Monosulfidic Black Ooze (MBO) formation, cycling and management in the Coorong

Luke Mosley, Juraj Farkas, Yuexiao Shao, Rob Fitzpatrick

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The Goyder Institute for Water Research is the delivery partner for research components of *Healthy Coorong, Healthy Basin*, providing independent research to inform future management decisions for the region.

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1. What is MBO?

Monosulfidic black oozes (MBOs) are a form of soil/sediment type typically found in waterways when specific environmental conditions exist. They are black gel-like materials (see Fig. 1) that are enriched in monosulfides, predominantly iron monosulfide (FeS), but also other compounds including hydrogen sulfide (H_2S). They are typically found in wet anoxic (oxygen-poor subaqueous) acid sulfate soils (ASS) and other sediments (Sullivan et al. 2018). The criteria used in Australia to define a soil or sediment as an MBO is based on the Australian Soil Classification (Isbell and National Committee on Soils & Terrain 2021) which defines monosulfidic material as that containing high concentrations of detectable monosulfides ($\geqslant$ 0.01% acid volatile sulfide, AVS) (Sullivan et al. 2018). MBOs are also typically high in organic matter (i.e. often greater than 10% organic carbon) and can form thick (> 0.5-1 m) accumulations in waterways (Sullivan and Bush 2002; Bush et al. 2004a; Isbell and National Committee on Soils & Terrain 2021). While MBOs occur in both natural and modified waterways, conditions are often more conducive for formation in modified systems as discussed further below.

Figure 1: Photographs of Coorong monosulfidic black oozes (MBOs) sampled from subaqueous soil profiles in shallow water near Parnka Point (top left photo) and Pelican Point (top right photo) and a core from a deeper basin near Woods Well in the South Lagoon (bottom photo). At Parnka Point, the thin black MBO layer occurs at the surface and abruptly overlies a calcareous clay with abundant shell fragments. At Pelican Point the thick black MBO layer (> 20 cm) abruptly overlies a thin (< 5 cm) brownish algal gel (< 5 cm). In the deeper South Lagoon basin core, a thick (> 10 cm) MBO layer overlies a grey sandy sediment.

2. How are MBOs formed?

Algae (e.g. filamentous algae, phytoplankton) and cyanobacterial/algal mats contain proportionally high levels of organic carbon (~50%), nitrogen and phosphorus. When the algae die, bacteria use oxygen to decompose the organic carbon to form carbon dioxide (CO_2), gaining energy through this process. Monosulfidic black ooze (MBO) or monosulfidic material forms under anoxic conditions, where oxygen is unavailable for aerobic bacteria to breakdown organic matter (e.g. in sediments and/or interior of algal mats). Under suitable anoxic conditions, sulfate reducing bacteria readily convert dissolved sulfate (SO_4^{2-}) in the seawater and/or sediment pore water to hydrogen sulfide (H_2S). H_2S is volatile as a foul-smelling gas, often referred to as 'rotten egg gas', which is released when MBOs are disturbed. Dissolved sulfide (H_2S and HS^-) ions sourced from sulfate reduction can react with dissolved ferrous iron (Fe^{2+}) under anoxic conditions (produced via iron oxide (Fe^{III}) reducing bacteria) to form iron monosulfide (FeS) precipitates, and eventually also iron disulfide (FeS_2, pyrite) minerals. These materials typically have a black colour (Fig. 1). The FeS is the 'active ingredient' in MBO or monosulfidic material and is estimated by laboratory measurement of AVS (Sullivan et al. 2018), as a direct measurement of FeS concentration is difficult (Rickard and Morse 2005; Isbell and National Committee on Soils & Terrain 2021).

According to the national guidelines (Sullivan et al. 2018), MBO forming conditions in Australia typically occur in the bottom sediments of poorly circulated and oxygen-depleted waterways affected also by increased salinity and nutrient loads. These conditions are more common in human-impacted coastal zones and areas influenced by seawater intrusion such as tidally affected estuaries, and also saline inland waterways. The association of MBO formation with increased salinity and/or seawater influence is due to the co-occurrence of sulfate, which is one of the main anions comprising the salinity in oceanic or saline ground water, and is utilised by the sulfate reducing bacteria as described above. The formation and accumulation of MBOs is also common in acid sulfate soil affected areas and can build up to form thick layers in relatively enclosed or stagnant waterbodies such as drains and waterways behind floodgates and barrages and semi-enclosed coastal lagoons (Bush et al. 2004a).

