

Controls on water acidification and de-oxygenation in an estuarine waterway, eastern Australia

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Abstract

The quality of soil and water was investigated in an estuarine floodplain system, eastern Australia. The backswamp portion of the floodplain is underlain by sulfidic sediments at depths about 0.5–0.9 m below the ground surface. Actual acid sulfate soils have developed due to sulfide oxidation as a consequence of land drainage since the early 1900s. These acid sulfate soils have a high measured total actual acidity (TAA, up to 500 mmol H⁺/kg). However, only a very small proportion (<2%) of this TAA occurs in a water-soluble form.

Water quality monitoring in the creek (Rocky Mouth Creek) draining the estuarine embayment during the period from May 1998 to July 2000 shows that acidic flows (pH < 4.5) of several months occurred intermittently in the upper reach of the creek. This may be attributed to the hydrolysis of Fe³⁺ after the oxidation of Fe²⁺ that is exported into the creek from acid sulfate soils through an artificial drain network. It is hypothesized that Fe²⁺ is being generated by biological iron reduction, which consumes H⁺ and thereby drives the conversion of retained acids to soluble acids. This allows the release of retained acids and subsequently the translocation of acids from soils to the adjacent waterway.

Monitoring results also show clear responses of pH and dissolved oxygen (DO) to heavy rainfall events during the period of alternating high (>6) pH-dominated flows. Frequently, pH and DO levels in the creek water drop during flooding. Results from field investigation and experimental simulation suggest that DO depletion associated with organic matter decomposition takes place rapidly in the floodwater inundating the soils and this DO-depleted water has a significant capacity to further de-oxygenate any receiving water. However, the consumption of DO in floodwater is not clearly related to oxidation of Fe²⁺. It is not certain what other DO consumers are involved in the process and further research is needed to fill this knowledge gap.

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1. Introduction

Coastal wetland soils frequently contain metal sulfides (predominantly pyrite), which oxidize in aerated conditions. Sulfide oxidation produces sulfuric acid and creates actual acid sulfate soils (ASS) in drained coastal backswamp areas. Under natural conditions, many

coastal wetlands remain inundated for much of the year or are subject to regular tidal flooding, which may effectively prevent or inhibit sulfide oxidation. Therefore, in many cases, the development of ASS relates to coastal land disturbances that cause the exposure of sulfidic materials to air (e.g. Dent, 1986). Estuaries and their associated floodplains are highly productive systems that attract human settlement. The draining of large areas of similar sulfidic wetlands in many coastal areas around the world has brought about severe ecological degradation due to the lack of awareness of the environmental impacts from improper uses of sulfidic wetlands (e.g. Dent and van Mensvoort, 1993; Lin et al., 2002a).

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In eastern Australia, extensive areas of sulfidic coastal floodplains and wetlands have been drained, primarily for cattle grazing and sugarcane cropping, since European settlement in the 19th century (Tulau, 2002). Flood mitigation structures (including drains and floodgates) have been constructed to accelerate the removal of surface water from the floodplains during heavy rainfall events and protect low-lying backswamps from regular tidal inundation (Haskins, 2000; Lin et al., 2001). Such engineering works have resulted in the lowering of water tables down to and below the sulfidic layer in the floodplains with the resultant development of ASS (e.g. Walker, 1972; NSW Agriculture, 1989). Extreme soil acidification (pH below 3.5) can occur in many drained sulfidic floodplains and wetlands (e.g. Lin et al., 1999). In addition to acidification, de-oxygenation of floodwater is also of great concern (Sullivan et al., 2002; Johnston et al., 2003). The water draining from ASS landscape has caused severe ecological degradation in the receiving estuarine waterways (e.g. Easton, 1989; Callinan et al., 1993; Hyne and Wilson, 1997; Roach, 1997; Corfield, 2000). Flood mitigation work significantly reduces the duration of flood inundation in the floodplains, which could result in increased organic debris due to intensified water stress for wetland vegetation during dry seasons. On the other hand, some water-intolerant vegetation species have replaced original water-tolerant species in the emergent zone of some backswamps that have been created following flood mitigation. During extended flooding, debris from these species may also contribute to total organic load. De-oxygenation can occur in water standing in floodplain backswamps following heavy rainfall events (Wood, personal observation) and it is likely that this is linked to the degrading organic matter derived from the inundated water-intolerant vegetation species (e.g. Wilkinson, 2000). In extreme situations, the floodwater may appear dark in colour (locally called “black water”) and may cause skin and eye irritation on contact. Although “black water” has been locally recognized for over two decades (Salisbury, 1977), detailed studies on its formation and environmental impacts are lacking.

In the current work, we investigate the chemical and biochemical characteristics of the soil and water in a sulfidic distributary floodplain system that experienced long-term artificial land drainage and tidal exclusion. The objective is to understand the major chemical and biochemical processes that contribute to the discharge of acidified and de-oxygenated water in this estuarine waterway.

