

SULFIDIC MATERIALS: AN EMERGING ISSUE FOR THE MANAGEMENT OF SALINE AREAS THE RIVER MURRAY FLOODPLAIN

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Until recently, the occurrence of sulfidic materials in saline areas of the River Murray floodplain was not known. When present, they represent a significant hazard for the remediation of wetlands and other habitats through water regime management, such as wetting and drying cycles. This presentation will provide background for research on sulfidic materials in the floodplain environment. The known distribution of these materials and the known or speculated hazards they pose the floodplain environment will be discussed. The key areas for future research will be highlighted.

FLOODPLAIN SALINITY – A CHALLENGING ENVIRONMENTAL ISSUE

It is currently estimated that 25% of the lower River Murray floodplain is impacted by salinity, with this proportion potentially increasing to 50% by 2050 (RMCWMB 2003). Salinity is threatening the health of many ecosystems in this floodplain, including several Ramsar-listed wetlands and large tracts of red gum forests. Floodplain salinity is a complex problem that will be more difficult to manage than the better known issue of river salinity. The causes for the salinisation of the floodplain include: (i) decreased flooding frequency; (ii) disposal of irrigation water in wetlands; (iii) increased saline groundwater discharge caused by irrigation mounds along the margins of the floodplain; and, (iv) high water tables caused by raised weir pools (Jolly 1996, Figure 1). A number of “environmental flows” initiatives are currently considered to help improve floodplain salinity. These include managed water level manipulations in wetlands, weir draw downs, and increased frequency and duration of overbank flow events through carefully timed releases from reservoirs (MDBC 2000, RMCWMB 2003). In areas impacted by irrigation mounds, salt interception schemes are now designed to improve both river and floodplain salinity. Despite ongoing efforts, halting the ecological decline of the floodplain will be a difficult task.

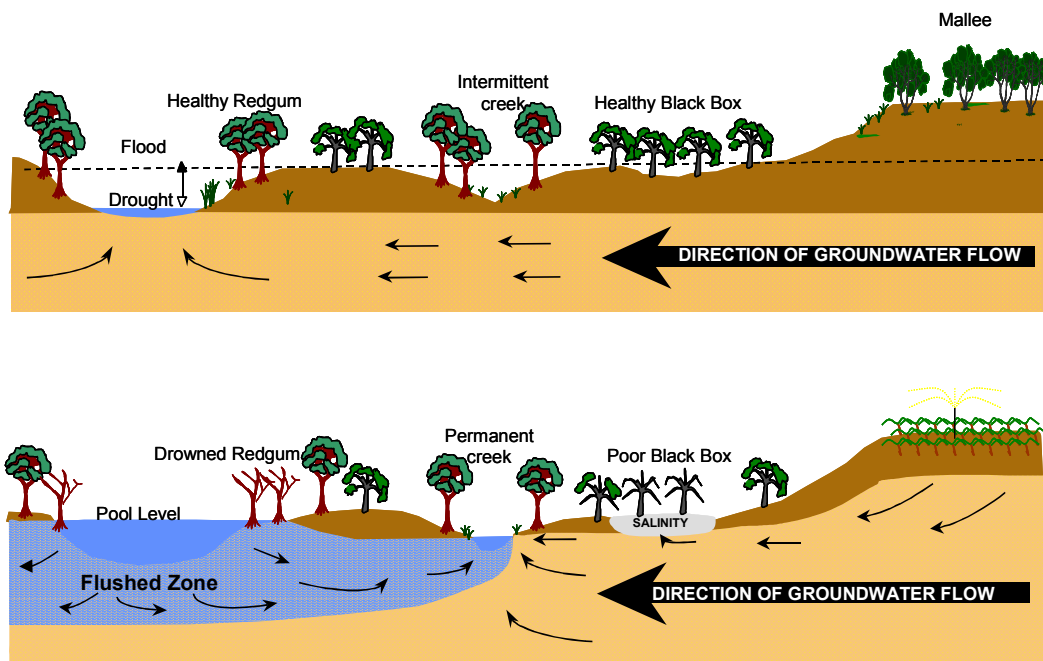


Figure 1: Change in groundwater - surface water interactions before (top) and after (bottom) European settlement in the River Murray floodplain (I. Jolly, CSIRO L&W).

