

# **Use of Active Barriers To Reduce Eutrophication Problems In Urban Lakes**

Barry Hart, Water Studies Centre, Monash University, Clayton, Australia  
Simon Roberts, Water Studies Centre, Monash University, Clayton, Australia  
Robert James, Water Studies Centre, Monash University, Clayton, Australia  
Jeff Taylor, Earth Systems Pty Ltd, Melbourne, Australia  
Dietfried Donnert, Research Centre Karlsruhe (FZK), Karlsruhe, Germany  
Rudiger Furrer, Research Centre Karlsruhe (FZK), Karlsruhe, Germany

## **ABSTRACT**

Excessive concentration of phosphorus is one of the main causes of algal blooms and eutrophic conditions in lakes. In many urban lakes, it appears that a large proportion of the phosphorus in the water column comes from the sediments, particularly when these are anaerobic.

Sub-aqueous capping is a relatively new method that has become an attractive option for isolating contaminated sediments from the environment, thus preventing or delaying the release of contaminants into surface waters. Active barrier materials (i.e. capping layers that consist of one or more reactive components) are gaining increasing attention for their greater efficiency in inactivating contaminants held in sediment layers.

This paper reports laboratory bioreactor experiments to test the effectiveness of three forms of calcium carbonate ( $\text{CaCO}_3$ ) in reducing the release of phosphorus from anaerobic sediment from Lake Carramar, a small urban lake in Melbourne.

Two of the  $\text{CaCO}_3$  active barrier materials tested proved to be quite effective, the most effective materials being the fine particle size, precipitated forms of  $\text{CaCO}_3$ . Over the 20-day experimental period, a 2% layer of the German material SoCal reduced the amount of phosphorus released by almost 100 times over that occurring with no barrier. The Australian product ESCal, while not as effective as the SoCal, still reduced the phosphorus released by around 15 times that with no barrier. A finely ground Lilydale limestone was essentially ineffective in reducing phosphorus release from the sediments.

A preliminary cost-benefit analysis suggests that SoCal unlikely to be attractive for use in Australia, given the estimated application cost of around \$3,800 per tonne. However, although the ESCal is slightly less effective in retaining phosphorus, its potential application cost estimated at \$2,000 per tonne, makes it an attractive option.

On the basis of these most promising preliminary results, we intend to further test the use of the ESCal. Further investigations will include: longer term laboratory studies using ESCal, optimisation of the barrier layer and methods for applying this material, mesocosms and full lake studies, and risk assessment studies to ensure there are no adverse ecological effects from its use.

## **KEY WORDS**

eutrophication, phosphorus, contaminated sediments, active barriers, calcium carbonate

## INTRODUCTION

Many water bodies in Australia and elsewhere in the world are experiencing an increased number of algal blooms, which can reduce the amenity value and ecological health of the water body. If the algae are predominantly cyanobacteria (blue-green algae), they can also be toxic.

Of the number of factors required for an algal bloom to occur, perhaps the most important is an excess of nutrients (particularly P and N). There are commonly two main sources of these nutrients: from the catchment; or internal release from the sediments.

Algal bloom management actions commonly focus on reducing catchment nutrient inputs, e.g. sewage discharges and diffuse runoff from agricultural land. But even in cases where these have been quite successful, the recovery of the water body may still be very slow due to in situ release from the sediments. Generally, it is only when the water body is stratified and the sediments become anaerobic that substantial amounts of nutrients (particularly FRP and ammonia) are released.

There are a number of methods available to reduce sediment release of nutrients. The most common include: artificial destratification, nitrate addition, oxygen injection and dredging of the contaminated sediments.

In recent years, the application of "capping" materials to contaminated sediments has found favour as a low-cost and low-technology alternative to the more conventional methods (Jacobs & Forstner, 1999). The concept of capping sediments in situ involves the placement of a cover over the sediment to seal it off and minimise release of contaminants to the water column. The cover material may simply provide a physical barrier over the sediment (eg. sand, gravel), or may provide an active barrier. Active barrier systems are generally pervious geochemical materials capable of actively demobilising contaminants in the pore water by adsorption or precipitation processes.