2. Research methods

2.1. Study site

The study site, Rocky Mouth Creek floodplain, is located in the northern NSW coast, eastern Australia (see

Fig. 1). Rocky Mouth Creek is a distributary of the Richmond River and it drains a sub-catchment of about 65 km². Much of the sub-catchment is low-lying floodplain (about 24 km²). The Rocky Mouth Creek floodplain system has been significantly modified by human activities since early 1900s. The floodplain has been drained for cattle grazing and sugarcane growing. Main drains and smaller farm drains were constructed to accelerate the removal of surface water following heavy rainfall events and to drain the soils as well. During the 1960s, the creek was straightened by a constructed cut-off at the location approximately 3.5 km upstream of its confluence with the main channel of the Richmond River. The natural channel section of the creek was blocked by a dike and a floodgate system was installed in a constructed channel section to prevent tidal water from flowing into backswamps upstream of the floodgate system.

2.2. Field methods

Field investigation was carried out during the period March–June 2001. Five soil cores were collected to a depth ranging from 1 m to 1.5 m using a Dormer Soil Sampler (Category No. 6-1-1-3-3) in two major backswamps (BS and HW, refer to Fig. 1). Immediately after soil core collection, soil pH (roughly 1:2.5, wet soil:deionized water) was measured at 10-cm intervals using a portable pH meter. Soil samples were then taken at 10-cm intervals and sealed in plastic bags and transported to the laboratory for oven-drying within 2 h of sampling. The pH, dissolved oxygen (DO) and electrical conductivity (EC) in backswamp surface water, drain water and creek water were also measured in the field using a water quality meter. DO was also checked with the iodometric titration method (APHA 4500-O-B) (American Public Health Association, 1992). A comparison of the results showed reasonably good agreement between both methods. A DO and pH transect along the Rocky Mouth Creek upstream of the floodgate (see Fig. 1) was also established on June 5, 2001. In addition, a “black water” sample was collected during a flood event (February 2001) for laboratory analysis of pH, Al, Fe, BOD₅ and total organic C.

2.3. Water quality monitoring

A submersible multi-parameter water quality data logger has been installed under the floodgate structure (see Fig. 1) by Richmond River County Council since May 1998. Water level, temperature, pH, EC, DO and turbidity at this point were monitored at 15-min intervals. In this paper, data recorded during the period from May 1998 to July 2000 along with other data that are relevant to the current discussion are presented.