SULFIDIC MATERIALS: A LEGACY OF FLOODPLAIN SALINISATION

Most studies on salinity in the floodplain have focused on the physics of salt and groundwater movement or

on the impacts of saline soils and groundwaters on phreatophyte health (summarised in Jolly 1996). An emerging concern arising from the salinisation of the floodplain is the development of sulfidic materials in soils and sediments in saline areas. Sulfidic materials are mostly accumulations of iron sulfide minerals, one of the end products of the process of *sulfate reduction*. Two forms of iron sulfide minerals are of interest on an environmental point of view: monosulfides (FeS) and pyrite (FeS₂). Soils or sediments rich in monosulfides (or “black ooze”) tend to be very dark and soft. Monosulfides can react rapidly when they are disturbed or exposed to oxygen. Pyrite will tend to occur as more discrete crystals in the sediment matrix and will react more slowly when disturbed. Sulfidic materials have long been recognised as a significant environmental problem for large sections of the Australian coastline (National Working Party on Acid Sulfate Soils 1999). It is now recognized that similar sulfidic materials can develop inland, for example in areas impacted by dryland salinity (Fitzpatrick *et al.* 1996, George 2002). However, little is known about the distribution of inland sulfidic materials and their potential hazards to ecosystem health.

WHY SHOULD SULFIDIC MATERIALS FORM IN THE FLOODPLAIN ENVIRONMENT?

Sulfidic materials will develop when conditions are favourable to high rates of sulfate (SO₄²⁻) accumulation and reduction (i.e., use of SO₄²⁻ instead of O₂ during microbial respiration). Conditions favourable to sulfate reduction are: (i) high concentration of sulfate in surface or groundwater; (ii) saturated soils and sediments; (iii) anaerobic conditions; and, (iv) the availability of labile carbon to fuel microbial activity. Saline wetlands in the floodplain environment have ideal conditions for SO₄²⁻ reduction because they have high sulfate concentration in surface and nearby groundwater, have become permanently flooded, and have anoxic sediments. External sources of carbon to fuel microbial activity in saline wetlands include terrestrial leaf litter and dissolved organic carbon in surface runoff or groundwater. Internal sources of carbon would include macrophytes (sedges, etc.), phytoplankton and benthic algae (i.e., algae growing on or near the surface of the sediments). Because most saline wetlands are shallow and have light reaching their sediments, it is expected that benthic algal growth will be a major source of carbon to fuel sulfate reduction. This problem will be compounded by elevated salinity, which will tend to decrease the turbidity of surface water and increase light penetration through the water column.

WHERE IS SULFATE COMING FROM?

While salinity is often equated with chloride (Cl⁻), SO₄²⁻ contributes between 10% to 20% of the salinity in rainfall, surface water and groundwater (Table 1). In unpolluted areas, the main source of SO₄²⁻ in rainfall is from ocean aerosols (sea spray). Near urban areas, the burning of fossil fuels may also contribute to SO₄²⁻ in rainfall. Other sources of sulfate in the environment will include gypsum deposits, fertilisers, and sulfide deposits. In saline floodplains, it is likely that most of the sulfate will originate from cyclic salts (i.e., will be rainfall-derived) but other sources may also be important locally. Overall, saline waters in the Murray-Darling basin have an ample supply of SO₄²⁻ to sustain high rates of sulfate reduction when conditions are favourable.

WHAT ARE THE POTENTIAL HAZARDS ASSOCIATED WITH SULFIDIC MATERIALS IN THE FLOODPLAIN ENVIRONMENT?

