

# Assessment of sulfidic sediments at Back Creek, NSW

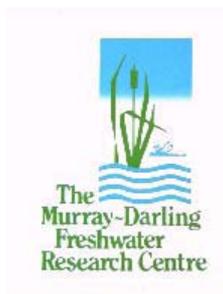


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**An MDFRC Consultancy Report for the  
Murray-Darling Basin Commission**

**May 2008**



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This report may be cited as:

Baldwin, D.S., Fraser, M.A. and McCarthy, B. (2008) Assessment of sulfidic sediments at Back Creek, NSW. Report to the Murray-Darling Basin Commission. Murray-Darling Freshwater Research Centre.

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## **Cover photograph**

A dry Site 3 at Back Ck in March 2008. The wetland had almost completely dried at the time of sampling. Photo: R. Durant, MDFRC.

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## Summary

Sediment cores (to a depth of 30 cm) were taken from six sites at Back Creek on 28 March 2008 to determine if sulfidic sediments were present, following the protocol outlined in Hall *et al.* (2006). There were only small amounts of  $S_{Cr}$  at all sites of Back Creek, therefore the amount of reactive sulfide present in the sediment that could oxidise and lead to acidification is low. Even though there was high net acidity at all Back Creek sites there is also a low risk of net acidification related to sulfidic sediments if the creek was dry for periods of time. It is suggested that any intervention such as wetland refilling be accompanied by a monitoring program, with particular emphasis on water column pH and conductivity.

## 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 *et al.* 2004).

Under the current climatic conditions, New South Wales is imposing a drying phase on a number of wetlands in order to generate water savings as part of drought contingency measures. One of these sites is Back Creek, a wetland 9.5km in length that connects with the Edward River via a 2km reach of Yallakool Creek. This wetland is being monitored by the Murray-Darling Freshwater Research Centre (MDBC Contract No. MD962) following its disconnection from the Edward River.

Back Ck was assessed in September 2007 for the occurrence of sulfidic sediments using the risk-assessment screening tool of Baldwin *et al.* (2007). The pH of sediment at the three sites assessed ranged from 4.1 – 4.4 (Durant *et al.*, 2008), and below the acceptable threshold of pH 4.5 (Baldwin *et al.* 2007). Hence, Durant *et al.* (2008) recommended that a more detailed investigation of the occurrence of sulfidic sediments occur at Back Ck through

the direct analysis of sediments as per the Baldwin *et al.* (2007) protocol. The results of this detailed analysis are presented in this report.