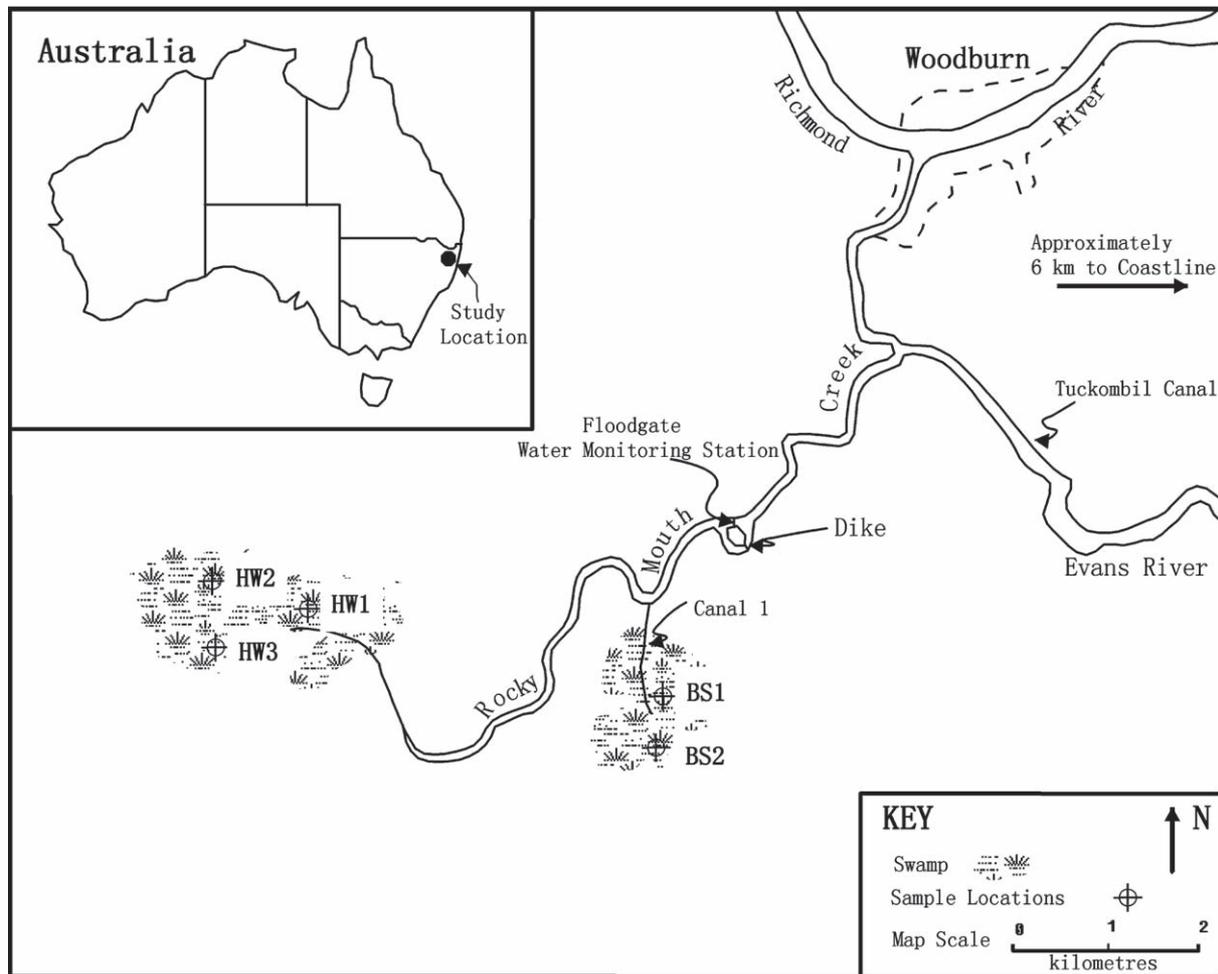


Fig. 1. Location map of the Rocky Mouth Creek floodplain showing the sampling sites.

2.4. Simulation experiments

Incubation experiments were also conducted to observe the chemical, biochemical and microbiological changes of the artificial floodwater overlying soil with growing grass. Two samples (approximately 600 cm³ of soil with growing grass) were placed in two 1.5-L wide-neck plastic bottles. Deionized water of known DO concentration and pH was added to a level very close to the top of the bottle (15 cm high). One bottle was capped (airtight, labeled as sample S&G-C) while another was left open (labeled as sample S&G-O, in duplicate). Another two pairs of samples were also prepared using underground portions (approximately 600 cm³ of soil with root material, labeled as sample S-C for the capped sample and sample S-O for the uncapped sample, sample S-C was in duplicate) and aboveground portions (50 g of fresh grass straw, labeled as sample G-C for the capped sample and sample G-O for the uncapped sample, both samples were in duplicate).

pH and DO were monitored in these six samples at the following times after the addition of deionized water:

20 h, 45 h, 70 h, 150 h, 290 h and 500 h. At 150 h and 290 h, Fe, microbial abundance and tannin were determined in the water samples. In addition, at 150 h of incubation, 25 mL of the water sample from each bottle was mixed with 25 mL of fresh deionized water with known DO concentrations. The de-oxygenated water was added to the fresh deionized water very carefully to minimize the introduction of atmospheric oxygen into the water samples. The DO of the mixture was then measured to determine the DO-consuming capacity.

2.5. Sample pretreatment and laboratory analytical methods

Soil samples were oven-dried at 60 °C and then ground to less than 2 mm. For each sample, three soil extracts were prepared: (a) 1:5 (soil:water), (b) 1:5 (soil:1 M NH₄Cl), and (c) 1:20 (soil:4 M HCl). pH, EC (electrical conductivity) and chloride ion in a 1:5 (soil:water) extract were measured using a calibrated pH meter, EC meter and Lachat FIA, respectively.

Titrateable acidity in water and the NH_4Cl extracts was measured by titrating an aliquot of each extract to pH 5.5 with 0.1 M NaOH solution (Lin et al., 2002b). Total actual acidity (TAA) was measured following the method of Lin et al. (2000). A range of elements in various extracts, including Al, Mn, Fe, K, Na, Ca, Mg, Zn, Cr, Co and S was measured using an ICP-AES. The water extract is used for determination of the amount of an element that is present in soluble form and the NH_4Cl extractable concentration of a metal is used as an estimate of the sum of soluble and exchangeable forms of that metal, whereas the HCl extractable concentration of an element represents a wide element pool including soluble, exchangeable and acid reactive mineral forms of that element.

Total carbon (C), sulfur (S) and nitrogen (N) concentrations in the topsoil samples were also determined using a Leco CNS Analyzer. Since inorganic C in strongly acidic soils is usually negligible, the total C measured can be used as a reasonable estimate of organic C. Sulfide-S was estimated in the form of chromium reducible sulfur (CRS) (Sullivan et al., 2000).

