

Assessment of sulfidic sediments at Washpen Creek, NSW

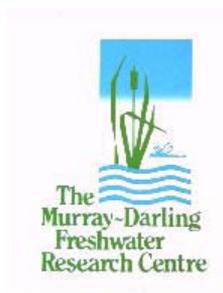


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Cover photograph

Washpen Creek in December 2007. Photograph: B.McCarthy, MDFRC.

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Summary

Sediment cores (to a depth of 30 cm) were taken from six sites in Washpen Creek on 7 March 2008 to determine if sulfidic sediments were present, following the protocol outlined in Hall *et al.* (2006). The elevated S_{Cr} and net acidity levels from the sediments at two sites are of some concern. There is potential for Washpen Creek to acidify if it was dried out. For the sites with elevated levels of reduced sulfur compounds, the sediment quality would benefit from maintaining the water level in Washpen Creek, which would prevent exposure of the sediments, subsequent oxidation and potential acidification. It is suggested that any intervention be accompanied by a monitoring program, with particular emphasis on water column pH and electrical 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 (Bottle Bend Lagoon) 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 the Euston Lakes system in south-west NSW. This wetland system comprises four separate wetlands including Washpen Ck, Taila Ck, Dry Lake and Lake Benanee. The wetlands are being monitored by the Murray-Darling Freshwater Research Centre (MDBC Contract No. MD962) following their disconnection from the Euston weir pool on the Murray River.

Washpen Ck and Taila Ck were assessed in August 2007 for the occurrence of sulfidic sediments using the risk-assessment screening tool of Baldwin *et al.* (2007). The pH of sediment at Sites 2 and 3 of Washpen Ck were 3.80 and 4.00 respectively (McCarthy *et al.* 2008), and below the acceptable threshold of pH 4.5 (Baldwin *et al.* 2007). Hence, McCarthy *et al.* (2008) recommended

that a more detailed investigation of the occurrence of sulfidic sediments occur at Washpen 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 Washpen Creek (Table 1; Figure 1) on 7 March 2008 using a dormer corer. Site 1-4 correspond to the sites sampled as part of the ongoing monitoring program (McCarthy *et al.* 2008) and sites 5 and 6 are additional sites. Samples were placed into plastic bags, frozen and shipped to the Environmental Analytical Laboratory, Southern Cross University, Lismore NSW for analysis.

Table 1. GPS locations of sampling sites at Washpen Creek.

Site	GPS
1	54H 667991 6175443
2	54H 667906 6174843
3	54H 669993 6173319
4	54H 671719 6172465
5	54H 667998 6173678
6	54H 671048 6173855

