# Marine disposal of monosulfide from a eutrophic estuary system and the impact on water chemistry

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## Abstract

The sediments of the Peel Harvey Estuary system (PHES) contain accumulations of monosulfidic black ooze (MBO) related to hypereutrophication and discharge from active acid sulfate soils. MBOs may release acidity and contaminants (nutrients, trace metals) when disturbed. We investigated release of acidity during resuspension of MBOs in a laboratory study and during a dredging event in the estuary. Selected samples from the laboratory study were analysed using XANES. In the laboratory study, decreases in pH (approx. 1 pH unit) of MBO suspensions coincided with the re-establishment of oxidizing conditions. Sediment analyses illustrated near-complete oxidation of acid-volatile sulfide (AVS, a proxy for monosulfide). The XANES data supported the chemical AVS analysis, showing the disappearance of peaks corresponding to mackinawite and greigite and appearance of the sulfate peak, consistent with AVS oxidation products. Pyrite and organic S peaks showing minimal changes throughout the resuspension. The data for estuary water quality from dredge monitoring showed consistent transient decreases in $E_h$ at the point of sediment disposal, but pH remained well-buffered. The decreases in $E_h$ were associated with increases in concentrations of ammonium and orthophosphate, with high variability. Laboratory experiments demonstrate the high reactivity of MBOs from the PHES following disturbance, but high variability and buffering in the field may limit the observation of these effects.

## Key Words

Sulfide, sediment, oxidation, pH, redox, resuspension.

## Introduction

Eutrophic estuary systems often contain an abundance of the acid sulfate material "monosulfidic black ooze" (MBO), which is an organic sludge enriched with highly reactive iron-monosulfide. MBO is a natural product formed during bacterially mediated sulfate reduction, and when undisturbed it is recognised as playing an important role in improving water quality by storing acidity and sequestering metals (Macdonald *et al.* 2004; Smith 2004; Smith and Melville 2004). However, contaminant stores in MBOs are temporary and can be released into the water column upon disturbance and oxidation (Smith 2004; Burton *et al.* 2006; Burton *et al.* 2009). Consequently, an understanding of chemical changes during MBO oxidation is critical to effectively manage water quality impacts during their disturbance and disposal. This is particularly important when such systems are subject to disturbance by development and recreation. The Peel Harvey Estuary system (PHES), located 70 km south of Perth in Western Australia has accumulated unusually large amounts of MBO related to contributions from hypereutrophication and active acid sulfate soils in it catchment. The Peel-Harvey MBO also have anomalously high acid-volatile sulfide (AVS, a proxy for monosulfide) contents; four 30 cm cores taken from the South Yunderup boating channel on the North-East of the estuary had AVS concentrations ranging from 33 to 335 µmol/g, with an average of AVS of 209 µmol/g. This study investigates a laboratory resuspension of sediment collected from the South Yunderup channel, and the water chemistry during a dredging event in 2008.

## Methods

### *Laboratory resuspension*

Three cores between 0-20 cm were collected from the South Yunderup boating channel in the PHES and homogenised in the laboratory under a stream of nitrogen gas. Three sediment to water ratios (50 g/L, 100 g/L and 200 g/L) and one control treatment (nil sediment addition) were resuspended in the laboratory with estuary water for two weeks, with humidified compressed air being continuously bubbled through the suspensions. Samples were collected immediately prior to MBO addition (0 hours) and at 0.33, 0.66, 1, 2, 3, 4, 24, 48, 72, 96, 168 and 336 hours and analysed for pH, $E_h$, alkalinity, ferrous iron, dissolved sulfide, orthophosphate, ammonium and dissolved metals. Sediment was analysed for AVS, CRS, elemental S and total extracted metals (Burton *et al.* 2009). Sulfur speciation at 0, 24 and 72 hrs was also investigated using K-edge X-ray absorption spectroscopy (XANES) using the Taiwan Synchrotron. Only the pH, $E_h$, and XANES data will be presented in this paper.

*Field dredge event*

The South Yunderup approach channel was dredged and the sediment disposed of in a submerged area of the estuary in 2008. Five water monitoring events were conducted between July 2008 and September 2008 to investigate the impact of the large scale MBO disturbance on the water chemistry of the estuary. The first site was 100 m upcurrent from the disposal point and was a reference for undisturbed estuary conditions. The second site was at the point of sediment disposal, with the remaining 3 to 4 sites were approximately every 100 m in a transect across the dredge plume moving away from the sediment disposal point. Water was analysed for alkalinity, ferrous iron, dissolved sulfide, orthophosphate, ammonium, dissolved metals, pH, $E_h$, dissolved oxygen and electrical conductivity. Only the pH, $E_h$, ammonium and orthophosphate data will be presented in this paper.