For the water samples, concentrations of various elements were determined by an ICP-AES. Tannin concentration was measured using an HACH DR 2000 Spectrophotometer. The following parameters were determined following the Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1992): DO (APHA 4500-O-B), biochemical oxygen demand (APHA 5210-B), and total number of microorganisms (APHA 9222-B).

3. Results and discussion

Fig. 2 shows the vertical variation of CRS along three selected soil profiles in the study site (refer to Fig. 1 for their locations). It can be seen that the depth of the sulfidic layer varies from about 0.5 m to 0.9 m below the

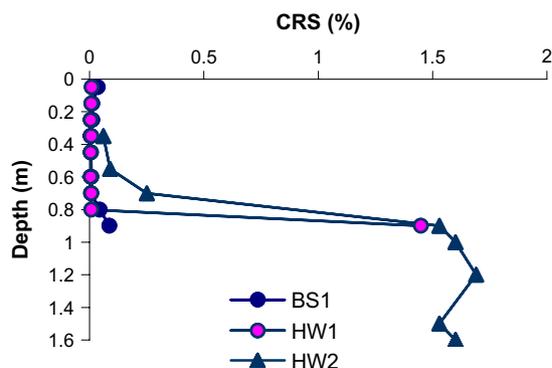


Fig. 2. Vertical variation of chromium reducible sulfur (CRS) contents along the soil profiles at three different locations.

land surface, which is similar to those found in the lower parts (backswamps or farmlands evolved from backswamps after intensive drainage) of other NSW estuarine floodplains (e.g. Lin and Melville, 1993; Lin et al., 1998).

Prior to artificial drainage, the floodwater was probably retained in the backswamps by the levees, which could effectively limit oxidation of sulfides. Following the construction of flood mitigation works, the floodwater is rapidly removed from the backswamps through the drainage systems within a few days while tidal inundation of land during dry periods is prevented due to floodgate closure. Under such conditions, the level of the water table in the floodplains can be lowered to below the upper boundary of sulfidic layer during dry seasons, particularly during extended dry spells. This allows the oxidation of sulfides to occur, and subsequently the oxidation products (sulfuric acid and ferrous sulfate) to react with other soil components. Part of the soluble acid can be permanently removed by reactions with carbonates and silicates, while a further part of soluble acid can be retained through cation exchange, protonation of variably charged particles and formation of basic sulfate minerals. Any remaining soluble acid becomes available for transfer into drains, primarily via the movement of ground water.

Fig. 3 shows the vertical variations of organic C, EC and pH along a selected soil profile (BS1). Organic C is enriched in the topsoil layer and sharply decreased in the subsoil layer (Fig. 3a). EC was lower in the topsoil layer than in the subsoil layer (Fig. 3b). The lowest pH in the investigated soils was below 3.5 (Fig. 3c), indicating that significant acidification has taken place in the site. It is interesting to note that the lowest pH point occurred above the sulfidic layer, reflecting the upward movement of acid materials from the sulfide oxidation zone, probably through capillary action. Fig. 4 gives a comparison of various acidity fractions along Profile BS1. It is clear from the figure that only a very small proportion (<2%) of total actual acidity was in water-soluble forms. The mean titrateable acidity (TA) (1:5 water extract) of the topsoil (top 0.5 m) in Profile BS1 was around 1.16 mmol/L, which is only slightly greater than that in the adjacent drain water (0.97 mmol/L, refer to Table 1). This is in contrast to some other NSW sites where soluble acidity can be as high as 50 mmol/L in a 1:5 (soil:water) extract (e.g. Lin et al., 1999). Clearly, the amounts of water-soluble acid stored in the soils of the Rocky Mouth Creek floodplain are far from sufficient to maintain the long-lasting acid tidal flows as shown in Fig. 5, where there are alternating low and high pH tidal flows of several months during the period from May 1998 to July 2000. It is interesting to note that the constant acid tidal flows only occurred during the winter–spring periods, and this pattern is in good agreement with previous

