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CHAPTER 19

ACID SULFATE SOIL MATERIALS AND SALT EFFLORESCENCES IN SUBAQUEOUS AND WETLAND SOIL ENVIRONMENTS AT TAREENA BILLABONG AND SALT CREEK, NSW: PROPERTIES, RISKS AND MANAGEMENT

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INTRODUCTION

In April 2007, Tareena Billabong (south-west NSW) was isolated by sandbagging from Salt Creek and the River Murray as an option to generate water savings and help mitigate drought-related problems in the Murray-Darling Basin. Because evaporation from the billabong surface is approximately 1GL per annum, it has been estimated that environmental flow savings of about this amount can be achieved at Tareena Billabong by preventing inflow from the Murray River. In addition, the proposed works will also direct flows down the Murray in order to maintain the Lock 6 weir pool, through restricting flows within Salt Creek.

Previous work by CSIRO Land and Water and others in subaqueous soil (lakes/rivers) and wetland environments in this region have identified various occurrences of sulfidic, sulfuric and monosulfidic black ooze materials (i.e. acid sulfate soils; e.g. Baldwin *et al* 2007; Fitzpatrick *et al* 2006, Fitzpatrick *et al* 2007; Hicks and Lamontagne 2007; Lamontagne *et al* 2004). Occurrences of these ASS materials would have serious environmental consequences relating to soil and water acidification, de-oxygenation of water, foul smelling (H_2S, organo-S compounds) and possible heavy and trace metal mobilisation – especially if these wetlands are to be slowly evaporated and experience wetting-drying cycles. Hence, characterisation of a range of representative subaqueous soils and sediments in the billabong and adjacent Salt Creek would allow identification of ASS hot-spots and contaminant types, and development of specific management options and contingency plans.

This chapter presents a summary of findings (Fitzpatrick *et al* 2008) and subsequent of Murray Darling Basin Commission actions on:

- The properties, extent, potential severity and management of the various subtypes of acid sulfate soils (ASS) currently present in Tareena Billabong and adjacent Salt Creek, based on field sampling (Figure 1), morphological descriptions and laboratory data
- Provide predictive capability when the area continues to be drained, partially drained and reflooded
- Recommendations for the sustainable management of ASS subtypes and identify mitigation strategies, especially their suitability for drying to generate water savings.

Field sampling of soils

Field work was carried out at Tareena Billabong and adjacent Salt Creek from 13th to 15th September 2007. Sampling sites are shown in Figures 1 to 3. Samples of soil profiles and salts (efflorescences) were taken from 21 sites at Tareena and 8 sites on Salt Ck (for detailed information see Fitzpatrick *et al* 2008).

We collected and analysed 80 samples from 29 sites for morphological, chemical, mineralogical and physical properties. These samples provided a comprehensive database to develop a user-friendly “Soil Identification Key” to allow the easy identification of the various subtypes of ASS in Tareena Billabong and Salt Creek areas. Identification of the various subtypes of ASS enabled us to assess soil condition across Tareena Billabong and Salt Creek. An understanding the properties, distribution, evolution and interrelationships of the seven subtypes of ASS identified has been vital for effective selection of appropriate management strategies.

