice field. The first two sites are located in small river systems on the eastern Australian coast and the third is part of the deltaic plain of the Pearl River, a large river system in the South China coast. It is found that the extent to which, and the processes through which, acid sulfate soil-derived degradation of aquatic ecology occur vary among these sites and this is attributed to their different soil characteristics, physical settings, and landuses. These results have implications for potential intensive aquaculture ventures in the different locations.

Introduction

It is now widely recognised that acid sulfate soil-derived water acidification causes great problems to estuarine fisheries and aquaculture (e.g. Dunn 1965; Callinan et al. 1993). Such estuary degradation is related to the transfer of toxic acid materials from acid sulfate soils to the surface waters through drainage, and at times when the output of acidity exceeds the neutralising capacity of the waters, fish kills and fish diseases may occur (Sammut et al. 1995).

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There has been, however, limited research on understanding the interaction of soil, physical setting and landuse on acid drainage from acid sulfate soils (White et al. 1993; Sammut et al. 1996). In this paper, we examined the controls of acid sulfate drainage in three sites selected from the eastern Australia and South China coasts.

Study Sites and Methods

The three sites selected for this study are: (1) the estuarine floodplain at McLeods Creek, a tributary of the Tweed River, Australia (Lat. 28°18'S; Long. 153°30'E; see Fig. 1a); (2) Tuckean Swamp, part of the lower Richmond River estuarine floodplain, Australia (Lat. 29°00'; Long. 153°15'; see Fig. 1b); and (3) Selou, part of the empoldered deltaic plain of the Pearl River, China (Lat. 23°8'N; Long.113° 5'E; see Fig. 1c).

A monitoring station was established in 1991 at a sugar cane block near McLeods Creek. Weather characteristics and watertable elevation in the cane block have been monitored at 10 minute intervals until 1997. Water chemistry (pH, EC, temperature, depth, and dissolved oxygen) have been monitored continuously for extended study periods of several months using a Yeokal Model 606 submersible datalogger and at high resolution until 1995. In the Tuckean Swamp, water measurements in drains and the nearby estuary commenced in March 1993, with detailed work during major rainfall events. In particular, detailed water chemistry (pH, EC, dissolved oxygen, temperature, and depth) was determined, and time series data on these variables were collected in drains and the adjacent estuary (see Sammut et al. 1994). At the Selou site in China, drainwater samples were collected in June, 1991 for laboratory measurements of pH, soluble SO₄ and Al.

Soil samples from the three sites were also collected and analysed in the laboratory for pH, soluble Na, K, Mg and Ca, and pyrite content. Methods for sampling, sample pretreatment and analytical techniques employed have been described in Lin and Melville (1993).

Results

McLeods Creek site

The site has been progressively reclaimed through drainage and cultivation for sugarcane farming since about 1890. McLeods Creek was widened and straightened to form the main drainage canal, which connects to numerous branch drains. The drainage density of the floodplain near McLeods Creek is now approximately 216.8 m/ha. The surface elevation of the monitored block ranges from 0.6 to 0.8 metres AHD (Australian High Datum = -0.046m relative to mean sea level).

The soil consists of four horizons: (1) a topsoil from 0-0.35 m; (2) a jarositic layer from 0.35-0.85 m; (3) a seasonally oxidised pyritic layer from



Fig. 1. Maps showing study sites.

0.85-1.50 m and (4) an unoxidised pyritic layer from permanently below the watertable. Some characteristics of the soil can be seen in Table 1.

The climatic pattern for our Australian study sites is of low rainfall and evapotranspiration (ET) during the Southern Hemisphere winter and of high rainfall and ET during summer. Fig. 2 shows the estimated ET and the measured rainfall and watertable 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 McLeods Creek site. It is clear that the rainfall events are responsible for the sudden rise of the watertable elevation recorded in most cases, but the long-term trend of the watertable position is controlled by ET. The mean watertable elevation in the soil was higher during the low ET period 15 February to 8 September 1992 than during the high ET period 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 watertable towards the centre of the cane block during the high ET, while the converse tended to occur during the low ET period. The pH of drainwater at Site 10 on McLeods Creek (refer to Fig. 1a) is markedly different during these periods. Drainwater pH measured from 8 May 1992 to 15 June 1992 (low ET period) was frequently below 4 (see Fig. 2c) 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, see Fig. 2c) when a negative water slope, away from the drain and into the cane existed.