## Results and discussion

During a laboratory resuspension of MBO material from the PHES a decrease in pH in all treatments was observed when the solution reached a redox potential of approximately + 400 mV (Figure 1a). The lower pH following oxidation of a higher mass of MBO reflected the greater acidity produced by oxidising higher quantities of AVS. In the highest sediment to water ratio treatment (200 mg/L) the pH dropped to a minimum of 6.99, before increasing to approximately the same pH that is observed at the end point of the other treatments (Figure 1b). This suggests that while the buffering capacity of the estuarine water prevents the severe acidification events that are observed during the resuspension of MBO in river systems (Sullivan *et al.* 2002).

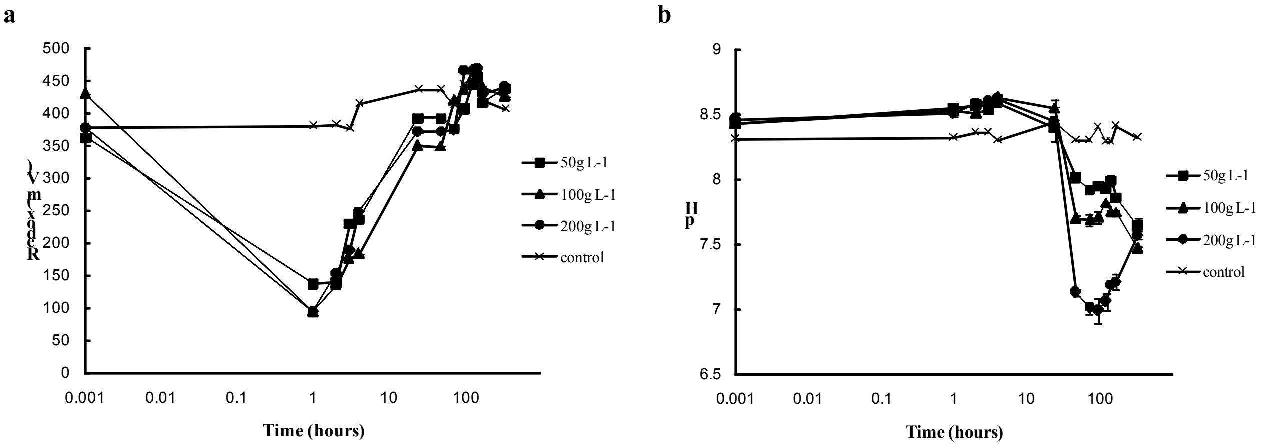

**Figure 1. The a) redox and b) pH of three sediment resuspension treatments and one control (no added sediment) were recorded for a two week period.**

This acidification is consistent with the disappearance of AVS and the appearance of the oxidation product sulfate observed in the peaks measured by XANES at 0, 24 and 72 hrs of resuspension for the 100 g/L treatment (Figure 2a). In a system not limited by oxygen, AVS has almost completely oxidised in all treatments by 24 hrs of resuspension, with the majority being oxidised within the first 4 hrs.

The results from monitoring a dredging disturbance also indicate redox and water quality changes. In the dredge plume, the localized impact zone can be distinguished by the decrease in redox potential at the point of sediment disposal (Figure 3a). The pH, however, is unaffected by distance from disposal site, and the variation observed between sampling dates is representative of normal estuarine processes (Figure 3b). The localised release of ammonium and phosphate was observed at the sediment disposal point in the dredge plume (Figure 4). The variation of concentrations measured at the disposal point is most likely a result of the heterogeneous nature of the dredge plume and hydrodynamic conditions in the estuary at the time of sampling.