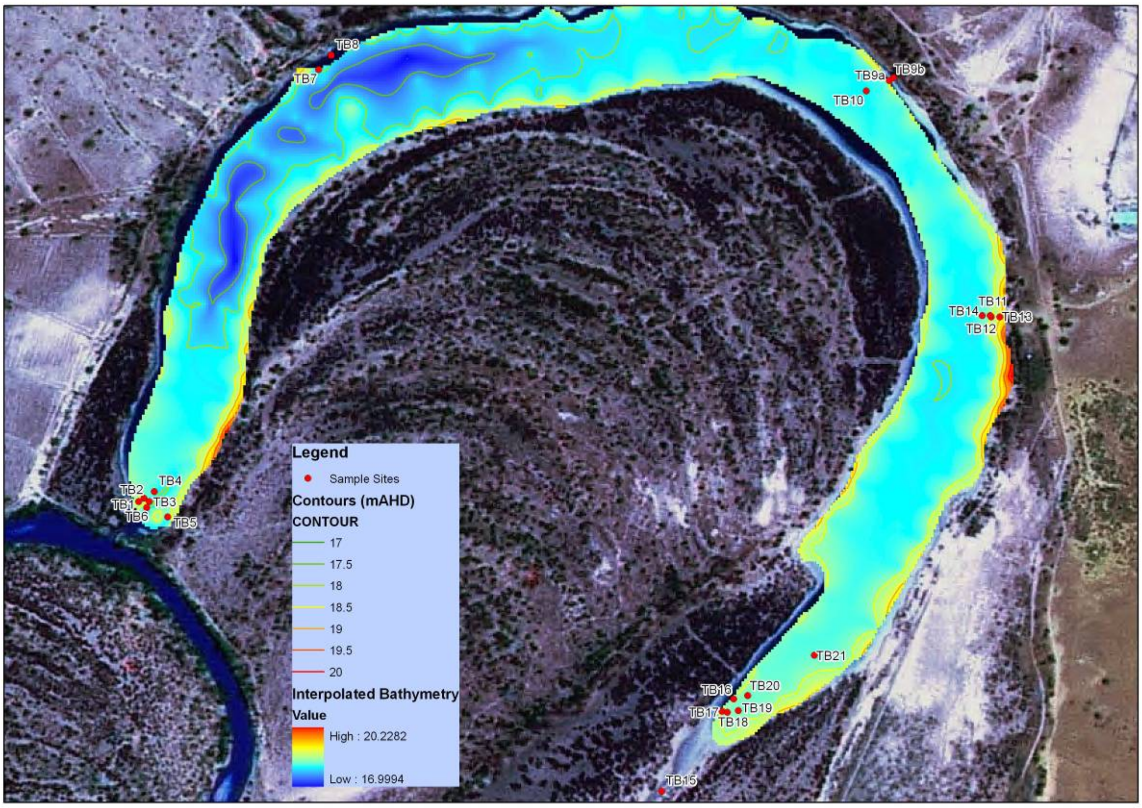

Figure 1. Sites sampled at Tareena Billabong.

Figure 2 . Sites sampled at Salt Creek. Tareena Billabong is on the right.

Figure 3. Detail of sampling sites SC3 to 6 on Salt Creek.

Results and discussion

We examined 29 sites for the occurrence of ASS. We found a wide range of ASS subtypes at these sites (Fitzpatrick *et al* 2008). We inspected 29 profiles and sampled 87 soil horizons/layers, which were stored in plastic chip trays to facilitate detailed soil morphological descriptions and mineralogical analyses. Eighty samples were analysed for chemical, mineralogical and physical properties.

These samples provided a comprehensive database to develop a user-friendly “Soil Identification Key” to allow the easy identification of the various subtypes of ASS in Tareena Billabong and Salt Creek areas. The key is based on the comprehensive data set of soil properties acquired in a range of subaqueous and wetland environments. The soil identification key essentially uses non-technical terms to categorise ASS subtypes in terms of attributes that are important for characterising soil and water degradation. Identification of the various subtypes of ASS enabled us to assess soil condition across Tareena Billabong and Salt Creek. An understanding the properties, distribution, evolution and interrelationships of the 7 subtypes of ASS has been vital for effective selection of appropriate management strategies.

Tareena Billabong

A range of subaqueous and wetland acid sulfate soil (ASS) subtypes with sulfidic and monosulfidic black ooze (MBO) materials are present in Tareena Billabong (ASS and non-ASS soils in subaqueous, waterlogged and drained soils). Sulfidic materials are expected, on oxidation, to result in pH values less the 4, measured in water (Isbell 2002). Although soil layers may be identified as sulfidic, acid generation on exposure to oxygen may be locally neutralised by carbonate minerals or by bicarbonate in the billabong and ground waters which can reach exposed soils by wind or wave action. On oxidation, MBO materials in soils do not usually produce a pH value lower than 4, the critical pH value for sulfuric material, unless other sulfidic minerals are also present. No sulfuric material (soil pH in water less than 4) was identified because the pH of most soil materials was alkaline, between pH 7 and 8.

Subaqueous ASS subtypes include:

1. Sulfidic subaqueous clayey soil with MBO (wet, soft, clayey MBO material overlying wet, heavy clay sulfidic material; Figure 4**Figure 4.**).

Figure 4. Sulfidic subaqueous clayey soil with MBO, in shallow water in the south east end of the billabong (Site TB21). This subtype has a thin surface layer (10 to 15 cm) of soft clayey monosulfidic black ooze (MBO) material, which overlies wet heavy clay sulfidic material.

