

Peel Harvey ARC Project Update: May 2012

PARTNER ORGANISATIONS

WA Department of Environment, WA Transport, WA Water, Murray Shire, Mandurah City Council, Southern Cross University, Curtin University, University of WA

PROJECT SUMMARY

The chemistry of anoxic aquatic environments such as the Peel Harvey estuary is dominated by reactions with reduced sulfur, yet many of the fundamentally important reactions are highly transient and elusive. This project is exploring the extreme sedimentary conditions of a eutrophic estuary where hyper-accumulations of iron monosulfide prevail. Reduced inorganic sulfur and organo-sulfur compounds occur in abnormally high concentrations in these sediments, providing an ideal natural material to unravel sulfur biomineralisation pathways.

KEY FINDINGS UPDATE (2011-2012)

Finding 1: Channels in the Peel-Harvey and deep holes in the lower reaches of the tributary rivers provide highly favourable conditions for monosulfidic black ooze (MBO) (this is well known).

Management Implication: Changes to bedform that result in sinkholes and troughs will enhance localised MBO accumulation. This has relevance to developments that involve new dredging and maintenance dredging of navigational channels.

Finding 2: The formation of MBO is strongly linked to the presence/deposition of fine-grained sediment (silt), '*find the silt and you find the monosulfidic sediments*'. The fine sediments appear to restrict oxygen diffusion into the sediment, enhancing the formation and preservation of otherwise labile iron monosulfide minerals.

Management Implication: Understanding catchment sediment yield and the mobilization and redistribution of fine sediments within the Peel-Harvey is necessary to predict the accumulation of MBO.

Finding 3: Fine sediments associated with MBO are likely to include both contemporary catchment inputs and sediment redistribution within the estuary.

Management Implication: The construction and on-going management of man-

made channels in the Peel Harvey estuary will need to account for the hazard of MBO accumulation in their design and on-going maintenance.

Finding 4: MBO are prone to scour and suspension.

Management Implication: The mobilization of fine sediments as a result of dredging will cause MBO materials to oxidize and release associated contaminants. Current hazards associated with the mobilisation of these sediments are poorly defined. A clear understanding of these hazards will improve the environmental assessment and management of MBO in areas of dredging and dredge disposal.

Finding 5: Coarser sediments (silty sands) hold only small amounts of iron monosulfide (FeS), but have high contents of pyrite (FeS₂), another major potential source of acidity and cause of deoxygenation.

Management Implication: The sandy textured sediments of the Peel Harvey estuary have exceptionally high pyrite contents. The oxidation and acidification hazard for these materials is substantial and should be a key aspect of environmental impact assessment for developments involving benthic sediment disturbance.

Finding 6: Thin, buried layers of monosulfidic sediments (e.g. resulting from incomplete removal during dredging) completely dominate the sediment porewater chemistry, providing nutrients and high levels of dissolved sulfide to the sediment porewaters and overlying water column.

Management Implication: Chronic impacts from even very small amounts of MBO material in dredge disposal areas may cause these areas to become hotspots for prolonged nutrient release and sulfide toxicity. The disposal of dredge materials containing MBO needs further consideration.

Finding 7: The availability of Fe limits monosulfidic sediment formation in the Peel Harvey. Fe-rich runoff or groundwater that enters the estuary will potentially increase the rate and magnitude of sulfidic sediment accumulation. The sensitivity of the Peel Harvey estuary to the addition of Fe is yet to be fully quantified.

Management Implication: Activities in the catchment (particularly near shore), that may enhance the supply of Fe to the estuary in either run-off or groundwater, are likely to directly enhance iron sulfide formation.

Finding 8: Although phosphorus burial is limited in the MBO sediments, stable Fe oxides seem to play an important role in long-term phosphorus retention from the overlying water column.

