

## RISKS OF WATER QUALITY DEGRADATION DURING THE REMEDIATION OF FLOODPLAIN SALINITY IN THE RIVER MURRAY

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Acid sulfate soils (ASS) have long been recognized as a significant environmental problem for large sections of the Australian coastline (e.g., Sammut & Lines-Kelly 1996, National Working Party on Acid Sulfate Soils 1999). It is now recognized that ASS and sulfidic sediments have developed inland, for example in areas impacted by dryland salinity (Fitzpatrick *et al.* 1996, 1997, George 2002, Fitzpatrick 2002) and in groundwater discharge areas. However, the assessment of impacts on environmental quality and the development of management strategies have been limited. Potential impacts include: ecological changes due to elevated hydrogen sulfide concentrations in sediments; changes in nutrient cycling; the delayed recovery of riparian vegetation in previously saline areas due to soil acidification; export of acidity and heavy metals to wetlands; acidification and increased dissolved iron concentration in pore waters; and, anoxia in streams or wetlands following flooding.

In this study we conducted a preliminary assessment of the occurrence and potential risks associated with sulfidic soil and sediments in the salinised floodplains of the River Murray. We chose wetland sites representing a range of salinities from hyper-saline disposal basins to low salinity managed lagoons. Our aim was to obtain an indication of their prevalence, make field and laboratory measurements of their properties, and assess the risk associated with their occurrence in the context of wetland management options. A secondary aim was to evaluate the methodology used in the assessment of coastal ASS and its applicability to sulfidic floodplain sediments.

In April 2003, we sampled pore water from freshly dug pits and sediments from cores and pits. Analyses of pore water samples gave electrical conductivity ranging from 1.3 mS/cm to 120 mS/cm, pH from 5.5 to 9.4 and alkalinity from 1.5 to 670 mg CaCO<sub>3</sub>/L (Table 1). Field tests on the sediments identified both the widespread occurrence of sulfidic materials and sufficient neutralising capacity to prevent acidification of the sediments except at Cobdogla and Bottle Bend Lagoon, where an acidification event had already occurred (McCarthy *et al.* 2003). Table 2 compares laboratory and field tests for oxidisable sulfur, in situ pH and pH in hydrogen peroxide. While the pH did not fall below 4 (the diagnostic pH value) it should be noted that the pH drop after oxidation is dependent on both the oxidisable sulfur content and the texture so that for example Merriti and Clover Lakes showed a substantial drop in pH at low oxidisable sulfur concentrations. This is reflected in the South Australian acid sulfate soil guidelines, which set trigger values for further investigation of 0.01%, 0.03% and 0.10% oxidisable sulfur for light, medium and heavy textured soils respectively. Values for oxidisable sulfur obtained across the sites sampled ranged from <0.01% to 0.97% (Table 3) indicating further investigation is required. While laboratory analyses of oxidisable sulfur and carbonate carbon allow the calculation of total sulfidic acidity (TSA) and net acid generation potential for soils and sediments, these are only relevant to the sub aerial exposure of these materials through drainage or excavation. In riverine or wetland environments sulfidic sediments can also be oxidised through resuspension in the water column, potentially causing acidification and/or lowered dissolved oxygen (DO) levels. To test this potential we calculated the TSA and chemical oxygen demand (COD) using the maximum oxidisable sulfur concentration for surface samples (0 – 10 cm) found at the site. We then calculated the concentration of suspended sediment required to either neutralise the alkalinity present or to lower the DO level by a given amount. The TSA range was from 5.0 to 490 moles H<sup>+</sup>/t sediment and the COD range from 0.4 to 34 mg O<sub>2</sub>/kg sediment (Table 4). The alkalinity in the water was sufficient to neutralise the potential acid generated at any realistic suspended solid concentration, except for Bottle Bend Lagoon where only 100 mg/L of suspended sediment was required and Cobdogla where 3,000 mg/L was needed. We selected 3 mg/L as the indicative drop in DO concentration. The ANZECC guidelines recommend that DO should be maintained at least 60% of its natural level over at least one diurnal cycle, and given saturated DO concentrations of 6 to 8 mg O<sub>2</sub>/L depending on salinity, a 40% drop represents around 3 mg O<sub>2</sub>/L. In Bottle Bend Lagoon, Cobdogla and the Berri Evaporation Basin the chemical oxygen demand of the sediment is sufficient to cause such a drop in dissolved oxygen concentration at suspended solid concentrations of 760, 340 and 570 mg/L respectively (Table 4).