3. How much MBO is in the Coorong system?

Due to its current reduced flushing (i.e. due to reduced frequency of flood inputs and channel restrictions), high organic matter (i.e. due to eutrophic/algal-enriched state), and plentiful dissolved sulfate (sourced from seawater and magnified via evapo-concentration) content, the Coorong Lagoon is well suited for *in-situ* MBO production (Fitzpatrick et al. 2018;, Sullivan et al. 2018). Historical observations indicate black mud/ooze was observed in some parts of the Coorong in the 1950-1960s (Delroy 1966), and may have been present earlier. A wide range of acid sulfate soils with MBOs were first formally identified in 2008 in 7 out 10 soil profiles sampled in the Northern and Southern Coorong by Fitzpatrick et al. (2008).

MBOs have since been identified to be present across very large areas of the Coorong system, throughout both the North and South lagoons, particularly in the deeper basin areas and around Parnka Point (see Fig. 2). During sediment quality surveys undertaken in 2020-2021 as part of the *Healthy Coorong, Healthy Basin* Program, 18 out of 26 (69%) of the surface (0-5 cm) sediment core samples taken along the Coorong (were classified as MBOs based on AVS concentrations greater than the national guideline value of 0.01% (on a dry sediment weight basis). The average (± standard deviation) AVS concentration in Coorong sediment samples classified as MBOs was 0.046 ± 0.020 % (n = 18), which is over four times greater than the national guideline level. The exception to this general MBO distribution is when sediment salinity was comparatively low (i.e., dominated by freshwater) such as near the Murray Mouth or Salt Creek (salinity of < 10 dS/m, Fig. 3), likely because both sulfate and organic matter contents are lower in freshwater and flushing is higher at these locations.