There are two categories of environmental hazards associated with sulfidic materials: the ones occurring during their formation and the ones occurring when they are disturbed. For example, during their formation, monosulfidic black ooze will coat surface sediments of wetlands and reduce the habitat available to benthic invertebrates (yabbies, clams, snails, etc). In addition, the process of sulfate reduction can interfere with the cycle of some of the key nutrients in freshwater, especially phosphorus (Waite 1997). High rates of sulfate reduction can make phosphorus more available to algae and, indirectly, could foster algal blooms.

Many potential environmental hazards associated with sulfidic materials will arise when they are disturbed (i.e. resuspended in the water column or drained). These include:

- **Noxious odours:** Foul offensive odour problems have recently been encountered near areas rich in sulfidic materials in the River Murray floodplain (for example at the Loveday and Ramco evaporation basins in SA). The offensive smells occur when sulfidic materials that were previously covered with water are exposed to the atmosphere. Hydrogen sulfide production (H₂S, the rotten egg smell) by drying sulfidic materials is thought to be a significant cause of the noxious odours. Aside from the foul odour problem, H₂S is also of concern for human health at high concentrations (Department of Environment and Heritage web site). However, a number of malodorous organic-S gases (such as dimethyl oligosulfides) can also be produced under the conditions favourable to H₂S production (Franzmann *et al.* 2001). Thus, the exact cause of the noxious smells is not clear at the present;
- **Accumulation of radionuclides:** In addition to iron, many other metals—including radioactive ones like uranium—can form mineral deposits in the presence of reduced sulfur. Thus, there is a possibility that, in

some areas, the long-term accumulation of sulfidic materials can also lead to significant accumulation of radionuclides. Of special concern for water quality would be radium-226, a mobile progeny of the uranium-238 decay series (National Health and Medical Research Council 1996). An investigation is currently underway to characterise the accumulation of radionuclides in retention basins of the Murray-Darling Basin (A. Herczeg, CSIRO Land & Water, *pers. comm.*). In addition to the risk to water quality, radionuclides will complicate the handling of sulfidic materials when the best management option will be to excavate and dispose of them safely;

- **Water column deoxygenation:** When sediments rich in monosulfides are resuspended, they will rapidly oxidise, potentially removing most of the oxygen from the water column (Sullivan *et al.* 2002). This can lead to fish kills, especially in enclosed areas such as billabongs. Flushing of saline drains by high runoff event and resuspension of sediments during water level manipulations in wetlands could potentially induce deoxygenation;
- **Acidification and elevated metal concentration:** When sulfidic materials are drained and exposed to air, they oxidise and produce sulfuric acid (Sammot & Lines-Kelly 1996). If the amount of acidity produced exceeds the buffering capacity of the pore water and sediment matrix, soil acidification can occur. Prior to draining, such materials are called potential acid sulfate soil materials (PASS). They become actual acid sulfate soil materials (AASS) or sulfuric horizons once drained. AASS materials can acidify runoff when they are flushed by rainfall or other events. In addition to lowering the pH of runoff, activation of PASS materials can also lead to significant increases in dissolved metal concentration in surface water, including toxic species such as aluminium and cadmium. The increase in solubility of these heavy metals under acidic conditions may be more harmful to biota than the low pH itself.

Table 1. Representative rainfall, surface water and groundwater chemistry for the western Murray Basin (from Herczeg *et al.* 2001).

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Rainfall							
Horsham (mg L ⁻¹)	0.9	0.2	0.4	0.6	1.1	0.24	4.3
(meq L ⁻¹)	0.04	0.004	0.033	0.03	0.031	0.005	0.071
Walpeup (mg L ⁻¹)	1.7	0.4	0.5	3.2	2.1	0.9	13
(meq L ⁻¹)	0.074	0.01	0.041	0.16	0.059	0.019	0.213
Merbein (mg L ⁻¹)	1.7	0.3	0.4	4.4	2.4	1.8	14
(meq L ⁻¹)	0.074	0.008	0.033	0.22	0.068	0.038	0.23
Groundwaters							
Fresh (mg L ⁻¹)	170	6.6	36.7	75	287	39.4	293
(meq L ⁻¹)	7.4	0.17	3.02	3.7	8.1	0.82	4.8
Brackish (mg L ⁻¹)	1,964	28	157	67	2,560	654	921
(meq L ⁻¹)	85.4	0.71	12.9	3.3	72.2	13.62	15.1
Saline (mg L ⁻¹)	6,693	124	676	447	12,018	706	360
(meq L ⁻¹)	291	3.17	55.6	22.3	339	14.7	5.9
Sea wat. (mg L⁻¹)							
(meq L ⁻¹)	10,760	399	1,294	412	19,350	2,712	145
	468	10.2	106.4	20.4	545	56.4	2.38

