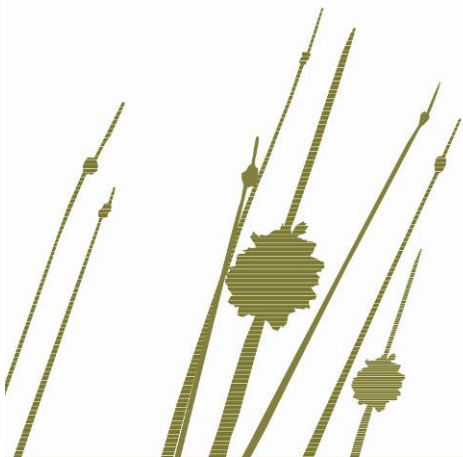


# Management of Acid Sulfate Soils in the Lower Murray Lakes

Technical Fact Sheet

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Department  
for Environment  
and Heritage



Government  
of South Australia

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## Acid Sulfate Soils (ASS)

The term 'Acid Sulfate Soils' refers to soils and sediments containing iron sulfide minerals such as pyrite (FeS<sub>2</sub>) and iron monosulfide (FeS). These minerals are the natural by-product of microbiological activity in coastal, estuarine and freshwater soils and sediments. Key ingredients in their formation include soluble sulfate concentrations, organic matter, (e.g. decaying vegetation), and a source of iron. Many sources of organic matter already contain suitable iron concentrations.

Whilst these minerals remain in water-saturated settings, they do not pose a hazard. Once exposed to the oxygen in air, they form sulfuric acid and metal salts that are highly soluble. When the acid salts are mobilised by water (e.g. river flows, rainfall or wave action), other minerals within the soils and sediments begin to dissolve, releasing a broad range of metals, often at toxic concentrations. Key elements of concern include iron, manganese, aluminium and arsenic.

The typical signature of advanced acid-generating processes from acid sulfate soils includes: drainage water with a low pH and elevated sulfate and metal concentrations, widespread secondary precipitates formed by water-soil interaction, extensive vegetation dieback, impacts on livestock and possible fish kills.

Figure 1 illustrates typical lake water levels post construction of the barrages and prior to the current drought (1940-2006), and identifies the natural processes and key reactions involved in pyrite and iron monosulfide formation in the lake sediments.

