Assessment of sulfidic sediments at Tumudgery Creek, NSW

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Cover photograph

Tumudgery Creek in March 2008. Photograph: R. Durant, MDFRC.

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Summary

Sediment cores (to a depth of 30 cm) were taken from six sites at Tumudgery Creek on 27 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 Tumudgery 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 most Tumudgery 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 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 Tumudgery Creek that branches from the Edward River approximately 40km north-west of Deniliquin, NSW. This wetland is being monitored by the Murray-Darling Freshwater Research Centre (MDBC Contract No. MD962) following its disconnection from the Edward River.

Tumudgery Creek 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 Sites 2 and 4 of Tumudgery Creek were 3.65 and 3.80, respectively (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 Tumudgery Creek 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 Tumudgery Creek (Table 1; Figure 1) on 27 March 2008 using a dormer corer. Sites 1-5 correspond to the sites sampled as part of the broader monitoring program at this site (Durant *et al*. 2008), and Site 6 is an additional site. 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 Tumudgery Creek.

Site	GPS
1	54H 286755 6080521
2	54H 286037 6080351
3	54H 284598 6079960
4	54H 282427 6081240
5	54H 282237 6081866
6	54H 283614 6080812

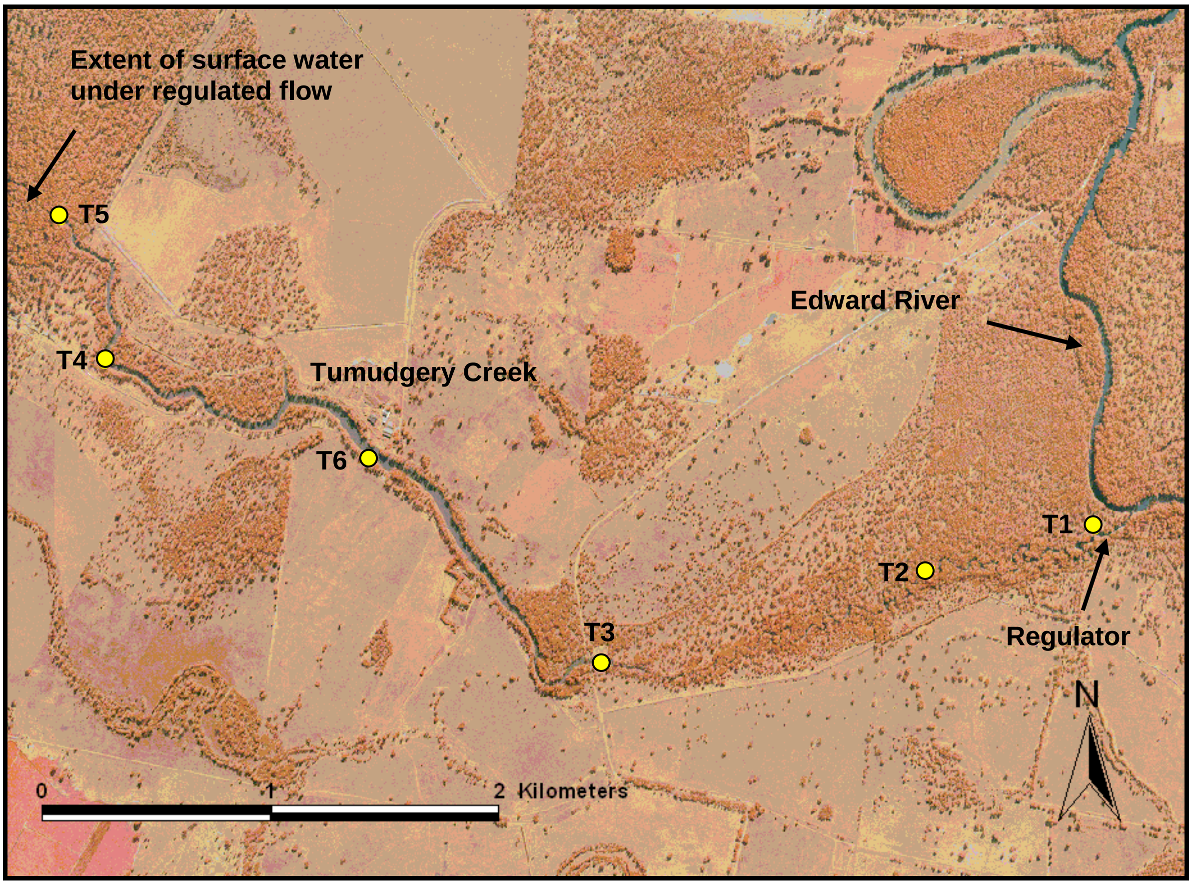

Figure 1. Sites of sediment collection at Tumudgery Creek.

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):

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). 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) recommends 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 Tumudgery 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 Tumudgery Creek; therefore the amount of reactive sulfide present in the sediment that could oxidise and lead to acidification was low. None of the Tumudgery Creek sites had concentrations of reduced sulfur in the sediments at the threshold that has been previously shown to cause ecological damage in wetlands if mishandled (Hall *et al*. 2006).

Tumudgery Creek sites 1, 3, 5 and 6 had TAA higher than 18 mol H^+/tonne, the value used to differentiate acidic sulfate sediments for coastal systems (Ahern *et al.* 2004). These same sites 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 Tumudgery Creek sites suggest that at present there is a low risk to this system from sulfidic sediments. S_{Cr}, which is the best indicator of reduced sulfur (Ahern *et al.* 2004), was low at all sites and therefore oxidation and subsequent acidification of sulfidic sediments that could be harmful is unlikely to occur. Even though there was high net acidity at some Tumudgery 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 be accompanied by a monitoring program, with particular emphasis on water column pH and conductivity.

Table 2. Results of sulfidic sediment analyses at Tumudgery Creek

Sample Site	Texture	pH (1:5 water)	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
Tumudgery 1	Medium	5.04	0.017	11	<0.005	0	48	0	48	59
Tumudgery 2	Fine	6.92	0.008	5	0.006	4	9	0	12	13
Tumudgery 3	Fine	5.95	0.003	2	0.007	4	22	14	26	23
Tumudgery 4	Medium	5.69	0.003	2	<0.005	0	16	10	16	18
Tumudgery 5	Fine	5.24	0.002	1	<0.005	0	54	37	54	55
Tumudgery 6	Medium	5.00	0.007	4	<0.005	0	50	27	50	54

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