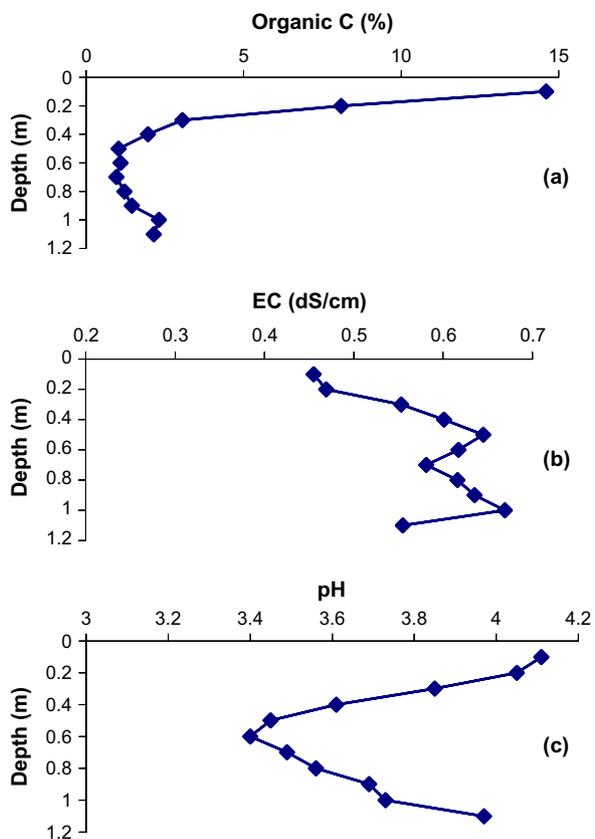


Fig. 3. Vertical variation of (a) organic C, (b) EC and (c) pH along a representative soil profile (BS1).

monitoring results obtained at the same location by Manly Hydraulics Laboratory (1997) during the period 1994–1996. The reason for this is unknown and further research is needed to explain it. Fig. 6a shows the pH transect along the Rocky Mouth Creek upstream of the

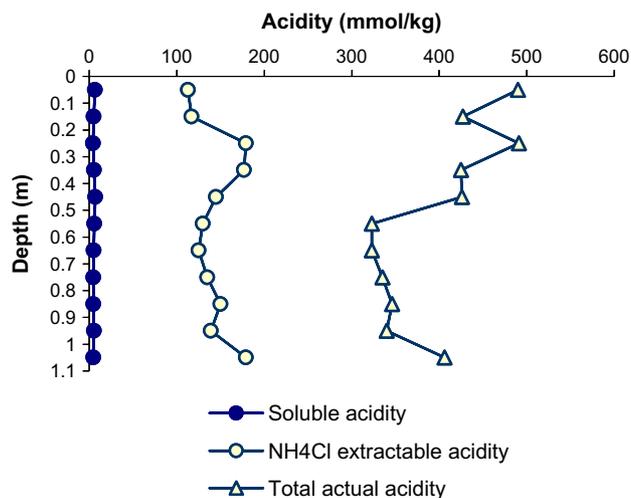


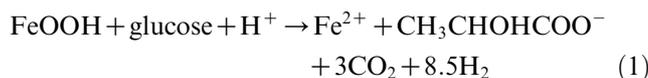
Fig. 4. Vertical variation of (a) soluble acidity, (b) NH₄Cl extractable acidity, and (c) total actual acidity along a representative soil profile (BS1).

Table 1
Chemical and biochemical characteristics of various water samples

Parameter	1:5 Soil extract	Creek water (near floodgate)	Creek water (head water)	Drain water (Canal 1)	Black water
EC (dS/m)	0.52	0.96	1.25	0.63	
pH	3.79	3.72	3.35	3.25	5.46
TA (mmol/L)	1.16	0.41	0.83	0.97	
Cl/SO ₄		0.45	0.69	0.36	
DO (mg/L)		5.60	3.60	0	
Al (mg/L)	3.90	1.49	2.35	0.79	0.66
Mn (mg/L)	0.56	0.75	1.03	0.39	
Fe (mg/L)	6.30	0.72	3.13	11.19	11.87
Zn (mg/L)	0.06	0.06	0.08	0.02	
BOD ₅ (mg/L)					7
Total organic C (mg/L)					25

floodgate, established using data recorded on June 5, 2001. It can be seen that the entire reach had very low pH (<3.5) with little vertical variation of pH in the water column at all measured locations.

These results suggest that transformation of retained acid to water-soluble acid must have taken place to sustain soil soluble acidity and thereby acid flow in the creek. A possible mechanism through which the retained acid is converted to water-soluble acid is biological iron reduction, as expressed by the following chemical equations:



and then

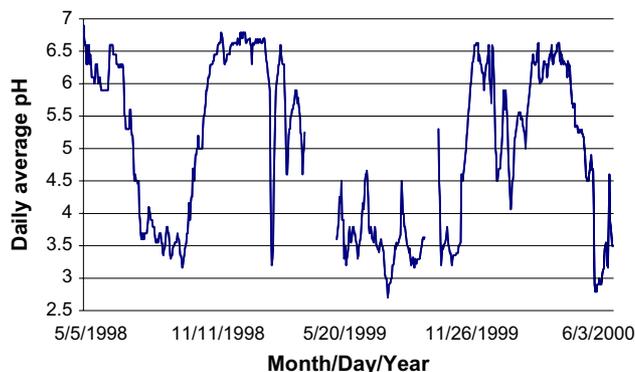
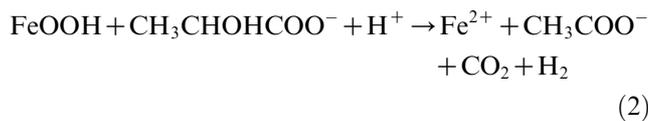


Fig. 5. Variation of daily average water pH in Rocky Mouth Creek at the water quality monitoring station during the period from May 1998 to July 2000.