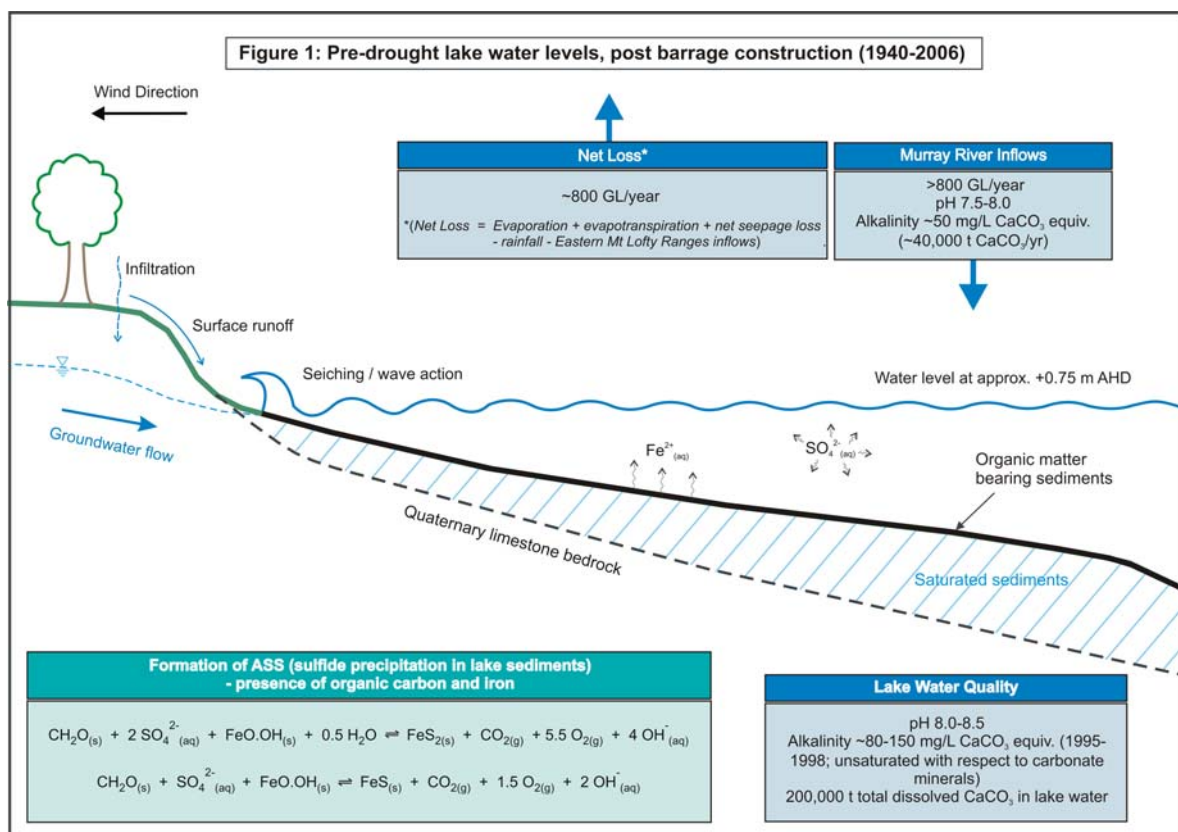


Figure 1. Pre-drought lake water levels, post barrage construction (1940-2006).

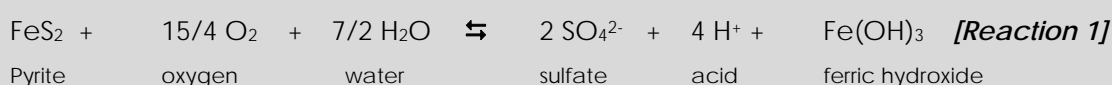
The primary management strategy for dealing with acid sulfate soils is to avoid or minimise exposure to atmospheric oxidation. Once acidity has been generated, natural bioremediation processes (i.e. microbiological activity under reducing conditions), should be encouraged to reverse acidification processes. Intervention with engineered solutions may become necessary when natural systems cannot deal with acidity loads.

## Implications of Acid Sulfate Soils in the Lower Murray Lakes

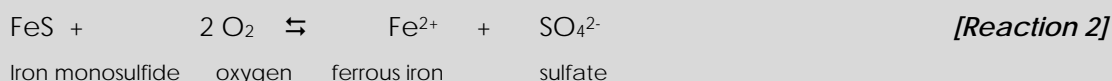
Water levels in the lower Murray lakes are declining as a result of the current drought affecting south-eastern Australia and over allocation of river flows upstream of the lake system. This lowering of lake water levels increases the mass (or volume) of sulfidic soils and sediments that are exposed to atmospheric oxygen. Hence, the mass of sulfidic material that generates acidic salts is progressively increasing as lake levels recede. If these acidic salts are washed into the lakes by rainfall, seiching or eventual refilling of the lakes, there is potential for serious ecological, human health or water quality impacts in the lower Murray lakes.

### Reactions involved in acidity generation in the lake soils and sediments

Acidity generation associated with pyrite and iron monosulfide oxidation is shown in the reaction below.



Acidity generation associated with iron monosulfide oxidation is shown below.



The oxidation of iron monosulfide is not "acid" generating but is "acidity" generating. The ferrous iron ( $\text{Fe}^{2+}$ ) produced in Reaction 2 may oxidise to ferric iron ( $\text{Fe}^{3+}$ ) and eventually precipitate as ferric hydroxide, which is an "acid" generating process.