Management Implication: Phosphorus cycling within the Peel-Harvey sediments may be sufficient to fuel major productivity and blooms, irrespective to the contemporary supply of nutrients in run-off. Activities that change the benthic sediment chemistry will have a direct impact on nutrient supply and potential to

trigger cycles of algae blooms.

Finding 9: Preliminary ²¹⁰Pb analyses indicate that the top ~ 20 cm of the sediment can be disturbed and readily remobilised by turbulent flows.

Management Implication: *The data indicates that MBO materials are impacting water quality continually as a result of even minor, but regular disturbances, such as general recreational boating.*

Finding 10: A detailed geochemical appraisal of the Murray River shows a dominance of terrestrial carbon input compared to the estuary.

Management Implication: *The processes driving MBO accumulation within the lower river systems differ somewhat to the open estuary. Different issues are at play in these adjacent waterways, resulting in the MBO's exhibiting different properties and hazards.*

UPDATE ON CURRENT WORK (2012 Jan – June)

Key Aim: *Determine the primary environmental constraints on sulfur biomineralisation and accumulation of iron-monosulfides in eutrophic estuarine sediments.*

Major Field Trip Three (Feb-Mar 2012)

The third field trip to the Peel-Harvey Estuary was undertaken between 13 and 25 February 2012, following earlier expeditions in April 2010 and March 2011.

Four sites were selected for further detailed analysis based on our findings during earlier trips (Figure 1). The sites cover a variety of depositional settings in the Peel-Harvey Estuary. Site 2 (Serpentine/Murray confluence) and Site 3 (South Yonderup Channel) are located in channels in the eastern part of the Peel Estuary, where the Serpentine and Murray flow into the estuary. The rivers are an important source of fine suspended sediment and nutrients to the estuary, with the former preferentially accumulating in geographic lows, e.g. channels. Site 6 (Harvey Estuary) is located in the western part of the Harvey Estuary, ~ 30 m off the Park Ridge boat ramp. This site is also located in a channel, yet far removed from riverine inputs. Site 8 (Central Peel) is near the Department of Water Scientific Platform in the centre of the Peel Estuary and functions as a control site which is not located in a channel. Due to issues with equipment (i.e. the transport company delivered the coring materials much too late), only three sites (Site 2, 6 and 8) could be cored.

Specific objectives and schedule

The February 2012 field trip addressed several key objectives, which were mostly aimed at improving our understanding of the geochemical processes around the sediment-water interface at the selected sites in the Peel-Harvey Estuary:

- Sample sediments and pore-waters at high resolution using a new coring system;
- Measure the benthic oxygen consumption rate and fluxes of nutrients using an core incubation setup;
- Determine the rate of dissimilatory sulfate reduction in sediment cores using the short-lived radioisotope sulfur-35 in tracer experiments; Investigate the 2-dimensional distribution of key dissolved pore-water species (ferrous and ferric iron, phosphorus and sulfide) using a novel gel-based approach.

Description of experiments

Water quality monitoring Key water quality parameters (temperature, pH, Eh, dissolved oxygen, salinity, chlorophyll a, turbidity and conductivity) were measured in-situ at 30-40 cm intervals in the water column at Site 2, 3 6 and 8 using a Hydrolab DS5 data sonde. In addition, filtered water samples were taken to quantify dissolved iron, sulfide, phosphate, ammonium, nitrite, nitrate and metals. These analyses together give a detailed snapshot of the water column conditions during sampling. These analyses have been performed during all three field trips, giving insight into the changes in water quality over the period 2010 -2012. These data are complemented by the extensive dataset gathered on a fortnightly and now monthly basis by the Western Australia Department of Water (Kwinana Peel region).