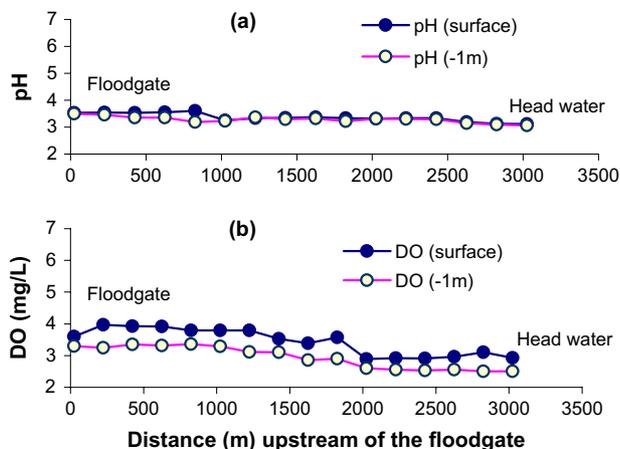
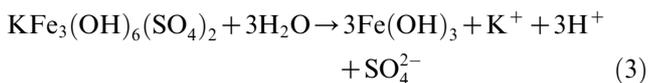


Fig. 6. pH (a) and DO (b) transects along the Rocky Mouth Creek upstream of the floodgate, established using data collected on June 5, 2001.

These reactions consume H^+ and raise soil pH, which could lead to the release of retained acids, e.g. hydrolysis of jarosite



If Fe^{2+} produced in Eqs. (1) and (2) is removed from the soils with draining water, then the location of acid re-generation through Fe^{2+} oxidation will shift to waterways and cause acid flows in the creek while Eq. (3) type reaction continues to supply H^+ for the processes in Eqs. (1) and (2) to take place. This assumption is supported by the fact that the drain water (sample Canal 1) contains much higher Fe (11.19 mg/L) than Al (0.79 mg/L) (see Table 1). It is unlikely that this Fe was mainly in ferric form because higher Fe^{3+} concentration than soluble Al^{3+} concentration in aqueous systems appears to occur only when $pH < 2.5$. The drain water sample (Canal 1) contained no dissolved oxygen, which suggests the consumption of DO by Fe^{2+} oxidation. The DO in the water sample near the floodgate was 5.6 mg/L, corresponding to a much lower Fe reading (0.72 mg/L). The maintenance of zero DO in the drain water prevents further Fe^{2+} oxidation from occurring before the drain water discharges into the creek and is mixed with the high DO creek water. This explains the occurrence of extremely high Fe concentration in the drain water. Fe concentration decreased in the creek water due to its oxidation and subsequent precipitation as iron hydroxide, which simultaneously acidifies creek water. The DO transect established on June 5, 2001 (Fig. 6b) shows that DO tended to increase downstream and this corresponds very well with the increasing pH downstream. This may reflect the decreasing rate of DO consumption downstream as a result of decreasing concentration of Fe^{2+} in the creek water.

In addition to continuous acidic flows of several months, it has also been frequently recorded that pH suddenly drops following heavy rainfalls during the periods between two continuous acidic flows. Fig. 7 shows an example of such events. During the period January 6–25, 2000, pH rapidly dropped from near 7 to about 4.5 following a heavy rainfall event (>200 mm) from January 11 to 15. Similarly, DO concentration also dropped from above 13 mg/L to 0 mg/L during the same period. It is possible that the DO depletion is related to the oxidation of Fe^{2+} , which acidifies the floodwater. However, considering that it requires at least 90 mg of Fe^{2+} to bring the DO of 1 L of floodwater from 13 mg/L to 0, it appears that Fe^{2+} is not a major DO consumer in this event. Analytical results of black