2. Sulfidic subaqueous clayey soil (wet, soft, clayey sulfidic material overlying wet, heavy clay sulfidic material; Figure 5)

Figure 5 . Site TB5 sampled in water (subaqueous) near the sand-bagged outlet to the billabong (Left side). Sulfidic subaqueous clayey soil (wet, soft clayey sulfidic material overlying wet heavy clay sulfidic material) (Right side).

3. Sulfidic subaqueous soil (wet, soft sandy sulfidic material overlying wet sandy to loamy sulfidic material). The upper layers often contain fine or medium sand of varying thickness, probably of aeolian origin.

In middle sections of the billabong (e.g. from Sites TB 7 to TB 10 to TB 13, Figure 1), the dominant subaqueous ASS subtype comprises mostly a thin layer (10 to 20 cm thick) of sandy to loamy sulfidic material overlying a heavy clay matrix with prominent slickensides and bluish or greenish diffuse mottles (Figure 6).

Figure 6. Sulfidic subaqueous soil (wet, soft, sandy sulfidic material overlying wet, heavy clay sulfidic material). This site, Site TB7, was sampled in water 20 cm deep.

3. Sulfidic subaqueous soil (wet, soft, sandy sulfidic material overlying wet, heavy clay sulfidic material). The upper layers often contain fine or medium sand of varying thickness, probably of aeolian origin.

Wetland (undergoing drying) ASS subtypes include:

4. Sulfidic cracking clay soil with MBO (dry to moist, hard to soft clayey MBO material overlying wet, heavy clay sulfidic material).

At the south-east terminal end of the billabong, as drying has proceeded for a much longer time period, the sulfidic heavy clays are overlain, above the shallow water table (Figure 7), by profiles with hard to friable cracked clayey MBO layers, which are surrounded by a brown hardened oxidised surface coating (Figure 8) with surface salt crusts (moist through capillarity or groundwater seepage) and dry, 'fluffy' surface with salt efflorescences. All of these materials show some evidence of accumulation of what we believe to be wind-blown fine sands and other materials.

Figure 7. Sulfidic cracking clay soil with MBO (Dry to moist, hard to soft clayey MBO material overlying wet, heavy clay sulfidic material). Site TB16 (left) is a groundwater seep surrounded by very thin (< 1 cm) dried surfaces with extensive cracking and salt efflorescences on edges of cracks. More extensive drying (0-10 cm) at TB 19 (right) displays hard crust.

Figure 8. Close-up view of a fractured piece of the dried and hardened surface material at site TB19 showing a brownish, platy surface layer (2 to 10 mm thick) abruptly surrounding the inner, black sulfidic-like material.

5. Sulfidic cracking clay soil (dry to moist, hard to friable clayey sulfidic material overlying wet heavy clay sulfidic material).

In the partly dried and evaporated area near the sand-bagged connection to Salt Creek (SW end; (site TB 4)) of the billabong, dry to moist, sulfidic cracking clay ASS subtypes occur with no MBO but with a thick, 'fluffy' surface with salt efflorescences.

Figure 9. Sulfidic cracking clay soil near Site TB4 at the south-western end of Tareena Billabong. The top 5 cm has potential to acidify significantly, depending on drying.

6. Sulfidic soil with MBO (dry to moist, soft to friable sandy MBO material overlying wet heavy clay sulfidic material). The upper layers often contain fine or medium sand of varying thickness, probably of aeolian origin.

Adjacent (5 to 10 m) to shoreline in the middle sections of the billabong (e.g. from Sites TB 8 to TB 13, Figure **Figure 1.**11, the dominant ASS subtypes comprise mostly a thin layer (10 to 20 cm thick) of sandy to loamy MBO material abruptly overlying a heavy clay matrix with prominent slickensides and bluish or greenish diffuse mottles (Figure 10).

Figure 10. Sulfidic soil in sandy MBO matrix, site TB9, 6 m from shoreline near the Telephone Station.

7. Sulfidic soil (dry to moist, soft to friable, sandy to loamy (thick 0 to 50 cm) sulfidic material overlying wet clayey sulfidic material).

On the upper shorelines (>10 m from shoreline at time of sampling), especially in the middle sections of the billabong (e.g. from Sites TB 8 to TB 13), the dominant ASS subtype comprises a thick layer (10 to 50 cm thick) of sandy to loamy sulfidic material overlying a heavy clay matrix with prominent slickensides and bluish or greenish diffuse mottles (Figure 11).