When completed the investigation will provide preliminary information to assess the risk of these sulfidic sediments to water quality and determine whether they may place constraints on floodplain salinity remediation techniques.

**Table 1:** Pore water analyses for Riverland water bodies

Sample	EC	pH	Alk	Cl	NH <sub>4</sub> N	NO <sub>3</sub> N	Ca	K	Fe	Mg	Na	P	S
	mS/cm		mg CaCO <sub>3</sub> /L				mg/L						
Ramco - surface	62.0	8.5	190	23000	0.19	0.037	150	300	0.05	600	15000	0.12	750
Ramco - inflow	2.4	8.3	670	510	0.29	0.36	34	9.8	0.05	31	370	0.021	70
Ramco - Pit 1	36	7.1	540	11000	2.0	0.069	280	67	0.05	490	8000	0.054	610
Ramco - Pit 2	32	6.8	450	10000	4.2	0.027	350	67	1.1	480	6900	0.093	410
Berri - evap. basin	120	7.5	220	51000	31	0.030	1200	820	0.05	2800	34000	0.51	3600
Bottle Bend Lag.	13	5.5	1.5	4100	7.0	0.063	320	18	0.71	360	1800	0.050	85
Hart - Pit 1	21	7.4	430	10000	0.78	0.11	220	130	0.05	370	7700	0.14	460
Merreti Lake	1.3	9.0	160	260	0.81	0.62	23	15	0.05	19	200	0.35	18
Ross Lag.	5.2	9.0	130	1500	0.25	0.027	50	13	0.05	83	880	0.046	66
Woolpolool Lake	5.0	9.4	38	1200	0.25	0.040	150	24	0.05	110	720	0.012	220
Cobdogla Pit 1	5.2	7.6	490	1100	8.5	0.65	76	36	0.029	72	950	-	150
Cobdogla Pit 2	-	6.5	75	23000	29	0.033	1200	200	3.4	1600	14000	-	2500

- not determined

**Table 2:** Laboratory determined oxidisable sulfur and field measurements of in situ pH and pH after treatment with 30% hydrogen peroxide

Site	Depth (cm)	Oxidisable sulfur (% S <sub>Cr</sub> )	pH <sub>soil</sub>	pH <sub>H2O2</sub>
Ramco Lagoon	20	0.18	7.7	4.7
Hart Lagoon	5+	0.19	7.2	5.9
Ross Lagoon	20	<0.01	6.6	5.8
Berri evap. basin	2.5	0.47	8.4*	6.3
Woolpolool Lake	1	0.07	7.3	6.4
Merriti Lake	2.5	0.01	6.1	4.6
Clover Lake	15	0.01	6.8*	5.5
Bottle Bend Lagoon	5	0.09	6.4	2.9
Cobdogla				

\* pH<sub>1:5 soil:water</sub>

**Table 3:** Sulfur analyses for soil samples from study sites

Location	Depth cm	Total S	Oxidisable S (S <sub>Cr</sub> )	
		%		
Bottle Bend Lagoon	upper section	0 - 10	0.39	0.35
		10 +	0.05	0.03
	middle section	0 - 9	0.12	0.09
		9 - 15	0.03	0.02
Clover Lake (dry)		0 - 10	0.04	0.01
		10 - 20	0.28	0.01
		20 - 25	0.27	0.00
Merreti Lake		0 - 5	0.02	0.01
		5 - 10	0.02	0.01
		10 - 20	0.01	<0.01
Woolpolool Lake		0 - 3	0.25	0.08
		3 - 6	0.14	0.04
		6 - 10	0.02	0.01
		10 - 20	0.04	0.01
Ross Lagoon		0 - 10	0.02	<0.01
		15 - 25	0.03	<0.01
		25 +	0.14	0.10
Hart Lagoon		0 - 5	0.36	0.22
		5 +	0.18	0.19
Ramco	pit 2	0 - 5	0.28	0.04
		5 - 10	0.16	0.11
		20 - 25	0.19	0.18
		30 - 37	0.02	0.01
Berri evaporation basin		0 - 5	1.38	0.29
		0.5 - 5	0.92	0.46
Cobdogla	site 1 pit1	20 - 30	0.72	0.72
		30 - 40	0.28	0.28
		0 - 1	3.49	0.78
	site 2 pit 1	1 - 20	1.38	0.43
		20 - 30	0.07	0.19
	site 2 pit 2	0 - 5	1.1	0.27
		5 - 30	1.0	0.97
		30 - 40	0.33	0.36