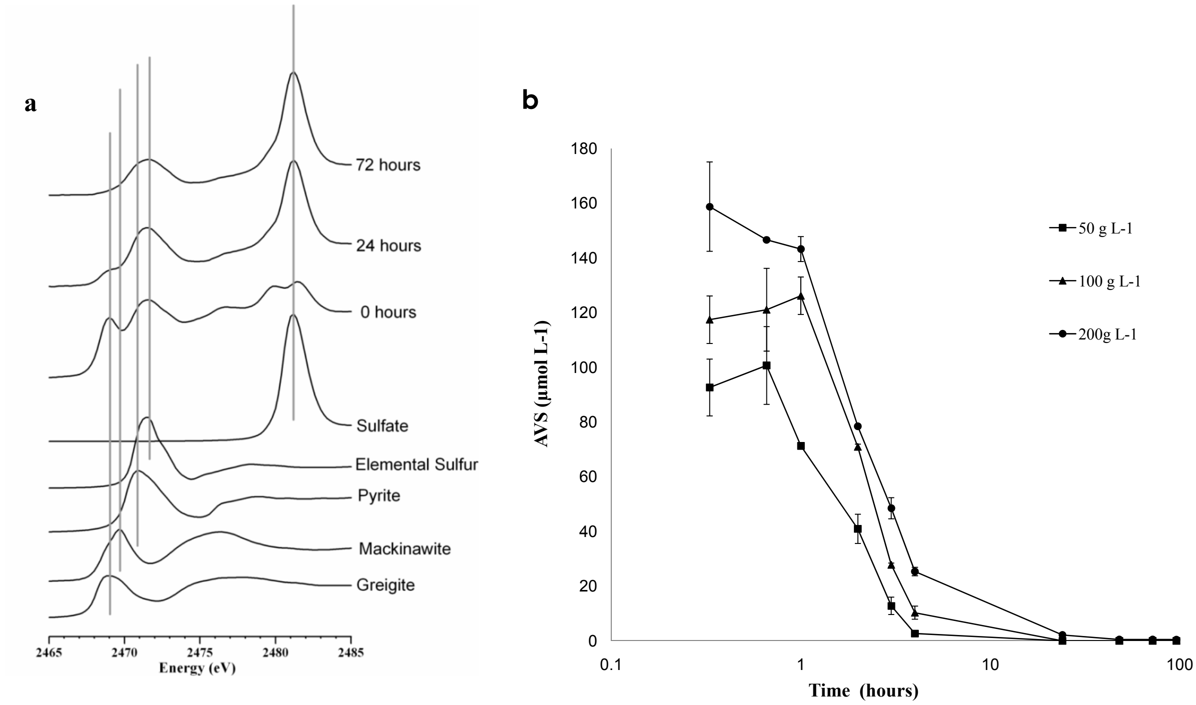

**Figure 2. a) Comparison between the X-ray energy of XANES peaks for reference phases and the XANES peaks in samples collected at three time intervals during the resuspension of 100 g/L of MBO from the Peel Harvey estuary system b) Acid volatile sulfide concentrations of laboratory MBO resuspension for all treatments. Starting (0 hr) concentrations of AVS are 4054 µmol/L for 50 g/L, 8108 µmol/L for 100 g/Land 16217 µmol/L for 200 g/L. These values are not graphed to maintain the clarity of the figure.**

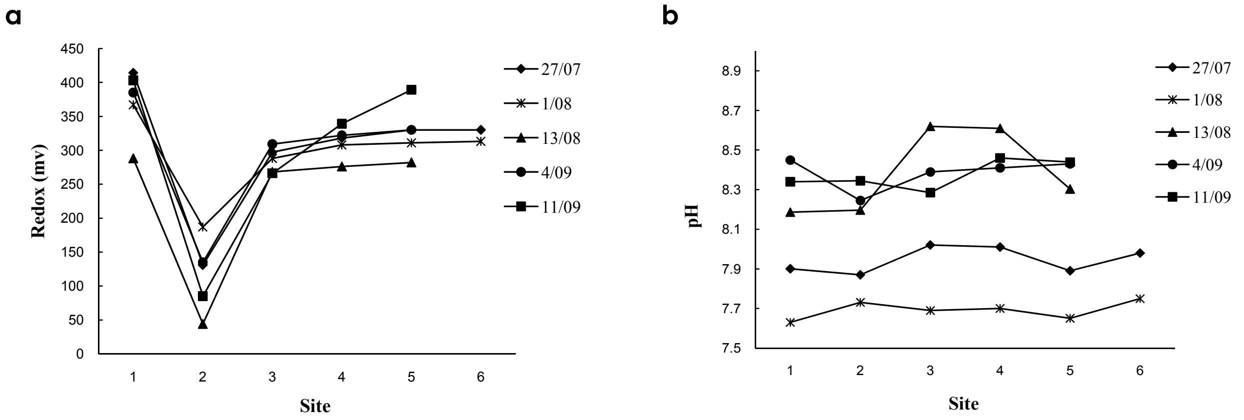

**Figure 3. a) The redox and b) the pH of surface water across a transect of a dredge plume; the sediment disposal point is at Site 2.**