Figure 11. Sulfidic soil at site TB 8 (on the upper shoreline) on the north-west side of the billabong. The dark bands at about 7 – 15 cm are sulfidic material and are likely to acidify on drying.

We also identified a sandy podsol soil with some ASS properties overlying a bluish-grey clay (site TB 11) on the upper shoreline with beach-line features (Figure 12). These are beach-like features - some of long standing in that they have experienced palaeo-environmental conditions where the climate was considerably wetter and suitable to develop a podsol (i.e. ‘Podosol’ according to the Australian Soil Classification: Isbell 2002). This soil may date from the earliest times of the billabong (Gell *et al* 2005) when it was a freshwater lagoon. Sand accumulation may also be a feature of where dry creek lines abut the billabong.

Figure 12. Sandy podsol soil overlying bluish-grey clay (site TB 11) on the upper shoreline with beach-like features.

Salt efflorescences containing mainly Na, Mg and Ca sulfate salts

The presence of several groundwater seepages with associated salt efflorescences containing mainly Na, Mg and Ca sulfate salts are most obvious at the south-eastern end of the billabong. However, some groundwater seepage is also evident at other places where dry gullies meet the billabong and near the sand-bagged connection to Salt Creek (SW end), with salt efflorescences containing significant concentrations of Mg and Na sulfate salts. These take the form of clearly defined seepages up to a few metres across, or much more extensive areas at some height above the billabong water level at the time of sampling, which may be kept moist by capillarity from the subsoil water table.

The pH of some soils at both ends of the billabong - which have likely been drained for the longest period - have pH values that are slightly acidic, about pH 6, similar to the groundwater in pits dug in these soils. Some localised, ‘spot’ pH measurements made in the field on naturally oxidised layers also showed pH values between 5.6 and 6. Soil pH after peroxide treatment, a quick measure of potential for acidification that simulates oxidation of sulfides on drying, indicates that there is acid neutralising capacity for most materials to maintain pH values above about 5.

More than 60% of samples exceed the highest trigger value for reduced inorganic sulfur concentrations (chromium reducible sulfur) for fine grained (clayey) soils. However, only around 40% of samples have a net acid generation potential (NAGP). Fourteen of eighteen profiles analysed had at least one horizon with a reduced inorganic sulfur concentration above the highest trigger value for fine grained soils. However, only five profiles have a net acidity (positive NAGP), although within profiles individual samples and the sum at shallower depths may have small net acidity.

Hence, we conclude that oxidation of the sulfides present are unlikely to produce very acidic soil profiles (pH less than 4) to a depth of 50 cm. Some limited layers in the upper 20 to 30 cm have potential to acidify more significantly, especially if the materials are sulfidic sands.

Two environmental features are likely to help mitigate acidification:

1. the evapo-concentration of alkalinity in the billabong water, and
2. the entry of alkaline groundwater to the surface soils.

The alkalinity of the billabong water is not known, but its pH is increasing as the billabong dries (ongoing MDBC Tareena Monitoring Reports). The alkalinities of the groundwaters are also not known, but the subsoils in seep areas are alkaline (pH > 8) and should be in equilibrium with the groundwater. The presence of groundwater leakage is also significant as it should maintain at least some areas of the billabong soils in a moist or wet state, and this will slow or prevent oxidation by excluding air. Any residual water that can be retained in the billabong will help this process as the heavy clays will wet up by capillarity (but not the sandy materials).

The rapid drying of the sulfidic material, especially the heavy clays, which cracks and lifts away from the moist, clayey subsoil and breaks the capillarity, slows the biological processes, which are responsible for oxidation of sulfides and thus the formation of acid.

White salt efflorescences containing Na, Mg and Ca-rich sulfate minerals have formed directly over the drying monosulfidic black ooze and sulfidic materials, with higher abundances of salt efflorescences occurring on the edges of cracks. The dominant salts are konyaite ($Na_2Mg(SO_4)2.5H_2O$), halite (NaCl), gypsum ($CaSO_4.2H_2O$) and thenardite (Na_2SO_4) with minor (trace) epsomite ($MgSO_4.7H_2O$), eugsterite ($Na_4Ca(SO_4)3.2H_2O$) and hexahydrite ($MgSO_4.6H_2O$). Salt efflorescences have potential for aerial transport and to be dissolved in surface flow waters. There is a need to prevent stock from ingesting these salts (e.g. similar to Epsom salts) because this is likely to lead to scouring in sheep and cattle. Magnesium salts are toxic when ingested in high levels.