Active barrier materials currently being tested include: calcium carbonate ( $\text{CaCO}_3$ ) (House, 1990), zeolites (Jacobs & Forstner, 1999), seawater-neutralised red mud (McConchie et al., 1998) and modified clays such as Phosloc (Douglas & Coad, 1996) and Kaolin Modified Derivatives (Mackinnon et al., 1998).

This paper reports a study to trial the effectiveness of three types of calcium carbonate ( $\text{CaCO}_3$ ) as active barriers to prevent phosphorus release from Lake Carramar sediments, and therefore reduce the risks due to algal blooms in this urban lake.

This work formed part of a broader investigation program undertaken by the International Research Alliance for Managing Contaminated Sediments (Alliance Project)<sup>1</sup> that aimed to develop, refine and apply the technological capacity for assessing the effectiveness of techniques for the management and remediation of contaminated sediments, and ensure the effective transfer of this technology to industry.

---

<sup>1</sup> The Alliance Project was funded by the Department of Industry Sciences and Research under the Targeting Research Alliances initiative, and involved five major scientific institutions, two from Germany (Technical University Hamburg-Harburg, Hamburg; Karlsruhe Research Centre, Karlsruhe) and three from Australia (Centre for Water and Waste Technology, University of New South Wales, Sydney; Water Studies Centre, Monash University, Melbourne; Centre for Advanced Analytical Chemistry, CSIRO Energy Technology, Sydney).

## EXPERIMENTAL DETAILS

### Lake Carramar

This lake is part of a man-made lake/estuarine system connected to the Patterson River in metropolitan Melbourne. Lake Carramar was selected for study because it has a history of algal blooms over the recent past (Coleman, 2000). Lake Carramar is approximately one hectare in area, has gently sloping sides, a maximum depth of 2.5m and sandy sediments. The water is brackish with a salinity of approximately 4 ppt.

### Chemical Barrier Experiments

Experiments were performed using sediment cores obtained from Lake Carramar in March and November 2001.

A simple model of phosphorus adsorption to iron hydroxide complexes in sediments predicted that under short-term anoxic conditions, a pool of phosphorus would be released as soluble inorganic orthophosphate. Most of the core incubation experiments included either replicate or triplicate aerobic and anaerobic treatments to test this hypothesis.

Two sets of barrier experiments using sediment cores collected from Lake Carramar were run to assess the effectiveness of chemical barrier materials on the interception of phosphate released from sediment pools under both aerobic and anaerobic conditions.

Sediment cores were obtained from the lake and returned to the WSC laboratory in Melbourne where experiments were conducted using laboratory bioreactors (see Figure 1). For each trial, duplicate cores for each treatment were run (most at 20-22°C) under either aerobic or anaerobic conditions. Aerobic conditions were maintained by leaving the cores on the laboratory bench. In Experiment 1, the anaerobic cores were contained within a glove box with continuous flushing of pure nitrogen. However, in Experiment 2, the glove box was flushed with a mixture of nitrogen and 0.03% CO<sub>2</sub> in order to maintain the carbonate balance in the cores' overlying water. The overlying water of all cores was continuously bubbled with either room air or the anoxic gas mix via a 0.5mm teflon tube.

Three barrier materials were tested:

1. Normal limestone (Lilydale) - this material was obtained from a limestone quarry at Lilydale. The crushed and finely ground material had the following characteristics: surface area - 1.3 m<sup>2</sup>/g, mean particle diameter - 3,500 µm.
2. SoCal - this material was obtained from Germany and is a precipitated calcite product with very small particle size (mean particle diameter - 33 µm) and large surface area (67 m<sup>2</sup>/g), making it an ideal phosphorus adsorbant.
3. ESCal - this material was obtained by precipitating CaCO<sub>3</sub> from waste product CaO. The product is very fine grained (mean particle diameter - 600 µm), but slightly larger than the SoCal. The surface area is smaller than the SoCal (7.7 m<sup>2</sup>/g cf 67 m<sup>2</sup>/g), but still considerably larger than the Lilydale calcite.