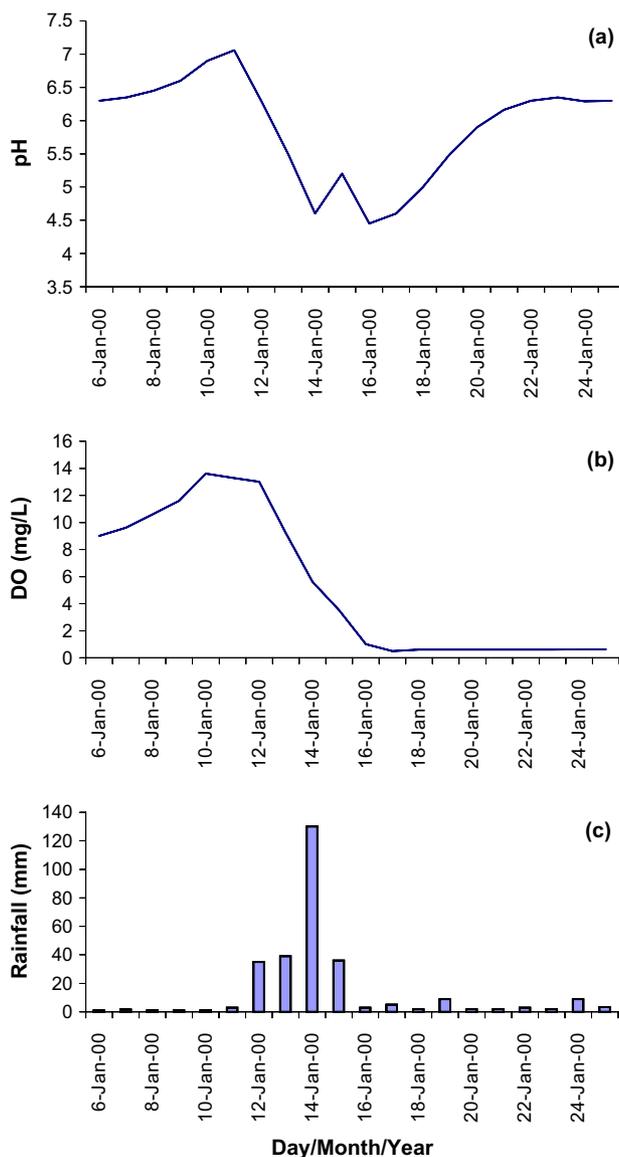


Fig. 7. Changes in (a) pH and (b) DO of creek water at the water quality monitoring station, during and following (c) a heavy rainfall event.

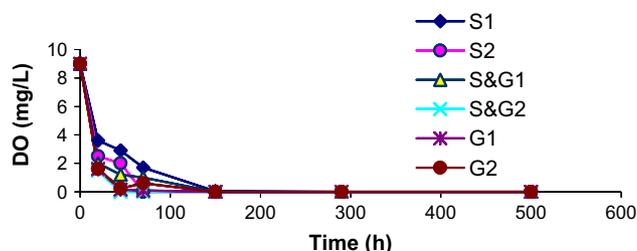


Fig. 8. Changes in DO of the artificial floodwater following inundation of six tested samples.

floodwaters on several occasions show that Fe concentration ranged from 1.99 to 11.87 mg/L (Collins, 1999 and Table 1) and it is not necessary that the Fe in floodwater is completely composed of Fe²⁺. This suggests that other DO consumers (e.g. ammonia, hydrogen sulfide and volatile organic compounds) may play more important roles in the process.

Results from simulation experiments reveal that the DO of the artificial floodwater dropped sharply after the six tested samples had been inundated for 20 h. After 150 h of inundation, no DO was detected in any of the tested samples (Fig. 8). Table 2 shows the abundance of microorganisms, tannin and Fe concentrations of various artificial floodwater samples at 150 h and 290 h after inundation. It can be seen that the total number of microorganisms, tannin and Fe concentrations increased from 150 h to 290 h for all the samples and the magnitude of increase was in the following decreasing order: grass only > soil with grass > soil only. These results indicate that increased biological reduction occurred after the DO in the artificial floodwater was depleted. The process was intensified when the bottles were capped, which prevented atmospheric O₂ from entering the artificial floodwaters. Parts of the grass straws used for the experiments were coated by films of

Table 2
Microbial abundance, tannin and Fe concentrations in various artificial floodwater samples at 150 h and 290 h after inundation

		Microorganisms per liter	Tannin (mg/L)	Fe (mg/L)
S&G-O	150 h	11,000,000	3.5	3.2
	290 h	19,000,000	9.7	6.3
S&G-C	150 h	15,000,000	11.0	7.9
	290 h	60,000,000	45.0	17.9
S-O	150 h	9,000,000	3.2	0.5
	290 h	16,000,000	7.9	2.3
S-C	150 h	12,000,000	9.2	5.2
	290 h	54,000,000	15.6	7.9
G-O	150 h	90,000,000	15.5	5.2
	290 h	360,000,000	40.5	11.5
G-C	150 h	162,000,000	16.9	8.9
	290 h	540,000,000	50.6	19.2

S&G-O: uncapped, soil with grass; S-O: uncapped, soil only; G-O: uncapped, grass only; S&G-C: capped, soil with grass; S-C: capped, soil only; G-C: capped, grass only.

