Assessment of Sulfidic Sediments in Coonancoocabill Lagoon

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An MDFRC Consultancy Report for

Water for Rivers

October 2008

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A report prepared for Water for Rivers
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This report may be cited as:
D.S. Baldwin (2008) Assessment of sulfidic sediments in Coonancoocabill Lagoon. A report to Water for Rivers.

Summary

Sediment and water quality was determined at 12 sites in Coonancoocabill Lagoon to determine if sulfidic sediments were present in the wetland. Overall, the sediment and water quality parameters at most sites indicate that sulfidic sediments are not prevalent in the wetland, but very high levels of reduced sulfur were found at two sites in the wetland - both deep pools associated with ancestral river bends. Notwithstanding the presence of reduced sulfur at both these sites, there would appear to be a low risk of acidification of the wetland as a whole if the water levels in the wetland are manipulated using a regulating structure (although localised acidification may occur if the remanent pools are taken to near dryness). It is noteworthy that the wetland was close to dry at time of sampling with no detectable ecological consequences.

It is important to note that the sediments have a low acid neutralising capacity (as evidenced by the low pH_{KCl} values) indicating that the lagoon would be susceptible to acidification if reduced sulfur was to become more prevalent in the sediments. Therefore, a principle objective for any management of the wetland should include preventing formation of new sulfidic material.

Before regulating water levels in the wetland it is recommended that:

1. The Kirkup Road Drain be totally cut-off from the lagoon, especially ensuring leakage from the regulator is fixed.
2. A hydrogeological study of the region be undertaken to determine possible groundwater inputs to the wetland.
3. Any drawdown/refilling of the wetland be accompanied by a monitoring program to look at changes in sediment and water chemistry. In particular, weekly monitoring of pH, dissolved oxygen and salinity is recommended at at least 4 sites in the lagoon including the deep holes at sites e and j..
4. A contingency plan is drawn up to detail appropriate management responses to any deterioration in water quality associated with draw down or refilling the wetland.

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INTRODUCTION

Sulfidic sediments (potential acid sulfate soils) are formed when sulfate reducing bacteria reduce sulfate to sulfide in the absence of oxygen. The sulfide then reacts with metals, particularly iron, to form metal sulfides. If exposed to the air, these sulfides can cause environmental damage- most notably producing a pulse of acid. Sulfidic sediments are considered a concern primarily in coastal regions, but mounting evidence indicates that they are also an issue in freshwater ecosystems (Fitzpatrick *et al*. 1996; Sullivan *et al*. 2002), particularly those impacted by secondary salinisation. (Sulfate, necessary for sulfate reduction, is often found in salt). In a recent survey of 81 wetlands in the Murray-Darling Basin, more than 20% had evidence for the presence of sulfidic sediments at levels that could lead to ecological damage (Hall *et al.* 2006). Implementing a drying phase in wetland management is increasingly common (Casanova and Brock 2000), but if sulfidic sediments are present, drying can oxidise sulfidic minerals and generate acid, thereby forming actual acid sulfate soils. For example, the partial drawdown of a wetland in western NSW resulted in an extensive fish kill because of exposure and oxidation of sulfidic sediments leading to acidification (McCarthy *et al.* 2006). Oxidation of sulfidic sediments can also cause other problems such as anoxia in the overlying water column, generation of noxious odours and mobilisation of metals from the sediments (Sullivan *et al*. 2002; Lamontagne 2004).

METHODS

Analytical Framework

Sediments were analysed according to methods developed for coastal acid sulfate soils (Ahern *et al*., 1998, 2004; Talau 2000). Although these methods focus on only one of the potentially harmful effects of sulfidic sediments (viz. acid production through oxidation), they serve as a useful guide to indicate the presence of sulfidic sediments in inland wetlands. The methods attempt to estimate Net Acidity (NA), which is a measure of the latent acid-producing capacity of the sediments due to the presence of sulfidic sediments. NA was estimated according to the following equation (Ahern *et al*., 2004):

Net Acidity (mol $H^+ t^{-1}$) = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – Acid Neutralising Capacity/Fineness Factor

The actual acidity is a measure of the current acidity of the sediment. It includes not only acidity due to sulfidic materials but also other sources (e.g. organic acids or the oxidation of reduced iron). The potential sulfidic acidity is an estimate of the net acid that can be liberated during the oxidation of sulfidic material — used alone, it may underestimate the quantity of sulfidic material because the total acid produced may be masked by the acid-neutralising capacity of the sediments. The retained acidity represents more recalcitrant sulfidic elements, like jarosite, that oxidise only slowly over time but can contribute to net acidity. The acid-neutralising capacity (ANC) is modified by a fineness factor to discount the neutralising capacity of larger particles of carbonates such as shell fragments.