Fine granular surface flakes containing “dried” sulfidic material may also form when the soils material dries. This material is also highly susceptible to wind erosion, especially on the extensive flat area of the bare, salty lake beds.

The concentrations of major and minor (or trace) elements determined using X-ray fluorescence spectroscopy (XRF) are considered to be in the normal range for most, if not all samples. Several elements – notably mercury (Hg), cadmium (Cd) and selenium (Se) – were present at concentrations below the lower limits of detection for the XRF method used. Evaluation of the potential toxicity of these and a few other elements requires other, more advanced techniques and, probably, the determination of the different species present in aqueous systems.

We recommend that the following steps be taken:

- The upper layers of soil materials be allowed to dry as quickly as possible
- The state of the drying billabong initially be monitored weekly for a period of three months – if there is little change in water pH (e.g. they remain in the range 6 to 9) reduce monitoring frequency to fortnightly
- People and farm animals be excluded as far as possible
- Develop a strategy for re-wetting based on the likely possibilities presented below.

Salt Creek

Salt Creek was sampled at five sites in the vicinity of Tareena Billabong. Mostly the banks are steep sided, with occasional reed beds and depositional areas with reduced soils and shallow water depth. Sampling and laboratory analyses of these subaqueous and near shore wetland soils indicate that the materials differ considerably from those in Tareena Billabong.

The subaqueous soils in Salt Creek mainly occur on steep sided banks (Figure 13) The dominant soil materials are grey clay to heavy clays with greenish or bluish diffuse mottles overlain by grey (sometimes yellowish grey) gel or ‘ooze’, or silty clay. In places where there are side channels, the layers may be silty or contain fine sand or grit. However, Site SC4 differed in having sand bars with rushes and reeds (Phragmites) (Figure 14). The heavy clays may show structure (lenticular or parallelepiped) and slickensides at depth. Where there was subaqueous weed, orange brown mottles are evident in the soils around the roots. Some of the heavy clays contained medium to fine sand.

Figure 13. Salt Creek near site SC1 with its steep sided banks.

Figure 14. Sulfidic subaqueous soil with thick (0 to 50 cm) soft, sandy, sulfidic material overlying wet clay. Site SC6 was sampled from the stream bed of Salt Creek mid way between the near bank and the reeds on the far side.

Subaqueous ASS subtypes include: Sulfidic subaqueous clayey soil (wet, soft, fine or medium, sandy or silty, sulfidic material overlying wet bluish grey, heavy clay sulfidic material with slickensides).

pH measurements show that these materials are mostly already acidic (pH less than 7 and lacking carbonate minerals) and that they contain sufficient sulfide, which, when oxidised, is likely to result in significant further acidification.

Wetland ASS subtypes include: Sulfidic cracking clay soil (wet, soft, fine or medium, sandy or silty, sulfidic material overlying wet, bluish grey, heavy clay sulfidic material with slickensides).

The alkalinity of the water in Salt Creek is not currently known but the low levels thought to be present may partially neutralise the subaqueous soils if they are exposed to drying. Otherwise, any acidity developed will be partially neutralised by the acidification and decomposition of the soil mineral matter. This may be effectively irreversible. Since the river water would also be expected to flush soluble sulfate salts from the system, the production of alkalinity by reduction processes that re-form sulfides may not be significantly retained for neutralising the soils. Water quality issues are also likely. Neutralisation by applying lime along the banks of the creek is not considered practical.

Management options based on subtypes of ASS
We developed the user-friendly "Soil Identification Key" to allow the easy identification of the various subtypes of ASS in Tareena Billabong and Salt Creek areas. The key is based on the comprehensive data set of soil properties acquired in a range of subaqueous and wetland environments. The soil identification key essentially uses non-technical terms to categorise ASS and other soils in terms of attributes that are important for charactering soil and water degradation. The key also describes practical, surrogate methods to assist managers and engineers to estimate hazard classes for the subtypes of ASS (High, Moderate, Low and Very Low).

Management strategies should to be based on adequate characterisation and mapping of the seven identified ASS subtypes. Understanding the distribution, evolution, nature and interrelationships of the seven subtypes of ASS is vital for effective planning of agricultural management and selection of appropriate remediation options. We recommend that the steps outlined below be taken.