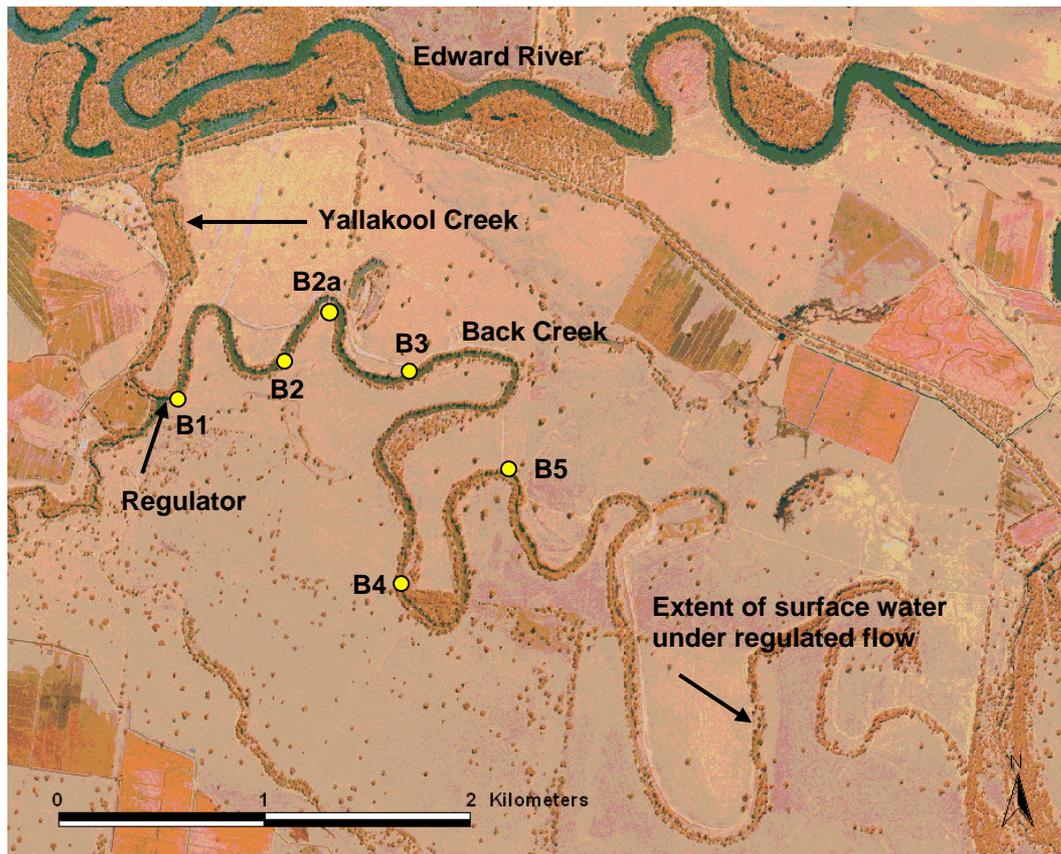
## Methods

### *Sampling*

Sediment cores (to a depth of 30 cm) were taken from six sites along Back Creek (Table 1; Figure 1) on 28 March 2008 using a dorrmer corer. The six sites correspond to those sampled as part of the broader monitoring program at this site (Durant *et al.* 2008). Samples were placed into plastic bags, frozen and shipped to the Environmental Analytical Laboratory, Southern Cross University, Lismore NSW for analysis.

**Table 1. GPS (UTM/UPS GDA94) locations of sampling sites at Back Creek.**

Site	GPS
1	54H 297771 6073590
2	54H 298302 6073768
2a	54H 298528 6074047
3	54H 298910 6073728
4	54H 298876 6072690
5	54H 299401 6073238



**Figure 1.** Sites of sediment collection at Back Creek.

### ***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):

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

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).

## Results and Discussion

The results of the sediment analyses at Back Creek are presented in Table 2.

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 (e.g. 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).

There were only small amounts of  $S_{Cr}$  at all sites of Back Creek, therefore the amount of reactive sulfide present in the sediment that could oxidise and lead to acidification is low. However, the amount of  $S_{POS}$  at sites 2A and 4 was at a level consistent with the threshold that has been previously shown to cause ecological damage in wetlands if mishandled (Hall *et al.* 2006).

All sites at Back Creek had TAA higher than 18 mol  $H^+$ /tonne, the value used to differentiate acidic sulfate sediments for coastal systems (Ahern *et al.* 2004). All samples had relatively high net acidities which would be classified as potential acid sulfate soils following the acid trail of the coastal classification scheme.

***Environmental considerations:*** The amounts of reactive sulfur at all Back Creek sites suggest that at present there is a low risk to this system from sulfidic sediments. Therefore, even though there was high net acidity at all Back Creek sites, there is also a low risk of net acidification related to sulfidic sediments if the creek was dry for periods of time. The higher  $S_{POS}$  values at sites 2A and 4 are unlikely to be of concern as  $S_{Cr}$ , which was low at these sites, is the best indicator of reduced sulfur (Ahern *et al.* 2004). It is suggested that any intervention such as refilling be accompanied by a monitoring program, with particular emphasis on water column pH and conductivity.

**Table 2. Results of sulfidic sediment analyses at Back Creek**

Sample Site	Texture	pH (1:5 water)	Peroxide oxidisable S- S <sub>pos</sub> %	S <sub>pos</sub>  mol H <sup>+</sup> /ton	Chromium Reducible Sulfur - S <sub>cr</sub> %	S <sub>cr</sub> mol H <sup>+</sup> /ton	Titratable Actual Acidity mol H <sup>+</sup> /ton	Titratable Potential Acidity mol H <sup>+</sup> /ton	Net Acidity based on S <sub>cr</sub> mol H <sup>+</sup> /ton	Net Acidity based on S <sub>pos</sub> mol H <sup>+</sup> /ton
<b>Back 1</b>	Medium	4.93	0.025	15	<0.005	0	58	13	58	73
<b>Back 2</b>	Coarse	5.24	0.022	14	<0.005	0	35	2	35	49
<b>Back 2A</b>	Medium	5.11	0.033	20	0.006	4	48	18	52	68
<b>Back 3</b>	Medium	4.77	0.026	16	0.007	4	54	15	58	70
<b>Back 4</b>	Medium	5.30	0.031	19	0.007	4	35	3	39	54
<b>Back 5</b>	Medium	5.19	0.014	8	<0.005	0	23	3	23	31

## Acknowledgements

This work was funded by the Murray-Darling Basin Commission. The authors thank Rebecca Durant and Christine Reid for collecting sediment cores at Back Creek, and Graham Lancaster from Southern Cross University for conducting the analyses.

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