The potential sulfidic acidity is either measured directly by titration according to the ‘acid’ trail, or indirectly by measuring the concentration and reactivity of sulfur in the sediment and then estimating the amount of acid that would be produced if the sulfur was oxidised (the ‘sulfur trail’; Ahern *et al*., 2004). In the current study sulfidic acidity is estimated from the concentration of chromium reducible sulfur - S_{cr}.

Sampling and Analysis

Sediment cores (to a depth of 20 cm) were taken from 12 sites in Coonancoocabill lagoon in September 2008, using either a hand auger (dry sites), shovel (shallow sites) or Ekman grab (deep water sites) - Figure 1. The water and sediment pH and electrical conductivity at each site were measured using standard methods (Hall et al., 2006) In addition, a water sample for sulfate analysis was also taken, stored on ice and frozen prior to analysis by ion chromatography. To estimate the likelihood of acidification on oxidation, a sediment sample from each site (ca. 35 cm^3) was placed in a 70 cm^3 polypropylene jar, capped and kept moist and allowed to oxidise in air for a period of 6 weeks, after which time the pH was remeasured. Sediment samples for extractable pH, titratable actual acidity and chromium reducible sulfur were placed into plastic bags, and shipped to the Environmental Analytical Laboratory, Southern Cross University, Lismore NSW for analysis.