**Figure 1: Experimental set-up of sediment core reactors in laboratory**

### **Experiment 1 - SoCal And Limestone**

A total of 24 cores (96 mm diameter) were collected from Lake Carramar at a depth of 2.5m on 30 March 2001. The barrier experiments were incubated at room temperature (20-23°C) for sixty days. All barrier cores were bubbled with the ambient atmosphere, room air for the aerobic cores, nitrogen gas for the anaerobic cores. Anaerobic barrier cores were contained within a glove box that was constantly flushed with nitrogen.

Two types of calcium carbonate barrier material were tested, a very fine precipitated German product (SoCal) and a fine ground limestone (Lime) from Lilydale. In this set of experiments, the barrier material was applied as a dry sand/barrier material mix, this being the method used by our German colleagues (however in subsequent experiments we dispensed with the sand).

The sand depth was set at 10mm (approx. 400g dw/core) and the barrier material was added at two concentrations 2% and 5% of the sand dry weight (2%=8g/core, 5%=20g/core). Loading rates for these materials are equivalent to 55.2 kg/m<sup>2</sup> of dry sand and 1.1 or 2.2 kg/m<sup>2</sup> of dry barrier material for the 1% and 2% treatments respectively.

In total, six treatments were run with duplicate cores of each in both aerobic and anaerobic conditions. The treatments were: Control (no barrier material added), Sand barrier, SoCal 2%, SoCal 5%, Lime 2% and Lime 5%.

### **Experiment 2 – SoCal And ESCal**

In this experiment we compared the effectiveness of SoCal against a locally produced (and less expensive) precipitated CaCO<sub>3</sub> (ESCal). Twenty-two cores (96 mm diameter) were collected at depth of 2.5m on 8 November 2001. These cores were incubated at room temperature (20-23°C) for sixty days. All cores were bubbled with the ambient

atmosphere, room air for the aerobic cores, nitrogen gas with 0.03% CO<sub>2</sub> for the anaerobic cores. Anaerobic barrier cores were contained within a glove box that was constantly flushed with the nitrogen/CO<sub>2</sub> mix.

The barrier materials were applied as a slurry mixed with site water. Barrier material was added at two concentrations 1% and 2% (1%=4g/core, 2%=8g/core). Loading rates for these materials are equivalent to 0.6 or 1.1 kg/m<sup>2</sup> of dry barrier material for the 1% and 2% treatments respectively.

In total, six treatments were run with duplicate cores of each in both aerobic and anaerobic conditions. The treatments were: Control (no barrier material added), ESCal 1%, ESCal 5% and SoCal 2%.

### Chemical Analyses

All samples for “soluble” nutrient analysis were filtered through 0.2 µm membrane filter at the time of collection. Samples were stored frozen at -20 or -70°C, and most of the samples were acidified to pH 2 with H<sub>2</sub>SO<sub>4</sub> at the time of collection.

Samples were analysed for ammonia (NH<sub>4</sub>-N), nitrate plus nitrite (NO<sub>x</sub>-N) and filterable reactive phosphorus (FRP) in the WSC analytical laboratory using a flow injection analyser (Lachette). The analytical methods and QC/QA procedures designated by the WSC laboratory were adopted.

## RESULTS AND DISCUSSION

### Experiment 1

There was no release of FRP until 12 days into the experiment (Figure 2), and then there was a fairly constant rate of release for the next 35 days.