There is at least one documented case of a wetland in the River Murray floodplain (Bottle Bend Lagoon, NSW) acidifying following a draw down event (McCarthy *et al.* 2003). This wetland was found to have PASS materials during a recent survey (see Hicks *et al.* 2003). However, it is also possible that acidification of Bottle Bend Lagoon was caused in part by an increased input of iron and manganese-rich groundwater following the draw down. Groundwater in the floodplain environment is frequently saline, anoxic, and rich in dissolved metal species such as Fe²⁺ and Mn²⁺ (Forward 2001). Especially where water tables tend to be elevated, a surface water level draw down can induce an increase discharge of groundwater to wetlands. Following discharge to surface water, the oxidation of Fe²⁺ to Fe³⁺ and of Mn²⁺ to Mn⁴⁺ followed by the precipitation of Fe and Mn oxides will produce acidity (Appelo & Postma 1993). Thus, in River Murray floodplain environment, activation of PASS materials and increase discharge of groundwater may have additive impacts on wetland acidification.

WHAT PART OF THE FLOODPLAIN ENVIRONMENT WOULD BE MOST AT RISK?

Only limited information is currently available on the properties and distribution of sulfidic materials in the River Murray floodplain environment. However, information collected to date indicates that sulfidic

materials are common in permanently flooded saline areas, such as evaporation basins (Hicks *et al.* 2003). It is possible to speculate on which parts of the floodplain would be most at risk of impact from sulfidic materials. Susceptible environments would include: (i) evaporation basins and permanently flooded saline wetlands; (ii) wetlands and billabongs that become disconnected from main river channels at low river levels; and, (iii) terrestrial habitats over shallow (< 2 m) saline water tables. Environments with reduced risk would include: (i) terrestrial habitat over deep or fresh water tables; (ii) wetlands with a good permanent connection to the main river channel; and, (iii) the main river channel. Wetlands well connected to the main river channels and the main river channels are probably not at risk because of the high dilution potential and generally high alkalinity of the river.

CONCLUSION

The understanding of the properties, distribution and hazards associated with sulfidic materials in the floodplain environment is currently limited but increasing rapidly. Sulfidic materials are stable as long as they remain in an undisturbed, saturated and anoxic environment. Consequently, management options that will expose sulfidic materials to the atmosphere will have environmental hazards associated with them. While it is now known that environmentally significant deposits of sulfidic material are present in the floodplain environment, many issues are still unresolved. Some of these issues include:

1. Incomplete knowledge of the properties and distribution of sulfidic materials in the floodplain;
2. Lack of predictive models to determine where and how fast these materials can develop under different conditions;
3. Limited knowledge of the hazards sulfidic materials pose to the environment, especially when disturbed;
4. An incomplete understanding of the contribution of metal-rich groundwater inputs and sulfidic materials to wetland acidification.

It is imperative that simple guidelines are developed and made available to floodplain managers to identify sulfidic material deposits of environmental significance. The issue is serious considering that managed water level manipulations are increasingly considered to provide a more natural water regime to many wetlands in the floodplain. While managed water level manipulations have many potential environmental benefits, these benefits may be negated if undertaken improperly when sulfidic materials and metal-rich groundwaters are present. Once identified, a risk assessment framework for sulfidic materials combined with appropriate management options must be designed to help maximise the benefits of managed water levels in wetlands and minimise potential hazards.

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