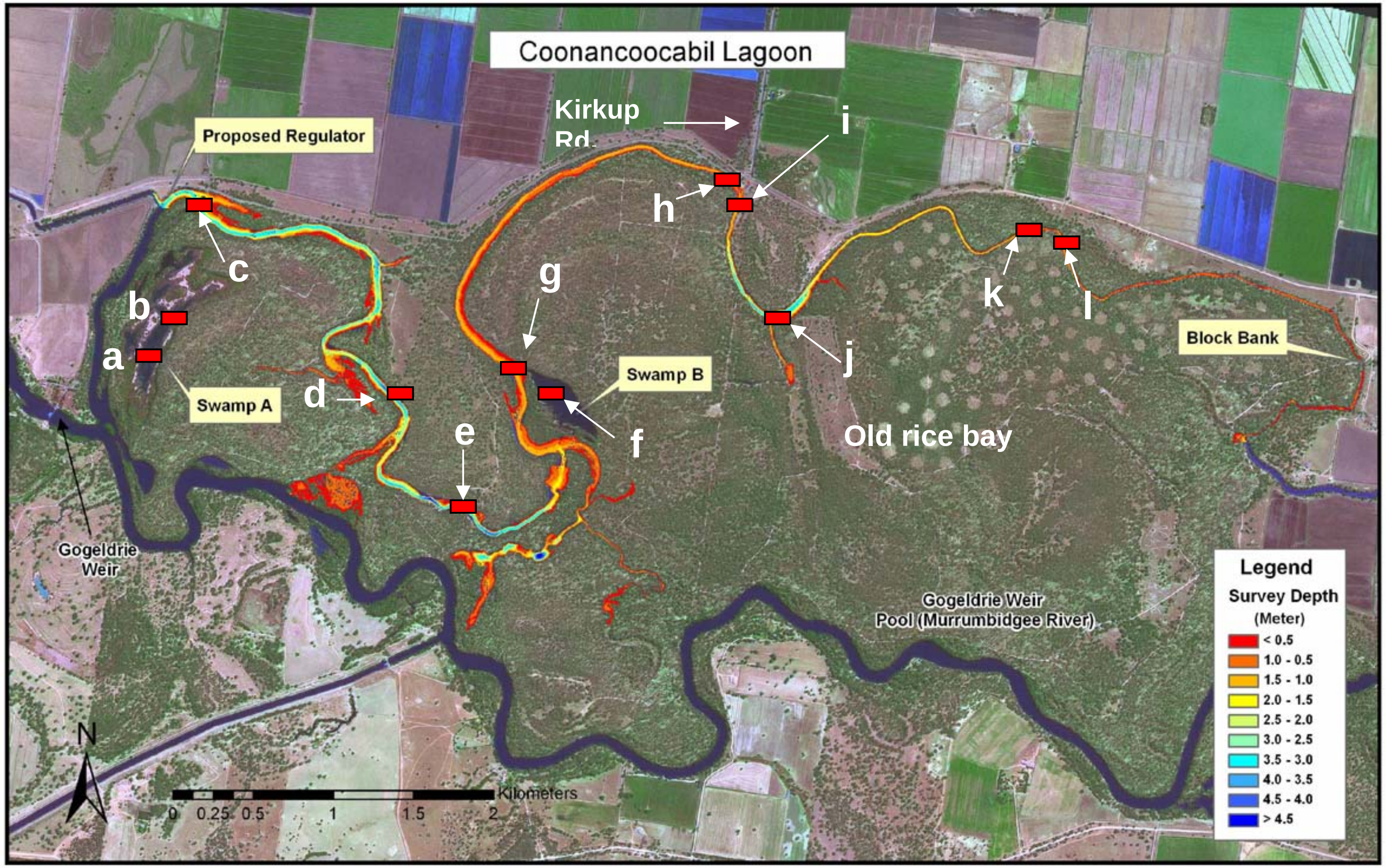

Figure 1 – Sampling Sites

Site	location (UTM Grid 55H)	Description	Water pH	Sediment $pH_{in\ situ}$ (after oxidation)	Soil pH_{KCl}	Water conductivity µS cm^{-1}	Sediment conductivity µS cm^{-1}	Water Sulfate (mg SO_4^{2-} /L)	Chromium Reducible Sulfur (% S_{Cr})	Titratable Actual acidity (mol H^+/tonne)	Net Acidity Cr Suite (mol H^+/tonne)
a	0432463/ 6169729	Swamp A - Dry	NA	5.3 (dry)	4.84	NA	55	NA	<0.005	37	37
b	0432487/ 6169572	Swamp A- Dry	NA	5.6 (dry)	4.80	NA	56	NA	0.005	35	38
c	0432828/ 6170570	Near outlet - shallow	7.3	7.6 (6.1)	5.05	178	75	7	<0.005	23	23
d	0434124/ 6169150	Wide but relatively shallow	7.3	6.1 (5.3)	5.34	193	75	9	0.011	13	20
e	0434607/ 6168551	Deep Pool	8.5	6.9 (NA)	5.00	326	224	27	0.104	48	113
f	0435040/ 6169364	Swamp B- dry	NA	5.2 (dry)	4.60	NA	1100	NA	<0.005	45	45
g	0434467/ 6169795	Almost dry	7.4	ND (6.3)	4.62	655	ND	49	0.036	13	35
h	0436293/ 6170638	30 M D/S of Kirkup Rd drain - shallow	8.6	7.5 (5.9)	6.20	1022	354	65	0.013	7	15
i	0436233/ 6170622	30 M U/S of Kirkup Rd drain - shallow	7.1	7.6 (6.0)	5.97	416	198	27	0.040	8	33
j	043636/ 616870	Travelling Stock route Deep pool	7.7	6.8 (NA)	5.29	354	324	26	0.168	26	131
k	0438114/ 6170364	50 m D/S of abandoned drain - residual pool	7.7	7.2 (5.9)	5.63	515	252	40	0.017	5	16
l	0438179/ 6170348	50 M U/S of abandoned drain - residual pool	7.8	7.1 (5.4)	5.50	520	186	44	0.010	8	14

Table 1 - Selected water and Sediment quality parameters at 12 Sites on Coonancoocabill Lagoon. NA = not applicable; ND = not determined.

RESULTS

At the time of sampling Coonancoocabill lagoon was mostly dry. Of the 12 sampling sites 3 (all in Swamp A and B) were totally dry, 6 were very shallow (with water depths less than about 30 cm), one (Site d) had a water depth of about 0.5 m and two (Sites e and j) had water depths of between 1.5 to 2 m - Figure 2.

The pH in the water column at the time of sampling at all sites was circum-neutral to slightly alkaline, ranging from 7.1 to 8.6 (Table 1). The pH of the sediments measured *in situ* suggests that they were circum-neutral to slightly acidic. The KCl extractable pH (measured on dried and ground samples) was 0.5 to 2.6 pH units lower (more acidic) than the pH of the sediments measured *in situ*. Similarly air oxidation led to a decrease in pH in most samples (noting that there was no evidence of oxidation in sediments from Sites e and j,)
The electrical conductivity in the water column varied from about 180 to about 1100 µS cm^{-1}; with the highest conductivity measured immediately downstream of the inlet of the Kirkup Road Drain. Sediment conductivity was also highly variable ranging from less than 100 to about 1100 µS cm^{-1}.