Study site	Soil horizon	Depth (m)	pН	S* (mg/kg)	P** (%)
McLeods Creek	Top soil	0-0.35	4.3	511	0
	Jarositic	0.35-0.85	3.9	420	0
	Partly oxidised pyritic	0.85-1.50	5.6	1146	0.89
	Unoxidised pyritic	1.50-2.00	7.0	1638	2.15
Tuckean Swamp	Peaty top soil	0-0.50	3.3	107	0
-	Partly oxidised pyritic	0.50-1.70	3.0	495	4.15
Selou	Tep soil	0-0.20	5.2	189	0
	Partly oxidised pyritic	0.20-0.80	3.6	289	0.95
	Slightly oxidised pyritic	0.80-1.00	4.5	497	0.98

Table 1 Soil properties of the three investigated sites.

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S*: Sum of soluble K,Na, Ca and Mg; P**: Pyrite content



Fig. 2. Changes in (a) evapotranspiration and (b) rainfall and watertables during the period 1 February 1992 to 3 September 1993; drainwater pH during periods (c) 8 May 1992 to 15 June 1992 and (d) 28 February 1993 to 27 March 1993.

Tuckean Swamp

Since the late 1800's, the swamp has been progressively drained for grazing and dairying. The drainage system comprises open-ditch drains 10-20 m wide and up to 5 m deep but generally less than 2.5 m deep and includes an eight-celled floodgated culvert, known as the Bagotville Barrage (Fig. 1). The barrage opens downstream on low tide but closes on high tide, thus limiting the inflow of tidal water.

Soil properties in the site are different from those in the McLeods Creek floodplain with a peaty topsoil of about 50 cm, above a pyritic layer. Jarositic mottles are not generally seen in soil profiles except for locations where nonpeaty soils occur. The pH ranges from 3.5 to 4.5 for the topsoils, but extreme acidity (pH<3) can occur in the partly oxidised pyritic layer. Some chemical properties of the soil can be seen in Table 1.

The pH of drainwater and river reaches downstream of the Bagotville Barrage were made for various times from March 1993 to 1996. Table 2 shows examples of water chemistry conditions during a wet period, for the tidal and drain water reaches.

Selou

The site is used for paddy rice cultivation which requires periodic innudation of the land. The abundant fluvial discharge of the Pearl River, combined with the lower elevation of the polder surface relative to high tide level, enables the irrigation of rice fields with the fresh tidewater during high tide stages. The irrigation water is then drained during low tide stages. This irrigation-drainage system consists of alternating inflowing canals and outflowing main drains approximately perpendicular to the river channel. Small field drains perpendicular to the outflowing main drains are dug about 10 m apart to assist in the drainage of soil water during low tides. During the rice growing period, the drainage-recharge cycle is normally completed in one or several days.

Acid sulfate soils in the site are characterised by the shallow occurrence of the pyritic layer (< 0.30 m below the surface, see Table 1). Drainwater quality measured (n=7) on 5 June 1991 shows pH range from 4.1-4.9; soluble SO_4^{2} range from 1.9 to 2.5 mM/L; and soluble Al range from 0.03 to 0.1 mM/L (Lin et al. 1995).

Discussion

The export of acidity from acid sulfate soils to aquatic ecosystems depends on two factors: (1) acid production; and (2) discharge of acid soil water. The first process is, in many cases, controlled by the elevation of the watertable relative to the depth at which the pyritic sediments occur because negligible pyrite oxidation, leading to soil acidification, occurs under water saturated conditions.

At the McLeods Creek site, the pyritic layer normally occurs below 0.85 m from the ground surface, and the watertable elevation below this can be reached frequently during the high ET period, which represents the major

Site	pН	EC (dS/m)	Cl (mg/L)	SO4 (mg/L)	Cl/SO4	Al* (mg/L)	Fe** (mg/L)
G1	3.2	7.25	1565	2100	0.75	90.2	33.4
Tl	3.6	0.22	30	48	0.63	2.0	0.35
S1	3.2	0.95	115	248	0.47	10.1	2.42
H1	3.1	1.71	317	335	0.94	17.5	1.81
B 1	5.1	0.47	102	43	2.4	0.61	0.05

Table 2. Chemistry of drainwater and tidal water at Tuckean.