High-resolution pore-water and sediment sampling

A new coring system with 10-cm diameter polycarbonate cores was used to increase the sediment sampling resolution without jeopardizing the collection of sufficient amounts of sediment and pore-water for all planned analyses. In addition, the use of transparent polycarbonate allows immediate assessment of core integrity. From all three sites (2, 6 and 8), three cores were taken and transported to the Chemistry Department at Curtin University (Perth, WA). For each site, one core was sampled at high resolution (0.5 -2 cm intervals, increasing with depth): one wet sample was immediately frozen for further analyses, another sample was centrifuged to extract the pore-water which was immediately sub-sampled for analysis of dissolved ferrous and ferric iron, nutrients, metals and organic carbon, pH, alkalinity. The second core was sub-sampled for bulk density and methane measurements. The third core was used to deploy a gel probe which allows for the ultrahigh-resolution, 2-dimensional analysis of pore-water iron, phosphate and sulfide (Figure 4). After this, two minicores were taken from the top 15 cm of the core for high-resolution analysis of the solid phase material. These high-resolution measurements will provide more detail about the geochemical processes occurring at small scales, which may greatly impact overall sediment chemistry.

Measurement of benthic oxygen consumption and nutrient fluxes

An incubation chamber was loaded with 9 surface sediment cores (3 replicate cores per site) and topped up with water from the Peel-Harvey Estuary and left to equilibrate. Subsequently the cores were capped and incubated over a ~ 10-hour period at constant temperature, during which measurements were performed and water samples were collected at set intervals (start, middle, end of experiment). Dissolved oxygen, Eh and pH were directly measured with electrodes. Samples were taken for analysis of all dissolved species described for pore-water analysis (see point 2, above). In this way, the activity of the benthic community can be assessed by quantifying the rate with which oxygen is consumed from the overlying water and the benthic fluxes of nutrients. The interaction between sediment and water column is of great importance to the overall water quality and nutrient availability in estuarine systems. Two incubation runs were performed, one during daytime and one during the night, to investigate the effect of benthic photosynthesis (i.e. net oxygen production) on net oxygen consumption and nutrient fluxes.

Measurement of sulfate reduction rates in sediment cores

The sulfur-35 radio-isotope tracer technique was used to quantify sulfate reduction rates in the sediments from the three investigated sites. More information on the activity of the sulfate reducing microbial community is important to understand the exceptional abundance of iron sulfide minerals in the Peel-Harvey sediments. In turn, these iron sulfide minerals are reactive and have the potential to acidify and deoxygenate the water column. During the tracer experiment, small cores are injected with radioactive sulfur-35 in the form of sulfate (SO_4^{2-}) at set intervals along the whole length of the core (Figure 6). These injected cores are incubated for ~ 1 hour, after which the cores are sampled and the samples are frozen in zinc acetate to stop any microbial activity. Reduced sulfur (sulfide, elemental sulfur) is subsequently extracted and its radioactivity is measured. This can be then used to calculate how much of the originally injected radioactive sulfate is reduced and thus how fast sulfate is reduced in the sediment.

New supporting external funds

We have received funding from the Australian Synchrotron Facility to unambiguously quantify the iron mineralogy in the Peel Harvey MBO sediments.

EXPECTED OUTCOMES (2012)

- 1) The high-resolution pore-water and solid-phase dataset will be used to quantify the processes that govern the accumulation of MBO. This is essential when considering how to predict the effect of bedform changes on MBO accumulation (e.g. channel excavation and dredging).
- 2) Quantified rates of sulfate reduction that together with sulfur isotopes, will be used

to identify the cause of the exceptional accumulation of MBO in the Peel estuary. Understanding the fate of sulfur in these sediments is required for predicting accumulation and foreseeing the triggers for MBO formation, and their potential environmental hazard (e.g. deoxygenation, acidification).

- 3) Quantified effect of Fe inputs to the estuary on MBO formation and phosphorus dynamics. This is important in assessing the phosphorus budget (and the role of sediments therein) for the Peel-Harvey Estuary and the role of MBO in the cycles of algae blooms.
- 4) A framework to describe the environmental role of MBO in nutrient cycling, contemporary impacts on water quality, and management practices that exacerbate or mitigate the MBO impacts.