The term "acid" quantifies only the actual concentration of  $\text{H}^+$  present in solution and is generally expressed as pH. The term "acidity", on the other hand, accounts for both the actual  $\text{H}^+$  concentration of the aqueous solution and the potential for acid generation due to mineral or latent acidity, ie  $\text{H}^+$  produced by metal hydroxide precipitation.

### Acidity generating capacity of the lake soils and sediments

The three key factors affecting the capacity of the lake soils and sediments to generate acidity are:

1. the mass (rather than surface area) of acid sulfate soils exposed to atmospheric oxygen
2. the mass of acid neutralising materials available to react with the acid and metalliferous drainage within the soils and sediments
3. the rate of sulfide oxidation (or oxygen consumption).

The mass of exposed acid sulfate soils is dependent on lake and groundwater levels as well and soil moisture content, which is affected by wave action/seiching and rainfall patterns. For example, a 1.0 metre drop in lake water levels from -0.5 metre AHD to -1.5 metre AHD has the potential to generate a total of around 680,000 tonnes sulfuric acid ( $\text{H}_2\text{SO}_4$ ), based on current estimates of the average sulfide content in the lake soils and sediments and the volume exposed.

The rate at which acidity is generated from exposed acid sulfate soils depends on the characteristics of the sulfide minerals (such as grain size), the type of sediment containing the sulfide minerals (e.g. sand or clay), and the sediment moisture content (i.e. ease of oxygen access). For example, an "effective" sulfide oxidation rate of 1 wt% of exposed  $\text{FeS}_2$  oxidising to sulfuric acid per year would correspond to the generation of 6,800 tonnes  $\text{H}_2\text{SO}_4$  annually. A higher oxidation rate (e.g. 10 wt%  $\text{FeS}_2$ /year), would correspond to the generation of 68,000 tonnes  $\text{H}_2\text{SO}_4$  annually.

While there is significant potential for acidity generation in the lake soils and sediments, this does not necessarily translate to acidification of lake waters. Factors that have the potential to mitigate lake acidification are described below.

### **Acidification of lake waters**

Any acidity generated within the lake soils and sediments has the potential to be transported into the lake waters by infiltration of rainfall or surface water runoff, and subsequent inflow to the lakes via groundwater flows. The effects of wave action and seicheing can also contribute to the flushing of acidic pore water from the soils and sediments into the lakes. However, the fate of acidity generated within the lake soils and sediments can be affected, to varying degrees, by the following processes:

- neutralisation of acidity by carbonate minerals contained within the lake soils and sediments
- neutralisation of acidity by aluminium silicate minerals (e.g. clays), contained within the lake soils and sediments
- re-precipitation of sulfides (e.g. pyrite or iron monosulfide), within the saturated zone of the lake soils and sediments, in the presence of organic carbon and iron (this is likely to occur relatively rapidly where the pH remains above 4.5).

Furthermore, any acidity that is transported to lake waters has the potential to be remediated by:

- neutralisation by soluble bicarbonate alkalinity within the lake waters
- microbial re-precipitation of sulfides (i.e. pyrite or iron monosulfide), within the lake soils and sediments, in the presence of some alkalinity, organic carbon and iron.

Water chemistry data for the lakes suggest that some re-precipitation of sulfides (i.e. natural microbial remediation), is already occurring within the system. It is vital for the ongoing health of the lakes that these processes are sustained in order to deal with any unavoidable acidity addition.

Key factors that have the potential to limit the efficiency of these remediation processes include:

- the quantity and availability of neutralising minerals within the lake soils and sediments
- the quantity of soluble bicarbonate alkalinity within lake waters
- the quantity of organic carbon within the lake soils and sediments
- the quantity and availability of iron within the lake waters and soils and sediments
- the rate at which acidity is flushed into the lakes by groundwater inflows, rainfall, wave action and seicheing processes.

Figure 2 depicts the current scenario in the lake, with water levels approaching -1.0 metres AHD, and identifies the processes and key reactions involved in acidity generation, neutralisation by carbonates and silicates (in saturated or unsaturated lake soils and sediments), re-precipitation of sulfides (in saturated lake soils and sediments), transport of residual acidity into the lake waters and subsequent neutralisation and re-precipitation processes.