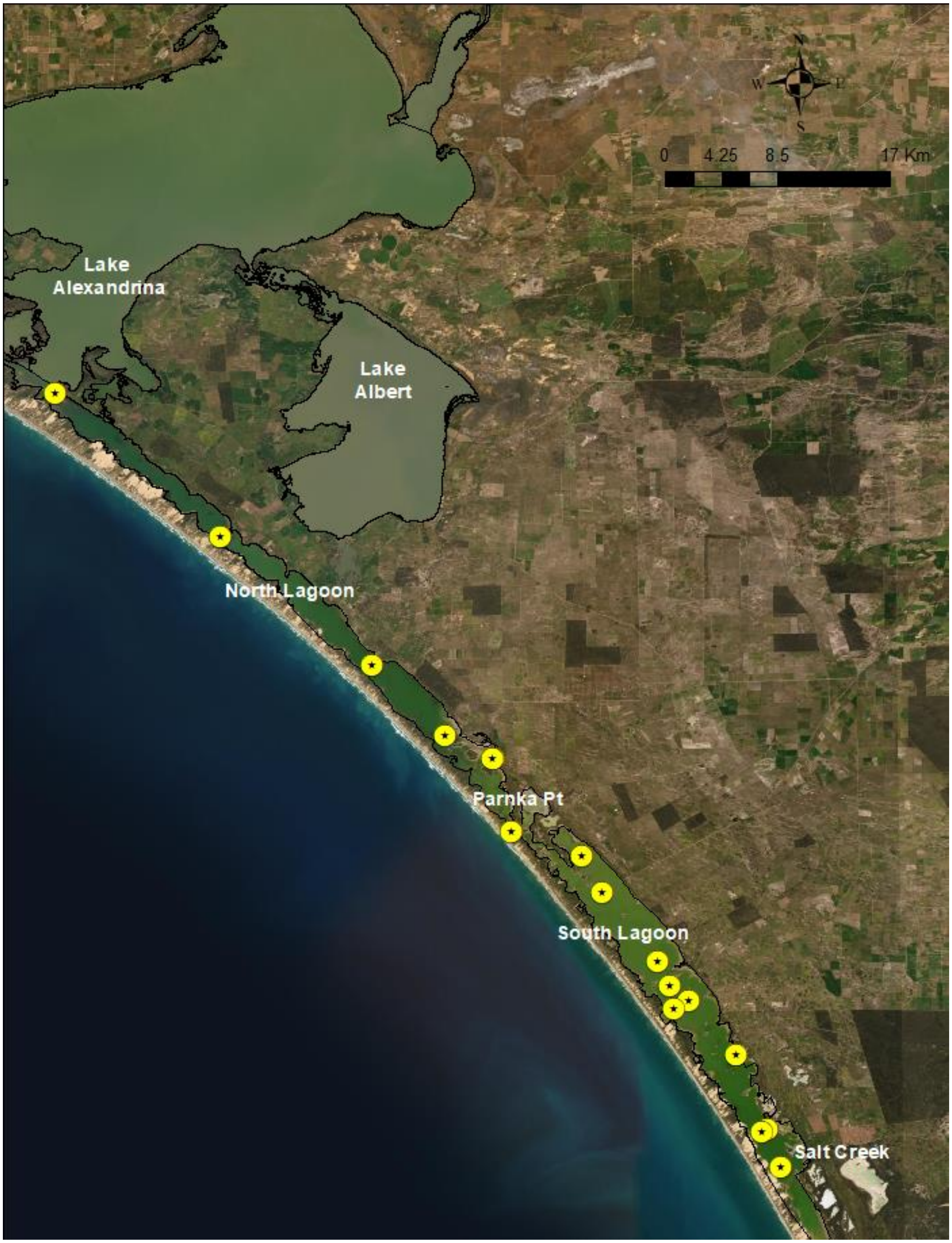

Figure 2: Locations (yellow symbols) where MBO (as defined by AVS > 0.01% dry weight as per the national guidelines, Sullivan et al 2018) was detected in the Coorong during 2020-2021 sediment quality surveys as part of the *Healthy Coorong, Healthy Basin* program.