Sulfate levels in the water column were relatively high and were highly correlated to the conductivity in the water column - Figure 3.

Chromium reducible sulfur levels in the sediments of Coonancoocabill Lagoon were also highly variable; although most sites had quite low levels of S_{cr}, Sites e and j had quite high concentrations of S_{cr}, while Sites g and i had moderate

Site

Site

Site

Site

Site

Site

Figure 2 – Sampling Sites

Site g

Site h

Site i

Site j

Site k

Site l

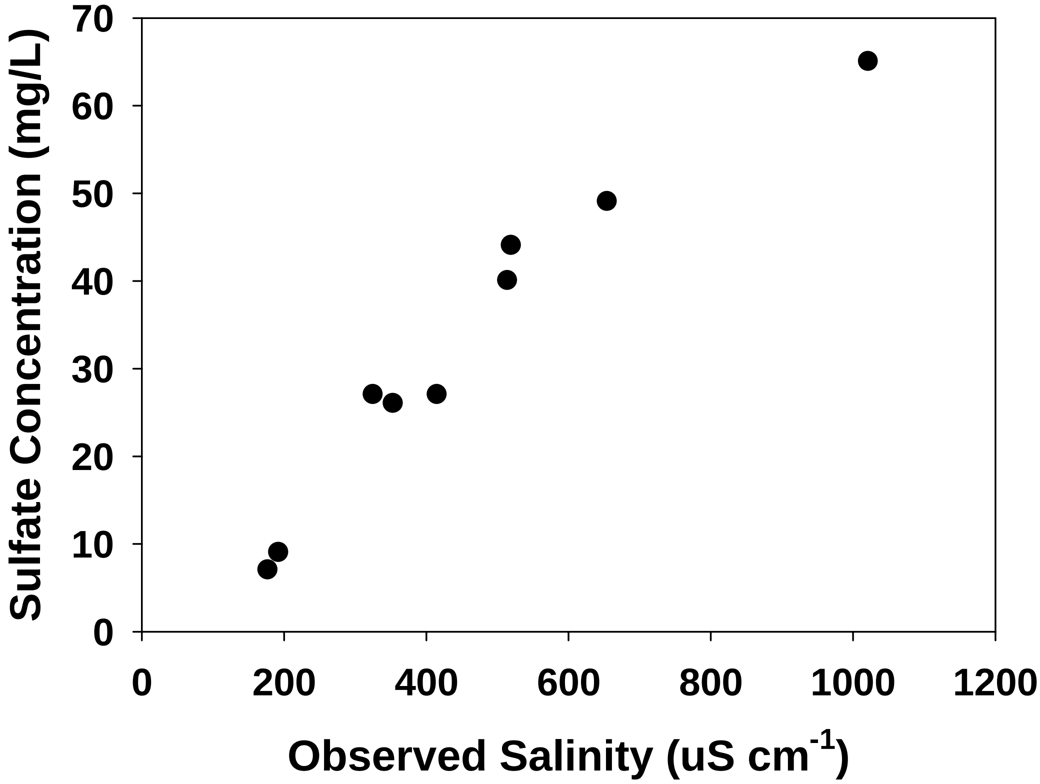

Figure 3 - Relationship between sulfate in the water column and measured electrical conductivity

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levels. The Titratable Actual Acidity was highest in sites that were dry at the time of sampling or had or had high levels of S_{cr} - Table 1.

DISCUSSION

Defining which sediments contain sulfidic materials at sufficient concentrations to cause death of biota if not properly managed is a complex task and usually involves the use of multiple lines of evidence. The distribution of sulfidic sediments in wetlands lies on a continuum ranging from none to highly sulfidic. Furthermore, the manifestation of attributes showing the presence of sulfidic sediments can vary depending on antecedent conditions such as prior oxidation or disturbance level, and, therefore, any definition of what constitutes a detrimental concentration of sulfidic material in sediments will be subjective and depend on the final use of the results. Ultimately, the question revolves around environmental risk assessment and management (*sensu* Hart *et al*. 1999; 2006).