Al*: Monomeric Al; Fe**: Filterable Fe.

period for pyrite-derived acid production in the site. As the hydraulic gradient at these times is from the drain towards the soil, there is therefore no outflow of soil water during this period. However, the pyrite oxidation products tend to be transferred upwards in the profile by capillary action and react with aluminium and iron hydroxides to form basic Al and Fe sulfate minerals. This explains the formation of a thick jarositic layer immediately above the pyritic layer:

$$2H_2S_4^\circ + 3Fe(OH)_3 + K^+ \rightarrow KFe_3(OH)_6(SO_4)_2 + 3H_2O + H^+$$
(1)

The reaction represents a major acid-buffering processs which prevents extremely low pH from occurring in the soil. The 1:5 soil:water extracts of the topsoils commonly have pH value ranging from 3.5-4. The outflow of acid soil water is generally controlled by the elevation of the soil watertable relative to the drainwater level. Because the base of most branch drains is above the pyritic layer and the subsoil has very small hydraulic conductivity, direct removal of the pyrite oxidation products from the pyritic layer through lateral flow is unlikely except for soils adjacent to the main drain which has a deeper base. Therefore, the large, infrequent outflow of acid soil water occurs during periods of high rainfall and low ET (see Fig. 2) so that the watertable rises through the jarositic layer and non-pyritic topsoil to above the ground surface or to provide a positive hydraulic gradient into the drain. Acid outflows from branch drains also occur with most rainfall events because of run-off from the adjacent soil surfaces and drain banks which have exposed jarositic material.

When the jarositic layer is saturated with soil water due to watertable rise, jarosite can hydrolyse to release H+:

$$KFe_3(OH)_6(SO_4)_2 + 3H_2O \rightarrow 3Fe(OH)_3 + K^+ + 3H^+ + 2SO_4^{-2}$$
 (2)

The control of acid generation through hydrolysis of jarosite at McLeods Creek is shown by the similarity of drainwater pH and the equilibrium pH for jarosite (van Breemen 1988).

Unlike the floodplain at McLeods Creek, a jarostic layer is generally absent in the peaty soils of the Tuckean Swamp. This is attributed to much less drain density and a thick peaty topsoil in the Tuckean Swamp, which limit the penetration of air and gives incomplete oxidation of pyrite. In such a case, the pyrite oxidation product is mainly ferro-iron sulfate rather than jarosite. The highly mobile ferrous iron is readily leached from the soils and then causes the acidification of drainwater and estuaries through its subsequent oxidation and hydrolysis:

$$2\text{FeSO}_4 + 1/2\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 4\text{H}^+ + 2\text{SO}_4^{-2}$$
 (3)

The release of acid through this chemical reaction is more rapid than through the hydrolysis of jarosite, and the pH of the soil-water is not buffered by jarosite formation. Therefore extreme pH values to much less than 3 can occur in the Tuckean Swamp soils and drains. Nevertheless, as Sammut et al.

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(1996) have shown, both the Tweed River floodplain and Tuckean Swamp provide annual discharges of several thousands of tonnes of sulfuric acid, causing major water quality degradation in these estuaries. These discharges occur during and following flood peaks.

The magnitude of acid discharges, and the severity of their biological impacts in terms of fish kills and EUS fish disease outbreaks vary with the nature of the flood events but tend to be greater following prolonged droughts (e.g. Dunn 1965; Easton 1989; Callinan et al. 1993; Sammut et al. 1995). Drought events lower the watertables in ASS landscapes enabling increased pyrite oxidation, and accumulation of toxic acid products in both soil profiles and drainage systems from where it is exported to the estuary in subsequent floods. The timing of these major droughts seems to coincide with the onset of El Nino-related ENSO events.

The natural controls and human activities over the past millenium have greatly reduced the accumulation of pyrite in the Pearl River Delta (Lin and Melville 1994). The present irrigation-drainage system there, reduces pyrite oxidation and acid formation because of the inundation under paddy rice. The cycles of water exchange every few days limit accumulation of toxic substances in the soils and drains. Finally, the large magnitude of the freshwater dilution and acidity buffering by tidal exchange provide a much greater overall buffering capacity of the Pearl River estuary system. Thus, fish mortalities have not been observed there. However, changed landuses and widespread disturbance of ASS landscapes could change this situation.

Conclusion

ASS-derived degradation of water quality occurs at the three examined sites, but the mechanisms controlling such a process vary due to differing soil characteristics, physical settings, and landuses. In general, the small river systems in the eastern Australian coast have greater acid hazards to aquatic ecosystems, compared to the much larger Pearl River on the South China coast. The results have also implications for potential intensive aquaculture ventures in these types of estuarine landscapes. With any such ventures, the existence, distribution and nature of acid sulfate materials, that might be caused to further oxidise during any construction, needs to be known. Any further oxidation needs to be managed so as to avoid acidification problems within the aquaculture ponds or in any estuarine area to which drainage is discharged. Finally, the total acidity load from all landuses on ASS must not exceed the estuary system's buffering capacity otherwise widespread water quality degradation and biological impacts will ensue.

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