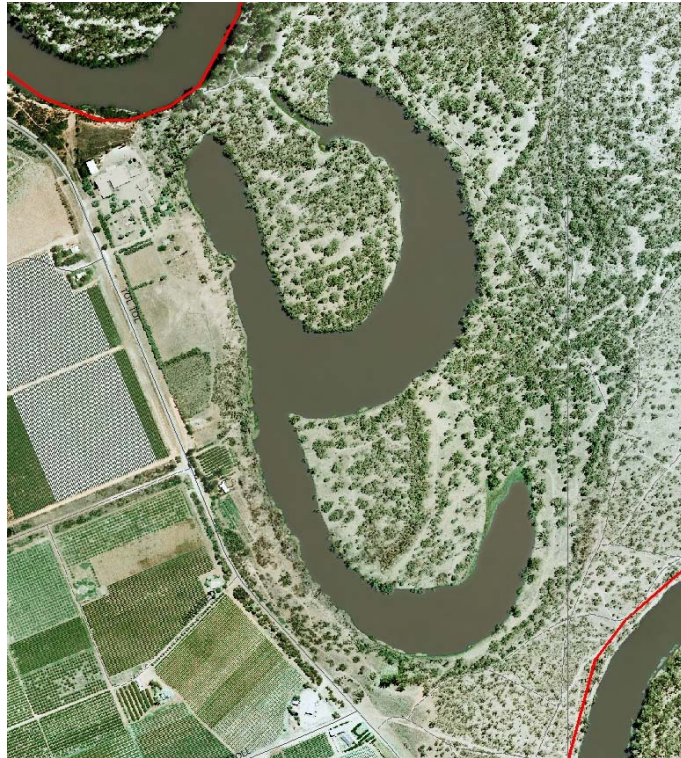


Assessment of Sulfidic Sediments in Margooya Lagoon

Darren S. Baldwin



The Murray-Darling Freshwater Research Centre
P.O. Box 991,
Wodonga, VIC 3698

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PO Box 5017, Mildura, Vic, 3502

For further information contact:

Dr Darren Baldwin
Murray-Darling Freshwater Research Centre
PO Box 991, Wodonga, VIC, 3689
Ph (02) 60582300

E-mail: darren.baldwin@csiro.au

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Summary Sediment cores (to a depth of 30 cm) were taken from seven sites in Margooya Lagoon in July 2007 to determine if sulfidic sediments were present in the wetland, following the protocol outlined in Hall *et al.* (2006). There is a low probability that Margooya lagoon would acidify if it was dried out. The elevated S_{Cr} and net acidity levels from the sediments at one site are of some concern, but given that samples were taken throughout the wetland, it is probable that sulfidic material are not widespread in the wetland. If there are only isolated patches with slightly elevated levels of reduced sulfur species, *the sediment quality in the wetland would benefit from introducing a regular wetting and drying cycle in the wetland.* It is suggested that any intervention be accompanied by a monitoring program, with particular emphasis on water column pH and conductivity.

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INTRODUCTION

Sulfidic sediments (potential acid sulfate soils) 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. 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 (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).

Under the current climatic conditions, New South Wales is considering imposing a drying phase on a number of wetlands in order to generate water savings. A preliminary assessment of these wetlands was undertaken to determine whether or not sulfidic material was present in the sediments of the lagoons at levels that could be of concern. Previous studies have shown that up to 20% of wetlands in the Murray-Darling Basin have some risk of acidification if dried out because of the presence of sulfidic sediments.

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):

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

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). The potential sulfidic acidity is an estimate of the net acid that can be liberated due to 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).

Acid trail

In this study, titratable actual acidity (TAA) provides an estimate of the actual acidity of the sediment and Titratable peroxide acidity (TPA) is used to estimate the potential sulfidic acidity of the sediment. Titratable sulfidic acidity (TSA) was determined from the difference between TPA and TAA. The retained acidity was estimated from the amount of sulfate that was retained in the sediment following extraction with KCl and the acid-neutralising capacity (ANC) of sediment was determined by titration.

Sulfur trail

Acidification is only one of the potential detrimental effects of sulfidic sediments. Other impacts include potential toxicity to aquatic plants and animals (Postgate 1984), deoxygenation of the water column as oxygen is consumed to oxidise sediments, and the creation of noxious odours (Lamontagne *et al.*, 2004). ANC may interfere with estimates of TSA by neutralising some of the acid produced from sulfidic materials. Therefore, Ahern *et al.* (2004) recommend that the amount of oxidisable sulfur in the sediment is determined and the potential amount of acid produced through oxidation be estimated — known as potential sulfidic acidity.

The reactive sulfides present in sediments can be determined as either Peroxide Oxidisable Sulfur (S_{POS}), which is a measure of the amount of sulfate produced when sediments are oxidised with a strong oxidising agent (30% peroxide), or Chromium Reducible Sulfur (S_{Cr}), which is the amount of hydrogen sulfide gas produced when the sediments are reduced with a strong reducing agent such as hot, acidic chromium chloride. Determining S_{POS} is considerably easier, safer and more environmentally friendly than determining S_{Cr} , but can overestimate reduced sulfur either by oxidising organic sulfur species to sulfate or leaching non-reduced sulfate from minerals like gypsum (Sullivan *et al.*, 2000).

Sampling and Analysis

Sediment cores (to a depth of 30 cm) were taken from seven sites in the wetland in July 2007 using a dorrer corer (Figure 1). Samples were placed into plastic bags, frozen and shipped to the Environmental Analytical Laboratory, Southern Cross University, Lismore NSW for analysis. At the same time as sediment sampling pH and conductivity were determined in the water column using a Quanta water quality meter.