The water and sediment chemistry in Coonancoocabill Lagoon is highly variable. While most of the sites sampled had water and sediment parameters which would suggest that there is little risk if the lagoon was allowed to dry out (and indeed, the lagoon was mostly dry at the time of sampling), nevertheless samples from two sites (Sites e and j) had very high levels of reduced sulfur and are therefore of some concern. These high levels translate into a high potential net acidity at both these sites. However, because high levels of reduced sulfur appear to be limited to the two residual pools, overall drying of the wetland shouldn't cause acidification of the entire lagoon; although localised acidification may occur. The pH in the water column at all the sites sampled was not at a level sufficient to cause environmental harm, even though the wetland had experienced a drying event. While the sediment pH was lower than that found in the water column, and oxidation lead to a further decline in pH; the pH didn't fall below 4.0 - a value associated with environmental harm. As an aside, given the generally low levels of reduced sulfur in the sediments, the decline in pH was probably not associated with the oxidation of sulfidic sediments, but may be caused by other mechanisms - in particular the oxidation of reduced iron in the sediments. (Iron mottling was evident in most sediment samples Figure 4).

It is important to note that the sediments have a low acid neutralising capacity (as evidenced by the low pH_{KCl} values) indicating that the lagoon would be susceptible to acidification if reduced sulfur were to become more prevalent in the sediments. Therefore, a principle objective for any management of the wetland should include preventing formation of new sulfidic material.

Figure 4 - iron mottling evident at Site k

Factors leading to the formation of sulfidic sediments in Coonancoocabill Lagoon

While it is not possible to definitively assign causative factors for the formation of sulfidic sediments in the wetland, nevertheless it is possible to hypothesise what the principle drivers are. To create sulfidic sediments it is first necessary to have a source of sulfate. As can be seen from Figure 3, sulfate in the wetland is highly co-related to electrical conductivity in the water column (a surrogate measure of salinity). The levels of salinity in the water column are generally significantly lower than levels typically found in wetlands with sulfidic sediments (> 1750 µS cm^{-1}; Baldwin et al, 2007). However, the presence of high levels of reduced sulfur in the sediments at Sites e and j clearly indicate that salt is entering the wetland. The salinity in both the water column and sediments is lowest near the entrance to the wetland and highest immediately downstream of the Kirkup Street drain. While the flow from the drain into the wetland is currently quite low (Figure 5a), and nominally controlled by a regulator (Figure 5b); nevertheless there is a distinct increase in salinity downstream of this input. The drain was probably a significant source of salt in the past and, while the drain is still connected to the lagoon, poses a threat in the future. The salinity further upstream of the drain is also elevated, suggesting another source of salt. However, the source is not as evident as at Site h. Site h is adjacent to an abandoned rice bay (Figure 1 - P. Deamer *pers. comm*), and therefore may have directly received irrigation return water in the past. Alternatively, It is possible there is still leakage from an abandoned drain located between Sites k and l (Figure 6) or there may be groundwater input to the lagoon, possibly from irrigated agriculture to the north and east of the wetland.

Notwithstanding the source of the salt, it is hypothesised that at certain times saline water accumulates in the deepest parts of the wetland, i.e. at Sites e and j, and the sulfate contained in the salty water is used for sulfate reduction, hence explaining why sulfidic sediments only occur at these two sites. However, there was no indication of a halocline at site j at the time of sampling - the conductivity at the surface and at depth was the same.

 

Figure 5 (a) outflow from drain (b) regulating structure

CONCLUSIONS AND MANAGEMENT OPTIONS

Based on the results of this study there is only a low risk that the wetland would acidify if totally drawn down and refilled. The wetland is currently at very low levels and there is little or no evidence for current acidification. While sulfidic sediments are present in the wetland, they are restricted to the deepest parts of the wetland. However, the observation that sulfidic sediments are present in the lagoon and the wetland sediments generally have a low buffering capacity suggests that the wetland needs to be carefully managed into the future. In particular sources of salt to the wetland need to be identified and controlled. Therefore it is recommended that:

1. The Kirkup Road Drain be totally cut-off from the lagoon, especially ensuring leakage from the regulator is fixed.
2. A hydrogeological study of the region be undertaken to determine possible groundwater inputs to the wetland.
3. Any drawdown/refilling of the wetland be accompanied by a monitoring program to look at changes in sediment and water chemistry. In particular,

weekly monitoring of pH, dissolved oxygen and salinity is recommended at at least 4 sites in the lagoon including the deep holes at sites e and j.

4. A contingency plan is drawn up to detail appropriate management responses to any deterioration in water quality associated with draw down or refilling the wetland.

Figure 6 – Location of abandoned drain between Sites k and l.

Acknowledgements: I would like to thank Mrs Kerry Whitworth and Dr Mark Fraser for assistance in field sampling and Mr Graham Lancaster from Southern Cross University and Mrs Whitworth for the chemical analyses. I would also like to thank staff from Forests NSW for giving access to the site.

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