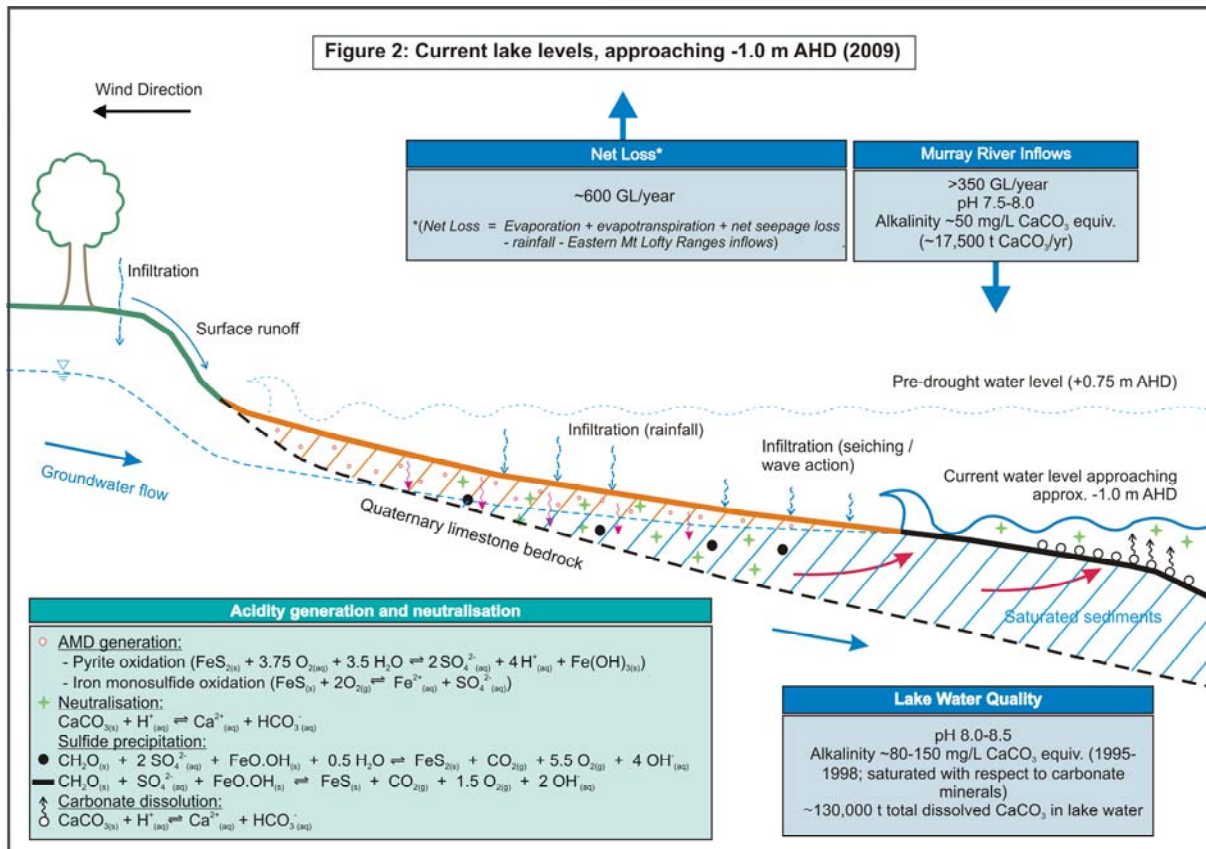


Figure 2. Current lake water levels, approaching -1.0 metres AHD (March 2009).

### Acid Sulfate Soils in the Coorong

The Coorong, situated downstream of the barrages, is currently influenced by seawater inflows. Water levels in the Coorong are therefore higher than those in the lower Murray lakes (upstream of the barrages).