Strategies for re-wetting based on likely possibilities
The results of investigations suggested that re-establishing the billabong to full capacity should result in the exclusion of oxygen to much of the cracked dry soils and the re-establishment of the more benign subaqueous acid sulfate soils with clayey or sandy monosulfidic black ooze overlying the clayey sulfidic materials that currently exist under water. Formation of sulfide minerals produces alkalinity (derived from organic matter) that may partially offset some of the acid formed, but only if this alkalinity is retained in the system. Re-flooding should manage potential acid formation of all soil types indentified in the billabong.

Management options for re-flooding and re-wetting dry wetlands
A strategy for re-wetting was prepared and implemented. For example, flood waters were held in Tareena Billabong for some weeks to permit anaerobic conditions to develop. This created reducing conditions for the oxidised sulfate to transform back to sulfide. Once this has occurred, and water quality is acceptable, then water can be allowed to flow back into Salt Creek.

A careful approach will be needed when re-wetting the adjacent Salt Creek to manage the increased salt loads and potential mobilisation of acidity and metals. Management to enable periodic flushing of the salts is recommended long-term, if possible, as this will decrease the sulfur load in Salt Creek and Murray River wetlands.

Monitoring of Salt Creek and adjacent wetlands was recommended and implemented as the wetting and re-filling occurs. It provided an opportunity to learn for future drought recovery programs.

Proposed monitoring strategy

For future work, it is strongly recommended that a detailed monitoring strategy be developed at the representative monitoring sites in the Billabong and Salt Creek for key field indicators and laboratory tests. The strategy will be to determine key trigger values to identify the onset of acidification and other ASS related problems (e.g. changes in pH, alkalinity, presence of indicator minerals, etc.), which needs to be site specific. Preliminary trigger values for pH of 6.5 is suggested since at pH values below this, significant impacts are likely for many natural ecosystems. However, part of the monitoring exercise should assess in detail site specific indicators for key indicator elements e.g. sulfur species.
A monitoring strategy should be based on data from the current ASS investigations, especially the identification of the sandy ASS "hot spots".

CONCLUSIONS

Tareena Billabong

Field and laboratory investigations led to the conclusion that significant acidification is unlikely to occur and become a problem if Tareena Billabong continues to evaporate to dryness, although minor local acidification within soil layers is likely. Acidity is likely to be neutralised by carbonate minerals present in the soils, by the entry of alkaline groundwater, wind and wave action on alkaline billabong water and by the accession of alkaline components of wind-borne dusts.

Salt efflorescences containing Na, Mg, Ca sulfate salts, their transport by wind (e.g. aerial transport of fine granular surface flakes containing sulfidic material) or water, and malodorous problems may become serious issues, though the latter is somewhat negated by its remote location. These efflorescences are mostly highly water soluble and can be expected to be easily entrained in and contribute to degraded quality of river water.

Monitoring of soils and waters for pH was recommended and implemented as the water in the disconnected billabong receded to confirm the expected course of acidification or alkalinisation (in this case, the latter). Murray Darling Basin Commission staff monitored the system, initially weekly for three months and subsequently fortnightly because pH levels remained alkaline. A similar monitoring program is recommended during reflooding of the billabong.

Finally, we also recommended:

- Removal of sandbags and installation of a floodgate and manual mini-sluice gate to enable controlled exchange of water between Tareena Billabong and Salt Creek
- Installation of a one-way hinged flap gate (floodgate) to regulate billabong water entering Salt Creek and the Murray River system, especially during reflooding of Tareena Billabong. The flood waters must be held in Tareena Billabong for some weeks to permit anaerobic conditions to develop. This will create reducing conditions for the oxidised sulfate to transform to sulfide
- Once anaerobic conditions have been re-established in the reflooded billabong, then water exchange with Salt Creek should be allowed, provided the water is of suitable quality. Self-regulating or manual mini-sluice gates allow better control of water exchange than raising floodgates.

Salt Creek

Field and laboratory investigations indicate that acidification is more likely to be a serious problem if the river bed of Salt Creek continues to be exposed. The higher quality river water contains relatively low alkalinity, as do the soils adjacent to the creek and in its bed. Generally these soils are already mildly acidic. Receding river water levels may allow significant entry of alkaline ground waters that should introduce alkalinity.

Should water levels decline further exposing more creek bed and bank, a monitoring program should be instigated and an assessment made of risks.

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