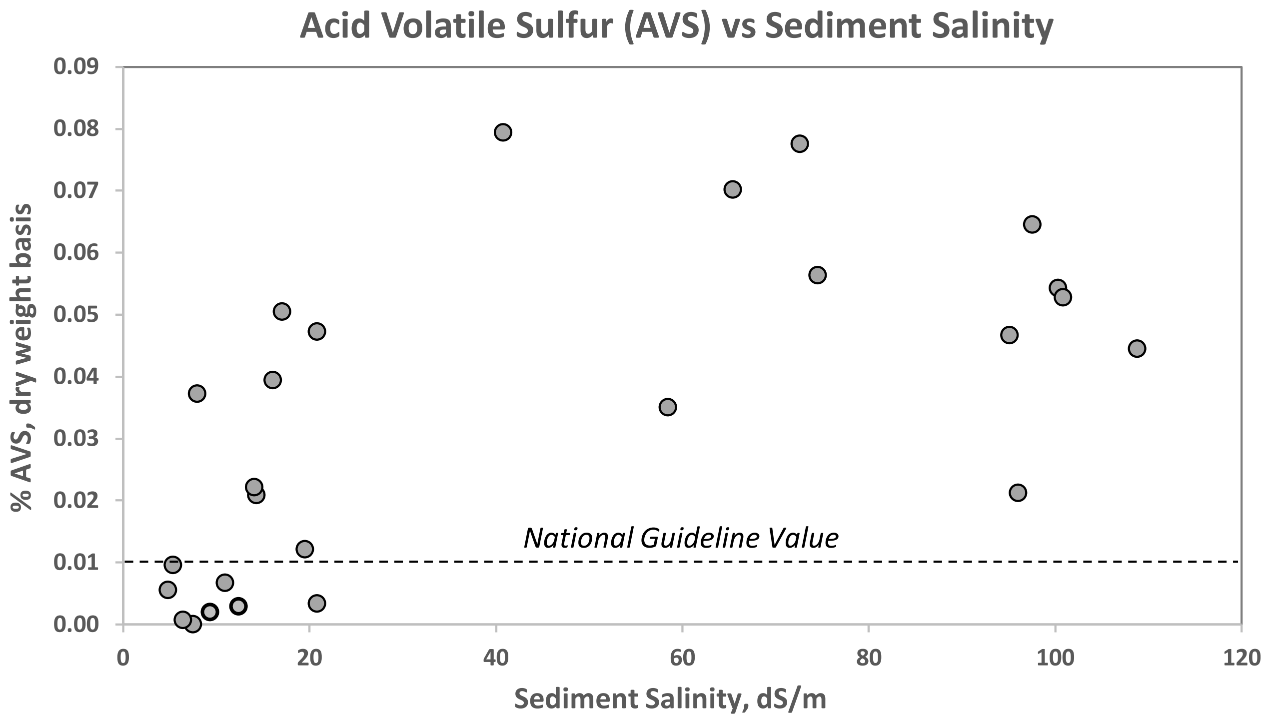

Figure 3: Acid Volatile Sulfur (AVS) content (%) versus sediment salinity (dS/m in a 1:5 sediment:water extract) in 26 surface (0-5 cm) core samples along the Coorong. The national guideline value (0.01% AVS), above which samples are classified as MBOs, is shown.

4. Why are MBOs a problem in the Coorong?

When monosulfidic black oozes (MBO) form, the sediment becomes less habitable for aquatic plants and macroinvertebrates due to the highly reducing conditions and elevated levels of hydrogen sulfide. The high sulfide concentrations can intrude into the roots of aquatic plants, reducing plant growth rates and contributing to die-off events. Low dissolved oxygen and high hydrogen sulfide levels also are also exacerbated by lack of bioturbating (i.e. organisms that burrow, mix and turn over sediment) benthic (bottom-dwelling) macroinvertebrates present in the South Lagoon of the Coorong, such as bivalves, gastropods and crustaceans (Lam-Gordillo et al. 2022a).

The formation of MBOs from dissolved sulfate in the water via diagenetic or post-depositional processes can lead to increased sediment build up in channels and deeper areas. However due to their high organic content, MBOs are also low density and readily resuspended by wind and wave action. This can further deoxygenate the water column as MBOs are reactive with dissolved oxygen and other compounds (Bush et al. 2004a,b). Such negative impacts of MBOs have potential to be greater in shallower and/or isolated areas of the Coorong lagoon with poor circulation (e.g. around Parnka Point to the Narrows region). While MBO resuspension is readily observed on windy days in the Southern Coorong, monitoring data shows there is no clear evidence of this causing actual deoxygenation due to effect of wind or sediment disturbance, and in general the main lagoon water in the Coorong appears to remain relatively well oxygenated via regular wind mixing of local water masses (Priestley et al. 2022a).

5. How can we reduce build-up of MBOs in the Coorong?

The *Healthy Coorong, Healthy Basin* Program is investigating the ways in which the high amount of MBOs in the Coorong can be reduced to restore a desired healthier state. According to the national guidelines (Sullivan et al. 2018), the accumulation of MBOs in waterways can be minimised by following one or more of four potential management strategies:

1) Maintain erosive flow rates (floodgate control, channel design).
2) Minimise organic matter accumulation.
3) Maintain regular wetting and drying cycles (in managed waterways and wetlands).
4) Minimise and limit the sources and inputs of sulfate.

Strategies 1 'maintain erosive flow rates' and 2 'minimise organic matter accumulation' are the main options that have the highest chance of success at a system level in the Coorong as outlined below.

Maintaining erosive flow rates
Improved inflows and flushing of the Coorong lagoons would be beneficial to create conditions where the nutrients and organic matter that form MBOs are exported to the coastal ocean. Project Coorong is investigating various management options to improve dilution, export, flushing and/or connectivity throughout the system.

Minimising organic matter accumulation in the sediment
MBOs are extensive and can form deep in to the sediment profiles of the southern Coorong due to the lagoons persistent hyper-eutrophic state. Lack of flushing has led to very high organic carbon and nutrient accumulation in the water column (Mosley et al. 2020), which has been deposited to the sediment (Priestley et al. 2022b). This has led to ongoing and excessive deposition of organic matter to sediments. This, coupled with very high salinity, which impairs the breakdown of organic matter, has created highly anoxic conditions and provided the 'fuel' for sulfate reducing bacteria to produce MBOs. Short and long term goals for the Coorong should aim to reduce the amount of organic matter being deposited to- and residing within sediments. Increasing flushing of the system and inter-lagoon connectivity are potentially feasible options to achieve this.