The processes of acid sulfate soils formation that are occurring in the lower Murray lakes are likely to be also occurring in the sediments of the Coorong. As long as water levels remain high enough in the Coorong to keep acid sulfate soils saturated, acidity generation is not expected to be an issue.

The accelerated accumulation of sulfidic sediments and odour issues associated with sulfate reduction to H<sub>2</sub>S may become an issue in the Coorong.

## General management approaches for acid sulfate soils in the lower Murray lakes

General acid sulfate soils management approaches for the lakes can be broadly categorised as follows:

1. Prevent further acidity generation by managing lake water levels to ensure that acid sulfate soils are permanently submerged, or at least saturated, and sulfide oxidation is therefore avoided or minimised.
2. Optimise and maintain conditions for natural bioremediation processes (addition of organic matter and/or iron to acid sulfate soils).
3. Control or treat acidity via neutralisation (addition of alkaline amendment to acid sulfate soils).

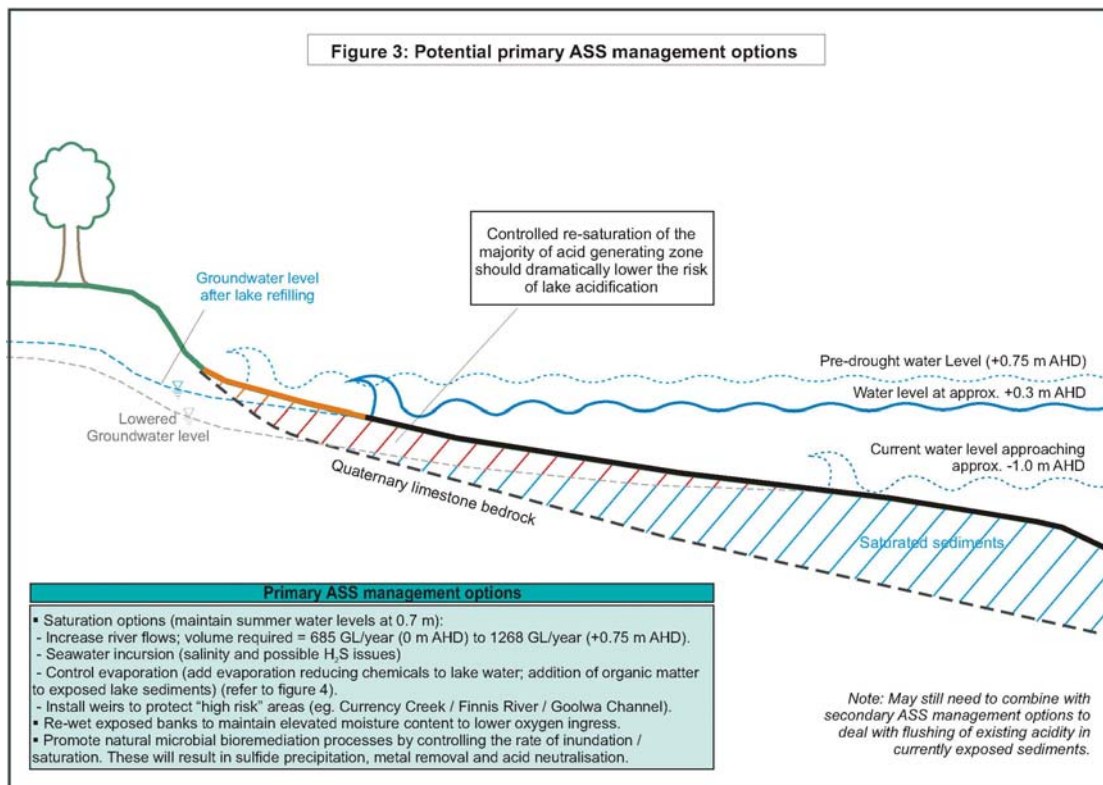
### Management options for preventing further acidity generation

Options for preventing further acidity generation by inundation or saturation of acid sulfate soils in the lakes (the first approach listed above and summarised in Figure 3) include:

- increasing river inflows to the lake system
- controlling evaporation (e.g. by adding evaporation reducing chemicals to lake water or adding mulch to the exposed lake soils and sediments)
- installing weirs or terraces at suitable locations to maintain saturation in higher risk areas (e.g. Currency Creek, Finniss River and Goolwa Channel)
- installing perforated pipe systems or surface irrigation systems along the lake shorelines to maintain saturated conditions in the shoreline soils and sediments using lake water or groundwater
- opening the barrages to allow seawater incursion to the lake(s).