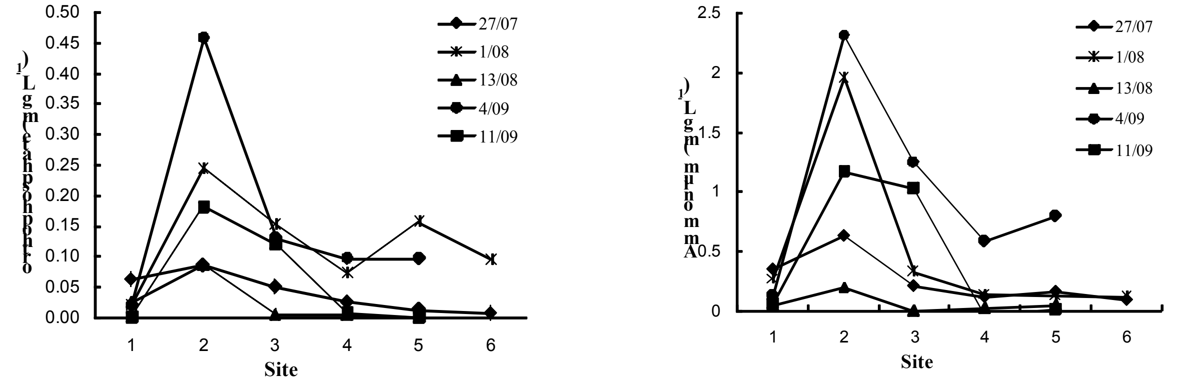

**Figure 4. Concentrations of a) orthophosphate and b) ammonium in surface water across a transect of a dredge plume; the sediment disposal point is at Site 2.**

## Conclusion

Laboratory experiments demonstrate the high reactivity of MBOs from the PHES following disturbance, but high variability and buffering in the field may limit the observation of these effects. Alongside the emphasis on acidification, deoxygenation and metal release during MBO resuspension, it is important to acknowledge the possibility of nutrient release from sediments in eutrophic estuaries.

## References

Brearly A (2005) 'Ernest Hodgkin's Swanland: estuaries and coastal lagoons of Southwestern Australia'. (University of Western Australia Press: Perth, Western Australia).

Burton ED, Bush RT, Sullivan LA, Hocking RK, Mitchell DRG, Johnston SG, Fitzpatrick RW, Raven M, McClure S, Jang LY (2009) Iron-monosulfide oxidation in natural sediments: resolving microbially-mediated S transformations using XANES, electron microscopy and selective extractions. *Environmental Science & Technology* **43**, 3128-3134

Burton ED, Bush RT, Sullivan LA (2006) Acid-volatile sulfide oxidation in coastal flood plain drains: iron−sulfur cycling and effects on water quality, *Environmental Science & Technology* **40**, 1217-1222

Burton ED, Phillips IR, Hawker DW (2005) Reactive sulfide relationships with trace metal extractability in sediments from southern Moreton Bay Australia, *Baseline/Marine Pollution Bulletin* **50**, 583-608

Bush RT, Sullivan LA, Fyfe D, Johnston S (2004) Redistribution of monosulfidic black oozes by floodwaters in a coastal acid sulfate soil floodplain. *Australian Journal of Soil Research* **43**, 603 – 607

Macdonald BCT, Smith J, Keene AF, Tunks M, Kinsela A, White I (2004) Impacts of Runoff from Sulfuric Soils on Sediment Chemistry in an Estuarine Lake. *Science of the Total Environment* **329**, 115 - 130.

Magni P, Montani S (2006), Seasonal patterns of pore-water nutrients, benthic chlorophyll a and sedimentary AVS in a macrobenthos-rich tidal flat. *Hydrobiologia* **571**, 297-311.

Smith J (2004) Chemical Changes During the Oxidation of Iron Monosulfide-Rich Sediment *Australian Journal of Soil Research* **42**, 659 - 666.

Smith J, Melville MD (2004) Iron Monosulfide Formation and Oxidation in Drain-Bottom Sediments of an Acid Sulfate Soil Environment. *Applied Geochemistry* **19**, 1837 - 1853.

Sullivan LA, Bush RT, Burton ED (2006) 'Acid sulfate soil development issues in the Peel Region'. (Department of Environment, Western Australia).

Sullivan LA, Bush RT, Fyfe D (2002) Acid sulfate soil drain ooze: distribution, behaviour and implications for acidification and deoxygenation of waterways. In 'Acid Sulfate Soils in Australia and China'. (Eds C Lin, MD Melville, LA Sullivan) pp. 91-99. Science Press, Beijing

Zimmerman AR, Canuel EA (2000), A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. *Marine Chemistry* **69**, 117-137.