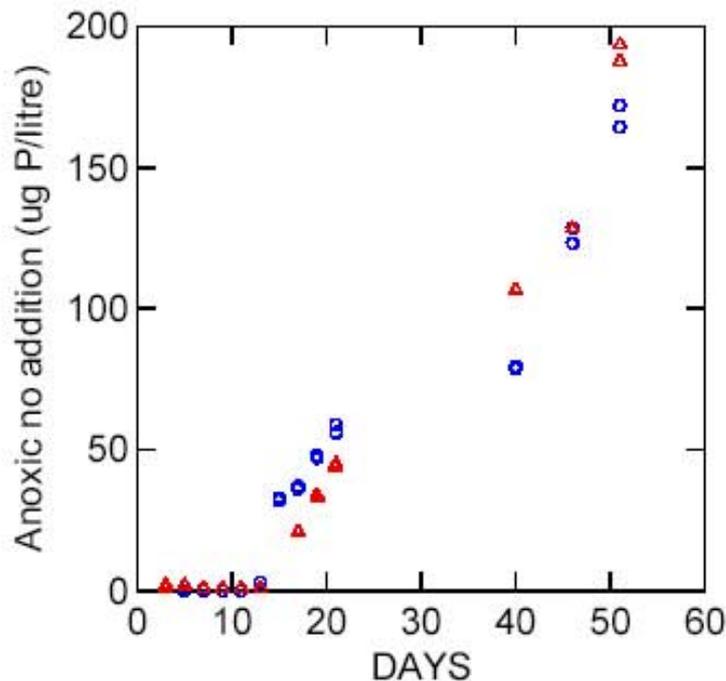


Figure 2: FRP concentrations (µg/L) in overlying water vs time (days) for Lake Carramar sediment sampled March 2001 –control, anaerobic conditions. Data shown for duplicate cores.

Figure 3 shows the FRP concentrations with time for the three different treatments and control, under aerobic and anaerobic conditions.

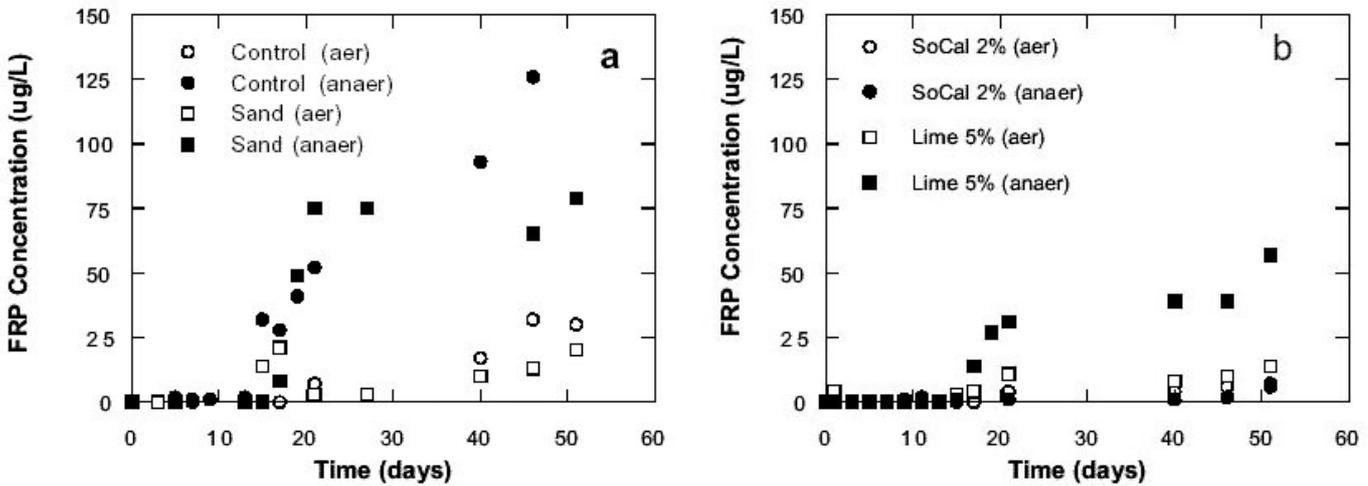


Figure 3: FRP concentrations (µg/L) in overlying water vs time (days) for Lake Carramar sediment under a range of different treatments.