For all of these options, permanent submergence of sulfidic materials would be required to prevent further acidity generation in the long term.

In addition, the rate of inundation or saturation would need to be controlled to ensure that flushing of existing acidity in currently exposed acid sulfate soils is minimised, and optimum conditions are provided for natural remediation of acidic soils and sediments (*in situ* neutralisation and sulfide re-precipitation processes).



*Figure 3. Primary acid sulfate soils management options – raise water levels to +0.3 metres to 0.7 metres AHD to saturate acid sulfate soils.*

### Management options for optimising bioremediation (microbial remediation)

Bioremediation options are those which utilise the natural process of sulfide reduction via sulfate-reducing bacteria (see Figure 4, potential secondary ASS management options).

If the availability of organic carbon and/or iron is found to be limiting the efficiency of natural sulfate reducing bacterial processes within the lake waters, the following bioremediation options could be considered:

- direct addition of organic matter and/or iron to the lake water bodies
- addition of organic matter and/or iron to the lake water bodies via inflowing tributaries
- addition of organic matter and/or iron to the lake water bodies via the shoreline soils and sediments.

Types of organic matter that may be suitable for application to the lower Murray lakes include: straw/hay, reed cuttings, timber waste/wood-chips, clean mulch, clean compost, fish waste, seaweed, recycled paper pulp or jute matting.

Another option to optimise bioremediation is to monitor and promote natural regeneration (succession) and revegetation so long as these processes do not cause further acidification to occur, such as through evapotranspiration by deep rooted plants or the establishment of oxidation pathways from densely rooted plants.

A combination of these sources, depending on their suitability in different regions, could ensure sufficient organic carbon is available along the lake shoreline and in bed soils and sediments to maximise sulfide re-precipitation.



### **Revegetation versus bioremediation**

It is important to distinguish between the terms 'bioremediation' and 'revegetation' in the context of acid sulfate soil management in the lower Murray lakes.

Bioremediation refers to management approaches that aim to promote microbial activity (sulfate-reducing bacterial activity) in order to convert dissolved sulfate to sulfide minerals, while consuming acid. This essentially reverses the pyrite/iron monosulfide oxidation reactions that generated acidity in the first place.

A common misconception is that revegetation is the same as bioremediation. Revegetation of exposed shoreline soils and sediments has the potential to assist in the process of bioremediation, but may also exacerbate acidity generation by lowering groundwater levels and exposing further acid sulfate soils to atmospheric oxygen.

If available iron is found to be a key factor limiting sulfide precipitation, addition of iron oxide ( $\text{Fe}_2\text{O}_3$ ) may also be required.

### **Management options for controlling or treating acidity by neutralisation**

Neutralisation options (see Figure 4) are those which enhance the natural alkalinity of the lake system via active or passive alkalinity addition methods. These may include:

- limestone addition to the lake water bodies via the shoreline soils and sediments
- limestone addition to the lake water bodies via inflowing tributaries
- direct limestone addition to the lake water bodies.

The key objective of neutralisation using limestone would be to distribute stored alkalinity, as evenly and rapidly as possible, across the lakes. This approach could be equally effective as a "passive" (pre-emptive) treatment option or an "active" (emergency response) treatment option depending on water quality monitoring results and whether agreed trigger levels (pH, alkalinity) were reached. Either way, ultra fine-grained limestone would optimally dissolve into the water column (if the water is not already saturated with  $\text{CaCO}_3$ ) in response to acidity generation from exposed shoreline soils and sediments and subsequent influx to the lakes.