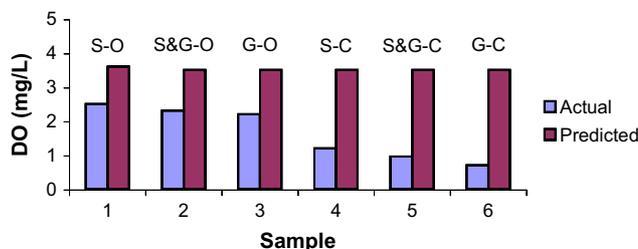


Fig. 9. Comparison between the actual and predicted DO levels in the mixtures of the oxygenated deionized water and different artificial floodwaters.

iron oxides/hydroxides, which act as sources of soluble Fe. This phenomenon is very common in the study site and analytical results show that the unwashed grass straw can contain up to 12,600 mg/kg of Fe, which is much greater than any other metals measured (our unpublished data).

When the de-oxygenated artificial floodwaters were mixed with oxygenated water, the DO levels in the mixtures were lower than that predicted based on dilution effect (Fig. 9). This suggests that the de-oxygenated artificial floodwater has the capacity to further consume DO in the freshly oxygenated water. It is clear from Fig. 9 that there is a marked difference in the DO-consuming capacity between two different treatments; all the capped samples had greater DO-consuming capacities than any uncapped sample. For the capped treatment where entry of atmospheric oxygen into the water was prevented, the DO-consuming capacity of various sample types was in the following decreasing order: grass only > grass and soil > soil, i.e. G-C > S&G-C > S-C. However, because one of these three samples was not replicated, the authors do not intend to draw a firm conclusion from these results. The substantial difference in the DO-consuming capacity between capped and uncapped treatments further suggests

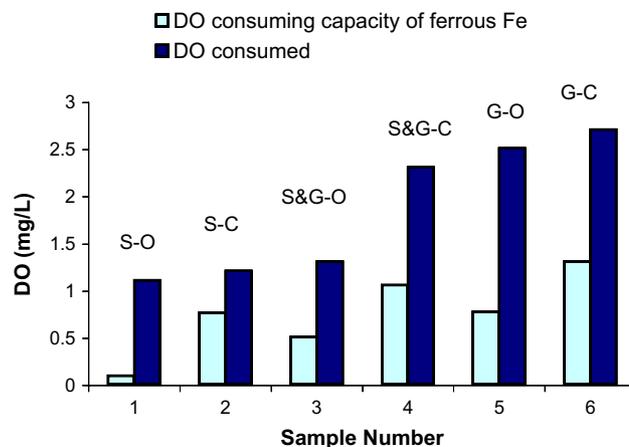


Fig. 10. Comparison between the DO-consuming capacity of the ferrous Fe and the DO actually consumed.

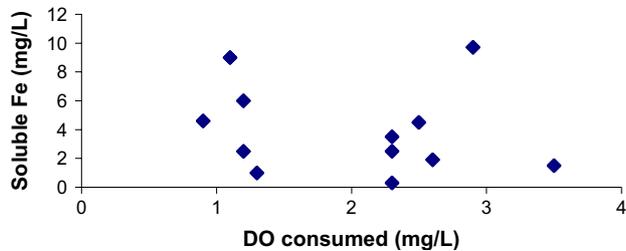


Fig. 11. Relationship between the amount of the DO consumed and the concentration of Fe contained in the artificial floodwaters.

that the samples with stronger biological reduction had larger DO-consuming capacities than that of the samples with weaker biological reduction. Possibly, the Fe^{2+} contained in the artificial floodwater contributed to the DO consumption. However, the DO consumption was beyond the DO-consuming capacity of Fe^{2+} contained in the water samples (Fig. 10). There is also no clear relationship between the concentration of Fe^{2+} and consumption of DO in the artificial floodwater (Fig. 11). This supports the above argument that other DO-consuming substances play more important roles in the DO consumption in floodwaters.

4. Conclusion

Continuous acidic flows of several month duration intermittently occur in Rocky Mouth Creek. It is likely that this is mainly caused by the oxidation of Fe^{2+} and the subsequent hydrolysis of Fe^{3+} , which acidifies the creek water. Fe^{2+} is produced as a result of biological iron reduction and exported to the creek with draining water from the adjacent acid sulfate soils. This process drives the conversion of retained acid to water-soluble acid, which provides the H^+ that enhances iron reduction. The acid sulfate soils in the study area contain considerable amounts of retained acid that has been accumulated in the soils due to sulfide oxidation following the construction of flood mitigation works.

A marked drop in the creek water pH also occurs following heavy rainfall events during high pH (>6)-dominated flow periods. This is frequently accompanied by a drop in DO in the creek water. Although the acidification and de-oxygenation in the creek water may be related to the oxidation of Fe^{2+} contained in the discharging water from the inundated acid sulfate floodplain, it appears that other DO-consuming substances play more important roles in the process. It is still unclear what these materials are and how they operate in terms of DO consumption. Further research is needed to fill the knowledge gap that clearly exists in the interplay of physical, chemical and biological drivers in the coastal floodplain environment.

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