Figure 4 shows the mean FRP flux rates for each treatment. The maximum rate of FRP release (16 mMole P/m<sup>2</sup>/day) was measured for the cores with no barrier material or sand present and under anaerobic conditions. The 10 mm sand barrier reduced this rate by more than 50% to 6.1 mMole P/m<sup>2</sup>/day.

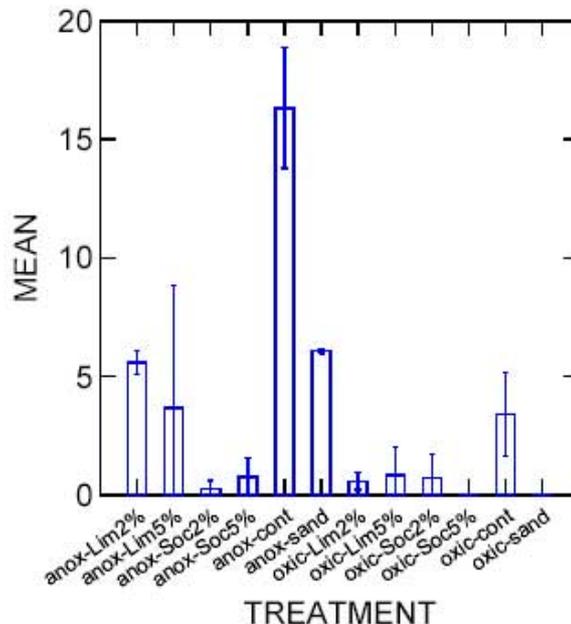


Figure 4: Mean FRP flux rates (mMole P/m<sup>2</sup>/day) from Lake Carramar sediments under a range of different treatments

Under aerobic conditions, the FRP flux rates were very much smaller than the maximum observed, reaching a maximum of only 3.4 mMole P/m<sup>2</sup>/day with no barrier material or sand, and less than 1 mMole P/m<sup>2</sup>/day under all the other treatments.

Under anaerobic conditions, the two calcite barrier materials gave very different results. The SoCal kept the FRP flux below 1 mMole P/m<sup>2</sup>/day for both concentrations of barrier applied, while the Lime (at both 2% and 5%) appeared to have little effect on the FRP flux when compared to the sand layer (Figure 4).

Thus, these experiments show that under anaerobic conditions, both 2% and 5% SoCal active barrier was very effective in reducing the FRP flux to around 1/20<sup>th</sup> that with no barrier. The SoCal was still effective at the end of the 60-day experimental period. It should be noted that even though the SoCal proved effective at reducing FRP release from Lake Carramar sediments, the amount released by the unprotected sediments would have had little effect on the overall water column FRP concentrations, even under prolonged anoxia. We estimated that the maximum release rate occurring for 20 days would increase the FRP concentration in a 2m water column by around 5 µg/L.

Interestingly, the maximum rate of FRP release (under anaerobic conditions) was around 170 times less than the rate of release of ammonia (2.8 ± 0.6 mMole N/m<sup>2</sup>/day) from the same cores. This very large ratio of the Nitrogen to Phosphorus fluxes (expected to be 15:1 if both due to breakdown of plant material) suggests that phosphorus is being retained in the sediments naturally or that the source of nutrients to the lake is very high in nitrogen relative to phosphorus.

## Experiment 2

Over the first twenty days of this experiment, as expected there was no release of FRP from any of the aerobic cores.

However, under anaerobic conditions, FRP was released from the control after four days incubation. However, the flux rates were relatively small, being 0.035 and 0.133 mMole P/m<sup>2</sup>/day for the two replicates.

Both barrier materials reduced the release of FRP from the anaerobic cores, with SoCal being more effective than the ESCal. The lack of data precludes an accurate estimation of the FRP flux rates, but we can say that the rate is less than 0.01 mMole P/m<sup>2</sup>/day.