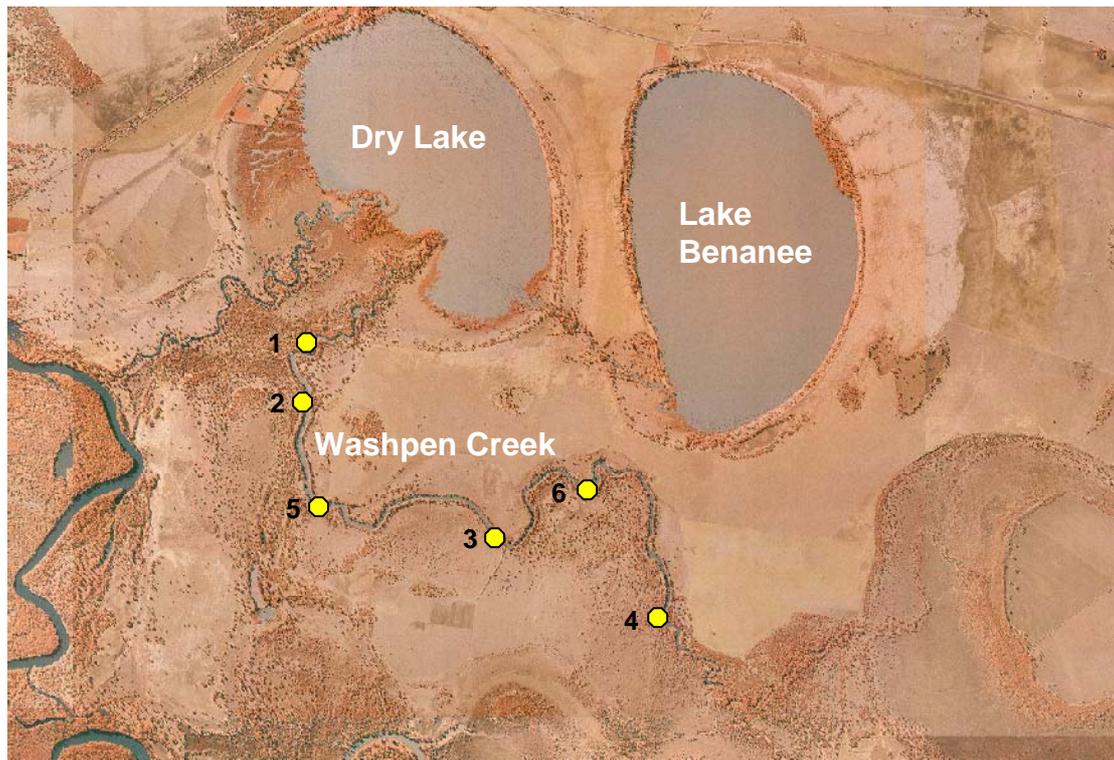


Figure 1. Sites of sediment collection at Washpen Creek.

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 from Washpen 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).

The results show that the concentrations of reduced sulfur in the sediments (S_{POS} or S_{Cr}) of three of the samples (Washpen Ck sites 1, 4 and 6) are close to the threshold that has been previously shown to cause ecological damage in wetlands if mishandled (Hall *et al.* 2006). At Washpen Ck sites 1 and 6, S_{Cr} was high and indicated a level of reactive sulfide present in the sediment that could oxidise and lead to acidification.

The Washpen Ck sites 2, 3, 4 and 5 all 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 quite high net acidities which would be classified as potential acid sulfate soils following the acid trail of the coastal classification scheme.

Environmental considerations: As there was high net acidity across all sites at Washpen Creek, there is a risk of net acidification if the creek was allowed to dry and the sediments to oxidise. The concentrations of sulfide at Washpen Ck sites 1, 4 and 6 suggest potential harm to this system. Although, as pointed out by Ahern *et al.* (2004), S_{Cr} is the best indicator of reduced sulphur and this would confine the potential acidification to Washpen Ck sites 1 and 6. However, the high S_{POS} and net acidity values for Washpen Ck site 4 indicate

that this site is of concern as it contains sulfidic sediments that may be an ecological risk. For the sites with elevated levels of reduced sulfur compounds, the sediment quality would benefit from maintaining the water level in Washpen Creek, which would prevent exposure of the sediments, subsequent oxidation and potential acidification. It is suggested that any intervention be accompanied by a monitoring program, with particular emphasis on water column pH and electrical conductivity.

Table 2. Results of sulfidic sediment analyses at Washpen Creek

Sample Site	Texture	Peroxide oxidisable S- S _{pos} %	S _{pos} mol H ⁺ /ton	Chromium Reducible Sulfur - S _{cr} %	S _{cr} mol H ⁺ /ton	Titratable Actual Acidity mol H ⁺ /ton	Titratable Potential Acidity mol H ⁺ /ton	Net Acidity based on S _{cr} mol H ⁺ /ton	Net Acidity based on S _{pos} mol H ⁺ /ton
Washpen 1	Medium	0.041	26	0.036	22	15	24	38	41
Washpen 2	Fine	0.006	4	0.012	7	27	23	34	31
Washpen 3	Fine	0.006	4	0.018	11	46	40	57	49
Washpen 4	Medium	0.036	22	<0.005	0	21	9	21	43
Washpen 5	Fine	0.011	7	0.026	16	41	29	58	48
Washpen 6	Medium	0.036	23	0.038	24	14	6	38	37

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