Maintaining regular wetting and drying cycles
Regular wetting and drying cycles can be applied in some locations to get atmospheric oxygen into the sediment, oxidizing the MBOs. However this strategy is not readily achievable at a system scale in the Coorong, sediment in deeper basins would likely stay wet as the lagoons are connected to the sea level, and drying could create severe ecological harm (e.g. due to drying, acidification, extreme hypersalinity) in this Ramsar-listed wetland. However, some consideration could be given to this strategy for smaller areas on the margins.

There are however ecosystem restoration strategies that could reduce MBOs in the Coorong via promoting oxygen transport into the sediment. Restoration of aquatic plants and the recolonisation of sediments by macroinvertebrates creates oxygen-rich zones in the sediment. Most burrowing and filter feeding macroinvertebrates require salinities below 60 g/L (approximately 1.7 times seawater salinity), which is often exceeded in the Southern Coorong at present (Lam-Gordillo et al. 2022a). *Ruppia* roots also oxygenate the sediment, but aquatic plant health and distribution is impacted by persistently high salinity (>70 g/L) and poor water quality that reduces light penetration (Dick et al. 2011). Improving connectivity and flushing will reduce salinity and improve overall water quality (i.e. reduce total nutrients, carbon and phytoplankton levels in the water – see Mosley et al. 2020)> Lower salinity will enable the benthic ecosystem (i.e. bioturbating macroinvertebrates) to reduce MBO and nutrient levels in the sediment (Lam-Gordillo et al. 2022b). Increasing oxygenation of sediment and reducing salinity will enhance nitrification-denitrification processes that can remove nitrogen (in gaseous form) from the system (Huang et al. 2022).

Minimisation of sources of sulfate
Minimising sulfate inputs is not a viable option for reducing MBOs in a system influenced by seawater and evapo-concentration, such as the Coorong, where there is plentiful sulfate. Nevertheless, enhancing freshwater inputs could help reduce MBOs in the lower salinity and well-flushed areas nearer the inflows (e.g. as per Fig. 3).

How could increasing seawater exchange influence MBOs?

Project Coorong is currently investigating options to improve flushing and export of organic matter, algae and nutrients from the Coorong.

It is useful to also examine how water chemistry may change and influence MBO formation during potential changed flushing and water import-export scenarios. This requires more detailed examination of the chemical reactions driving MBO formation and its relationship with carbonate cycles. The sulfate reduction reaction can be facilitated in various forms and bio-geochemical pathways. Turchyn et al. (2021) formulated the following equation for consumption of organic carbon (represented below as: $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$) via sulfate reducing bacteria to produce H_2S and bicarbonate (HCO_3^-) alkalinity:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} + 14CO_2 + 14H_2O \rightarrow 53H_2S + 120HCO_3^- + 16NH_4^+ + HPO_4^{2-} \quad \text{(Eq. 1)}$$

Dissolved ferrous iron (Fe^{2+}) in anoxic sediment pore water can react with the H_2S produced by sulfate reducing bacteria (Eq. 1) to form FeS, the 'active ingredient' in MBOs:

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \quad \text{(Eq. 2)}$$

In anaerobic sediments, Fe^{2+} can also react with carbonate ions (Jensen et al. 2002, Burton et al. 2006) to form the solid phase iron carbonate mineral – i.e. early diagenetic siderite ($FeCO_3$):

$$Fe^{2+} + CO_3^- \rightarrow FeCO_3 \quad \text{(Eq. 3)}$$

The generation of bicarbonate alkalinity via sulfate reduction (Eq. 1) can also lead to a reaction with dissolved calcium (Ca^{2+}) and the precipitation of calcium carbonate *in situ* within the sediments (Turchn et al. 2021):

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \quad \text{(Eq. 4)}$$

These reactions will largely govern how MBO will respond chemically to a hypothetical increase in seawater inputs into the Coorong. Firstly, it can be seen in Eq. 1 that reducing organic carbon availability on the left hand side will reduce formation of H_2S, and thus also subsequent FeS/MBO formation (via Eq. 2). Hence any infrastructure or other strategies to improve flushing have the potential to reduce organic matter availability and this key driver of MBO formation.