**Table 4:** Water pH and alkalinity, surface sediment TSA, COD and suspended solid concentration needed to consume the available alkalinity and to reduce the DO concentration by 3 mg/L

Sample	pH	Alkalinity mg CaCO <sub>3</sub> /L	Sediment TSA moles H <sup>+</sup> /t	Suspended solid conc to consume alkalinity mg/L	COD mg of O <sub>2</sub> consumed /kg of material	Suspended solid conc to consume 40% of DO mg/L
Ramco - surface	8.5	190	80	48,000	5.6	2,100
Ramco - inflow	8.3	670	80	170,000	5.6	2,100
Ramco - Pit 1	7.1	540	80	140,000	5.6	2,100
Ramco - Pit 2	6.8	450	80	110,000	5.6	2,100
Berri - evap. basin	7.5	220	290	15,000	20	570
Bottle Bend L	5.5	1.5	220	100	15	760
Hart - Pit 1	7.4	430	140	61,000	9.8	1,200
Merreti	9.0	160	5.0	640,000	0.35	33,000
Ross L	9.0	130	60	43,000	4.2	2,800
Woolpolool	9.4	38	50	15,000	3.5	3,300
Cobdogla Pit 1	7.6	490	490	20,000	34	340
Cobdogla Pit 2	6.5	75	490	3,000	34	340

**REFERENCES**

- ANZECC & ARMCANZ 2000. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. National Water Quality Management Strategy Paper No 4. Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- FITZPATRICK R.W. 2002. Inland acid sulfate soils a big growth area. *5th International Acid Sulfate Soils Conference, Tweed Heads, NSW, 25th to 30th August 2002*. Book of extended abstracts addendum. p 12.
- FITZPATRICK R.W., FRITSCH E. & SELF P.G. 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* **69**, 1-29.
- FITZPATRICK R.W., COX J.W. & BOURNE J.1997. *Managing waterlogged and saline catchments in the Mt. Lofty Ranges, South Australia: A soil-landscape and vegetation key with on-farm management options*. Catchment Management Series, CRC for Soil and Land Management, CSIRO Publishing, Melbourne, Australia, 36 pp.
- FITZPATRICK R.W., MERRY R.H, COX J.W., RENGASAMY P & DAVIES P.J. 2003. *Assessment of physico-chemical changes in dryland saline soils when drained or disturbed for developing management options*. CSIRO Land and Water, Adelaide, South Australia, **Technical Report 02/03**.
- GEORGE R. 2002. 'Secondary acidification' an emerging problem in wheatbelt. *Focus on Salt* **23**, 10.
- MCCARTHY B., CONALLIN A. & WALSH R. 2003. *Aquatic Survey of Bottle Bend Lagoon, near Buronga NSW: Salinisation and Acidification Impacts*. CRC for Freshwater Ecology Consultancy Report for NSW Murray Wetlands Working Group Inc. **Report No. 2/2003**. Murray Darling Freshwater Research Centre, Albury, New South Wales, Australia.
- NATIONAL WORKING PARTY ON ACID SULFATE SOILS 1999. *National Strategy for the Management of Coastal Acid Sulfate Soils*. NSW Agriculture: Wollongbar.
- SAMMUT J. & LINES-KELLY R. 1996. *An introduction to acid sulfate soils*. ISBN 0 642 24533 9. 23 p.