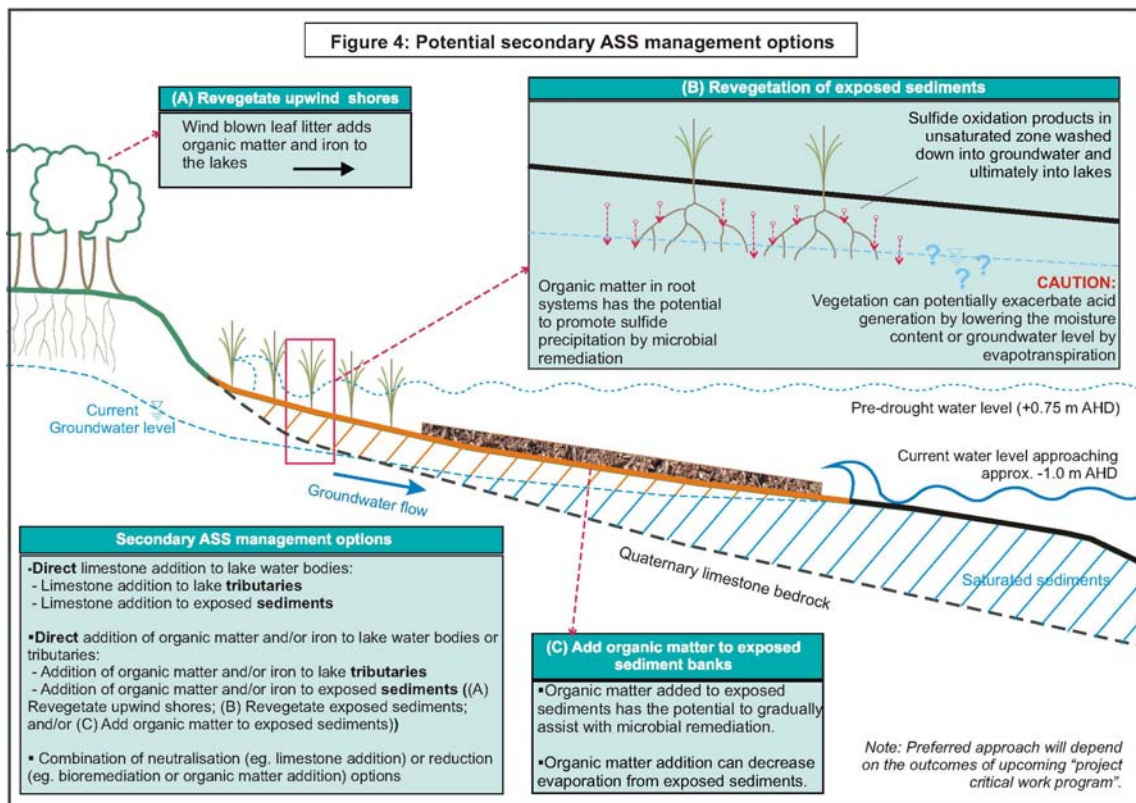


Figure 4. Secondary acid sulfate soils management options – bioremediation or neutralisation.

## How the South Australian Government is addressing the issue of ASS in the lower Murray lakes

The South Australian Government is developing a detailed work program for acid sulfate soils management in the lower Murray lakes. The immediate priority of the government is to address areas containing higher risk acid sulfate soils, including Currency Creek, Finniss River and the Goolwa Channel. A multi-faceted approach to acid sulfate soils management strategy has been developed for these areas for implementation over the next few months.

### Goolwa Channel, Currency Creek and Finniss River management strategy

This strategy comprises several stages, with the last few stages being subject to predetermined water quality and water level or soil moisture triggers. The approach is described in Table 1. A detailed monitoring program will be developed to guide the implementation of the staged management strategy shown in Table 1.

Table 1. Proposed strategy for acid sulfate soils management in the Goolwa Channel Currency Creek and Finniss River.