The formation of diagenetic siderite ($FeCO_3$, Eq. 3) is also potentially beneficial to prevent FeS formation, as it involves reaction with Fe^{2+} which is then not available to form FeS (via Eq. 2). It is noted however this mineral has not yet been formally identified in the Coorong sediments. In addition, enhanced seawater exchange with the Coorong Lagoon waters will supply abundant dissolved carbonate ions into the lagoon system. Related to that, the calcium carbonate ($CaCO_3$, calcite or aragonite) saturation state is also high, even in typical seawater (Saturation Index > 0), and particularly high in the South Lagoon (Saturation Index ~0.5-1.0, Shao 2021). This means that the dissolved carbonate concentration in lagoon waters is controlled by equilibrium (i.e., dissolution vs precipitation) with solid $CaCO_3$ minerals (Eq. 4). Indeed, carbonate precipitates (mostly aragonite) have been identified in surface sediments in the Coorong South Lagoon (Shao et al., 2018), and an active precipitation of $CaCO_3$ is also supported by elevated stable Sr isotope ratios ($\delta^{88/86}$Sr) in the South Lagoon water (Shao et al. 2018, Shao 2021), primarily controlled by salinity, followed by supply of alkalinity. Carbonate supersaturation and calcium carbonate mineral production has been observed in the Coorong for many decades (Delroy 1966), and is likely a natural feature of the South Lagoon.

Will increasing calcium carbonate saturation via a low-volume passive seawater input (with minimal flushing) effectively reduce MBOs in the Coorong?

A higher direct input of seawater is unlikely to change the calcium carbonate supersaturation state of the South Lagoon, and similarly pumping out of water to the coastal ocean (one of multiple management options being considered) is also unlikely to do this. As noted above, seawater is saturated with calcium carbonate in the local coastal waters. Hence, increased input of seawater is not expected to create undersaturation of waters or sediment with respect to calcium carbonate ($CaCO_3$) or siderite ($FeCO_3$) minerals, or influence availability of Fe^{2+} to form FeS/MBOs. Given the current supersaturated state with respect to $CaCO_3$ in both the Coorong and ocean water, with levels of dissolved carbonate ions, only a very high input of freshwater (i.e. sufficient to lower salinity below seawater levels, and create carbonate mineral undersaturation) would decrease local calcium carbonate mineral production in the Coorong Lagoons. However, there are large reservoirs of carbonate minerals in the sediment that likely buffer any changes in the calcium carbonate saturation state of the water, which appears consistent with contemporary observations (Shao 2021). Carbonate production facilitated via sulfate reducing bacteria activity (Eq. 1) will also continue, particularly in the deeper sediment layers.

Pathways to reduce MBOs via increased lagoonal flushing

Enhanced lagoonal flushing, via increased seawater exchange or facilitated export of South Lagoon water to the ocean would decrease organic matter availability for sulfate reducing bacteria (Eq. 1) and has the potential to reduce MBOs. This is via enabling more oxic sediment conditions with low Fe^{2+} that are not conducive for MBO formation, and that could lead to dissolution of the current MBO build up. Specifically, reducing organic matter deposition to a sediment (e.g. via reduced nutrient loading and eutrophication, or increased flushing) reduces the likelihood of anoxic sediment conditions that promote high Fe^{2+} availability. Anoxia leads to both a lack of Fe oxide formation in the top sediment, and results in high Fe^{2+} and thus high FeS and siderite formation, the latter at the expense of a more stable mineral pyrite (FeS_2, Burton et al. 2006). Restoring ecological functions provided by burrowing macroinvertebrates to the Southern Coorong by lowering average salinity (to <60 g/L) will lead to increased sediment oxygenation and reduction in sulfide levels (Lam-Gordillo et al. 2022a,b). Similarly, enhancing *Ruppia* health and distribution will reduce sulfides and MBO (i.e. via root oxygen transfer). A conceptual model of how the current MBO accumulation can be reduced, linked to key biogeochemical processes described earlier, is shown in Fig. 4.