RESULTS AND 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 interpretation of results is based on the previously reported study into sulfidic sediments in inland wetlands (Hall *et al.* 2006). The interpretation differs slightly from that used to classify sulfidic soils in coastal systems (e.g. Ahern *et al.* 2004). Like the coastal protocol, the current methodology uses a risk assessment approach to classification, but uses a more conservative value for differentiating between sulfidic and non-sulfidic material. This is based principally on the differing nature of sulfidic sediments in coastal soils and inland wetlands. In coastal soils, if sulfidic sediments are mismanaged and a plume of acidic and/or toxic (eg heavy metal rich) water is released, it is released as a pulse that usually enters a waterway (where it can cause short term ecological damage) before reaching the ocean. Most inland wetlands that are affected are terminal; or the drying phase that is imposed makes them behave as if they are terminal. Therefore the toxic material accumulates within the wetland, and the conditions may persist for extended periods of time. For example, the acidification event that occurred in Bottle Bend Lagoon in 2002 was still evident in September 2007 (pH in the water column was measured at 1.8 at that time).

The results from the analysis are presented in Table 1.

At the time of sampling the water level in the wetland was high and there was no evidence that the wetland had undergone a drying event in the recent past. The pH in the wetland was circum-neutral and the conductivity relatively low.

Sulfur Trail: The levels of peroxide oxidisable sulfur in the sediments were mostly quite low, with the exception of one sample (from Site 5), which had slightly elevated levels. Similarly, chromium reducible sulfur levels were generally low throughout the wetland, with the exception of two samples (from Sites 5 and 6), which were slightly higher than the threshold suggested by Hall et al (2006) to be of concern. The levels of reduced sulfur in the sediments was substantially lower than the levels used to classify potential acid sulfate soils in the coastal AAS framework.

Acid Trail: Sediment pH was circum-neutral in all samples and, also had a relatively low actual acidity. For most samples the latent acidity (net acidity) was about 20 moles H⁺/ton; the latent acidity from Site 5 was slightly higher (30 moles H⁺/ton).

There is a low probability that Margooya lagoon would acidify if it was dried out. The elevated S_{Cr} and net acidity levels from the sediments at Site 5 are of some concern, but given that samples were taken throughout the wetland, it is probable that sulfidic materials are not widespread in the wetland. If there are isolated patches with slightly elevated levels of reduced sulfur compounds, the sediment quality would benefit from introducing a regular wetting and drying cycle in the wetland. It is suggested that any intervention be accompanied by a monitoring program, with particular emphasis on water column pH and conductivity.

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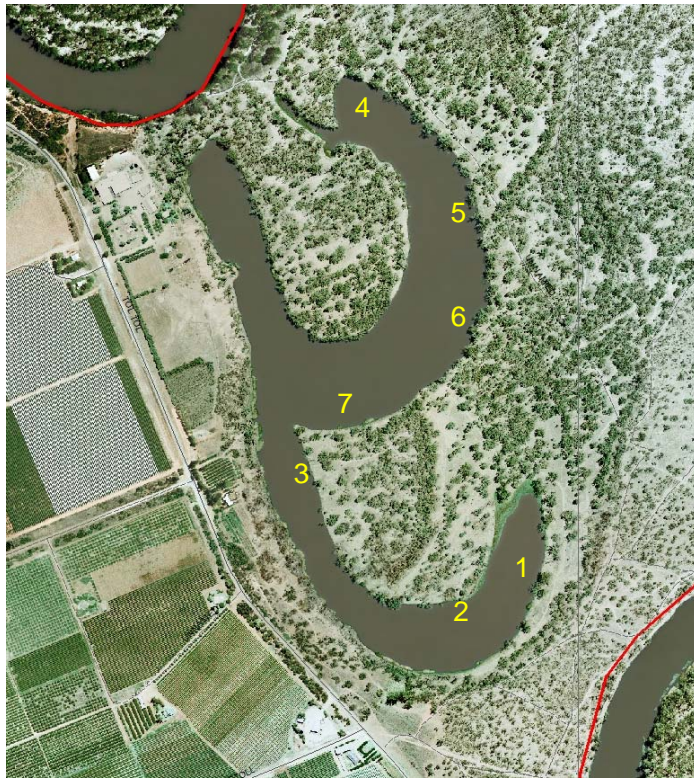


Figure 1 – Approximate Location of Sampling Sites in Margooya Lagoon

Sample #	Texture	pH (1:5 Water extract)	Peroxide oxidisable S- S _{pos}	S _{pos}	Chromium Reducible Sulfur – S _{cr}	S _{cr}	TAA pH _{KCl}	Titratable Actual Acidity	Titratable Potential Acidity	Net Acidity based on S _{cr}	Net Acidity based on S _{pos}
			%	mol H ⁺ /ton	%	H ⁺ /ton		mol H ⁺ /ton	mol H ⁺ /ton	mol H ⁺ /ton	mol H ⁺ /ton
1	Fine	6.61	0.003	2	0.003	2	4.92	19	0	21	21
2	Fine	6.99	0.000	0	0.005	3	5.22	16	0	19	15
3	Fine	6.74	0.011	7	0.007	4	5.30	14	0	18	20
4	Fine	6.53	0.013	8	0.007	4	5.17	18	0	22	26
5	Fine	6.25	0.033	20	0.034	21	5.29	10	0	31	30
6	Fine	6.63	0.026	16	0.021	13	5.68	6	0	19	22
7	Fine	6.01	0.021	13	0.011	7	4.89	16	0	23	29

Table 1: Results of assessment of sulfidic sediments for Margooya Lagoon.

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