Stage	Description
1	Promote carbonate saturation by strategic placement of ultra fine grained limestone in the creek bed of Currency Creek (and possibly the Finniss River) to provide pre-emptive alkalinity addition as stream flows commence.
2	<p>Ensure highest risk ASS are kept saturated (not necessarily inundated) by installing one or more weirs or blocking banks to control water levels at key locations. The objective of the weirs would be two-fold:</p> <ul style="list-style-type: none"> <li>to permit controlled saturation of soils and sediments to minimise sulfide oxidation</li> <li>to control downstream flow during rainfall events to minimise flushing and to optimise water retention so as to assist with natural, in-situ bioremediation within the water bodies.</li> </ul> <p>Instigate daily monitoring when significant stream flows commence, in preparation for Stage 3 if alkalinity decreases to below accepted levels.</p>

Stage	Description
3	Ensure carbonate saturation is achieved and maintained within the water bodies by direct application of limestone slurry to multiple locations in the Goolwa Channel, Finniss River and Currency Creek, if necessary, and water quality monitoring.
4	Ensure carbonate saturation is maintained within the water bodies in the longer term by fixed point dosing of limestone slurry and water quality monitoring in Currency Creek and the Finniss River. This approach would utilise wet season flows in these tributaries to transport ultra fine grained limestone into each stream and ultimately to the Goolwa Channel.
5	Increase organic matter via appropriate mulching and revegetation to assist with bioremediation on saturation.
6	Apply limestone slurry to exposed sediment banks to minimise acidity release to the water bodies associated with rainfall events and/or raised water levels.

### ***Broader lower Murray lakes management strategy***

In addition to addressing the short-term ASS risks in the Goolwa Channel, Currency Creek and Finniss River, the broader work program for the lower Murray lakes will most likely include:

- Continuing routine water quality monitoring throughout the lower Murray lakes, with a particular focus on key indicators such as pH, alkalinity, sulfate and salinity.
- Further characterisation of lake shoreline and bed soils and sediments to better quantify ASS risks throughout the lower Murray lakes and determine whether alkalinity, organic carbon and/or iron (in the shoreline and/or lake bed soils and sediments) are likely to be limiting factors in natural bioremediation - this will inform the selection of effective long-term acid sulfate soils management strategies.
- Investigation of local and regional groundwater influences on the water balance of the lower Murray lakes, and the implications of groundwater flows for acidity generation and management.
- Refinement of current estimates of the total amount of acidity that could potentially be generated in the lake soils and sediments, the rate at which this acidity is likely to be generated, and the degree to which natural remediation processes in the lake shoreline and bed soils and sediments may limit impacts on lake water quality.
- Establishment of field trials to quantify the potential decrease in acidity loads to the lakes associated with selected management options, to determine which options are likely to be most effective for large scale implementation (if required).
- Ongoing assessment of the relative merits of each of the management options available for long term ASS management in the lower Murray lakes, as critical data become available.

Several of these activities will occur over the next 12 months to more specifically quantify acid sulfate soils processes and management responses.

## **What the community can do and how the government will facilitate this**

The South Australian Government is working with the community to establish and implement adaptation, rehabilitation and recovery strategies for the lower Murray lakes and Coorong.

Projects identified during community consultation include:

- Ecological protection, rehabilitation and remediation works (e.g. fencing, revegetation, protection of critical plants and animals, weed and feral animal control).
- Supporting community action networks (e.g. knowledge sharing, environmental education, community participation).
- Rehabilitating, adapting and developing community infrastructure (e.g. adapting public places to the changing environment, developing environmental infrastructure and interpretation opportunities).
- Aboriginal cultural heritage and reconciliation of land and water management (e.g. restoring and protecting cultural sites, sharing of response and recover experiences).

Specific projects are currently being identified with a view to encourage robust partnerships for best-practice management of the region both now and into the future.

### **Further information**

Coorong, Lower Lakes and Murray Mouth Projects Team

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