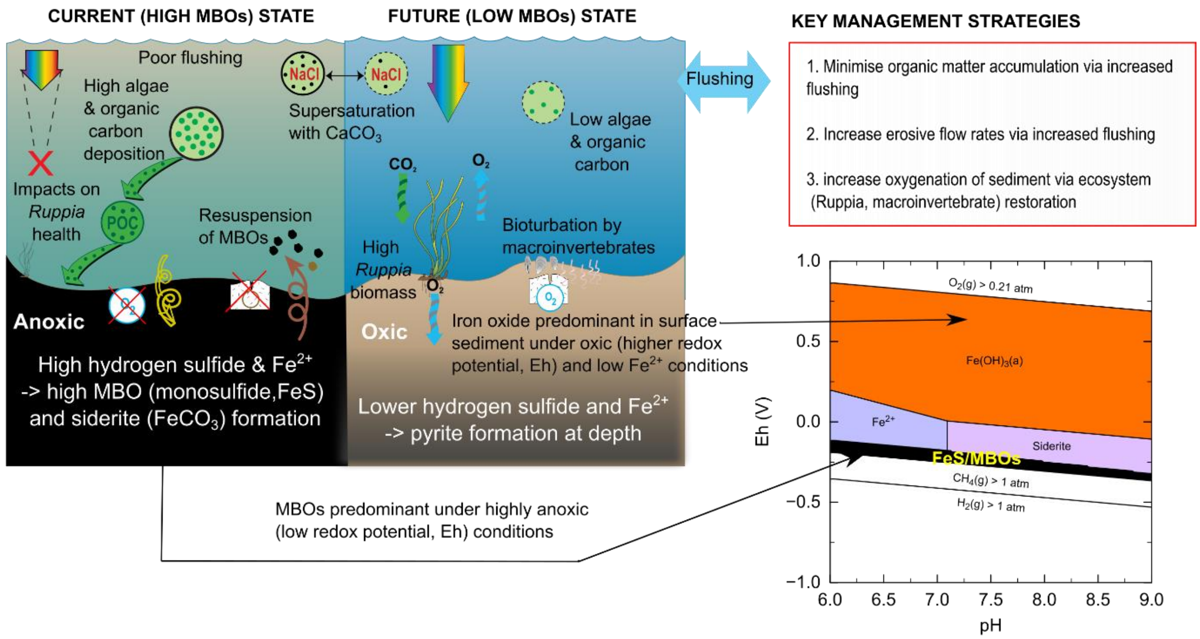

Figure 4: Conceptual model of current MBO issue in the Coorong and management strategies that can address this based on the principles in the national guidelines (Sullivan et al. 2018). A redox potential-pH diagram is shown to illustrate the current predominance of iron and sulfur in FeS/MBO form and desired future change for surface sediment to have iron oxide [$Fe(OH)_3$] predominantly present.

Conclusion

Monosulfidic black oozes (MBOs) are predominant over large areas of both the South and North lagoons of the Coorong. Their formation in the Coorong is mostly driven by algal organic matter deposition to the sediment providing the ‘fuel’ for sulfate reducing bacteria. Minimising organic matter accumulation and maintaining erosive flow rates are the key MBO management options that have the highest chance of success at a Coorong system level via implementing management options that increase lagoon flushing and connectivity. Enabling bioturbating macroinvertebrate recolonisation in the South Lagoon (requires salinity < 60 g/L) would also be beneficial and complementary to reduce MBO formation (i.e. via these organisms introducing oxygen to the sediments which reacts and breaks down the sulfide-rich materials). Enhancing *Ruppia* distribution and health will also result in more sediment oxygenation. Due to the predominance of carbonate saturation in coastal seawater, Coorong water and sediments, options to increase outflow and/or inflow of seawater are unlikely to result in major changes to the carbonate system or any iron-carbonate phases in the sediment.

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Acronymns

Acronym	**Description**
AVS	Acid Volatile Sulfur, a laboratory analytical technique that is used to classify a sediment as an MBO
$FeCO_3$	Iron carbonate (Siderite) mineral phase
H_2S	Hydrogen sulfide, present in dissolved form but also volatile as a 'rotten egg' smelling gas
MBO	Monsulfidic black ooze