Some measure of the effectiveness of the barrier materials can be obtained from the final FRP concentration in the reactor water overlying the sediment cores. After 20 days, the SoCal treated cores had the lowest mean FRP concentration (4 µgP/L) with the ESCal treated cores being around six-times greater (24 µgP/L). However, both these barriers released considerably less FRP than the control cores where the overlying water had an FRP concentration of 370 µgP/L.

Ammonia was released in all treatments, with the ammonia flux rates ranged from 1.1 to 2.2 mMole N/m<sup>2</sup>/day. The aerobic cores had rates some 20-30% higher than the anaerobic cores.

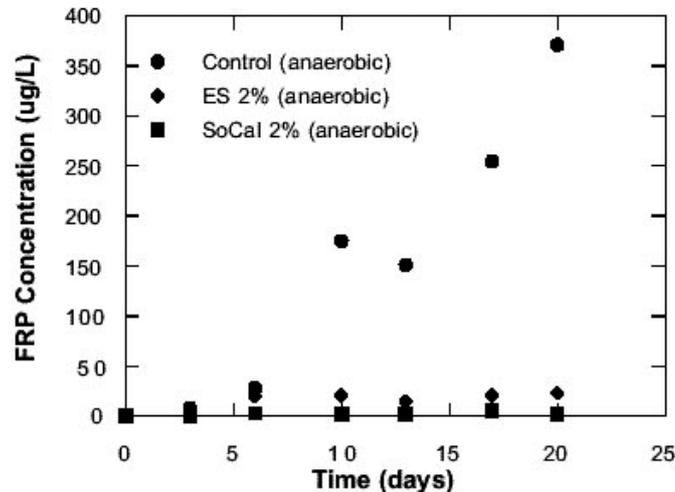


Figure 5: FRP concentrations ( $\mu\text{g/L}$ ) in overlying water vs time (days) for Lake Carramar sediment under different treatments.

## CONCLUSION

The experiments reported here show that sediment cores from Lake Carramar release both ammonia and FRP, particularly under anaerobic conditions. Ammonia, but not FRP, was also released by the cores under aerobic conditions.

Two of the  $\text{CaCO}_3$  active barrier materials tested proved to be quite effective at reducing the release of phosphorus from Lake Carramar sediments under anaerobic conditions, when tested in laboratory bioreactors. The most effective materials were fine particle size, precipitated  $\text{CaCO}_3$ , with the Germany material (SoCal) being the most effective. Over the 20-day experimental period, a 2% layer of SoCal reduced the amount of phosphorus released by almost 100 times over that occurring with no barrier. The Australian product ESCal, while not as effective as the SoCal, still reduced the phosphorus released by around 15 times that with no barrier. The Lilydale limestone material was essentially ineffective in reducing phosphorus release from the sediments.

A preliminary cost-benefit analysis suggests that the SoCal product is unlikely to be attractive for use in Australia, given the estimated application cost of around \$3,800 per tonne. However, although the ESCal is slightly less effective in retaining phosphorus, its potential application cost estimated at \$2,000 per tonne, makes it an attractive option.

On the basis of these most promising preliminary results, we intend to further test the use of the ESCal. These further investigations will include: longer term laboratory studies using ESCal, optimisation of the barrier layer and methods for applying this material, mesocosms and full lake studies, and risk assessment studies to ensure there are no adverse ecological effects from its use (Hart et al. 2002).

## REFERENCES

- Azcue, J.M., Zeman, A. & Forstner, U. (1998). *International review of application of sub aqueous capping techniques for remediation of contaminated sediments*. Proceedings of the 3rd International Congress on Environmental Geotechnics, Sept 7-11, Lisbon.
- Coleman, R. (2000). *Quiet Lakes blue-green algal bloom prevention study*. Melbourne Water Corporation, March 2000, Melbourne.
- Douglas, G.B. & Coad, D.M. (1996). *Review of estuarine sediment remediation techniques*. Technical report 96-11, CSIRO, Land & Water, Canberra.
- Hart, B.T., Roberts, S., O'Donohue, M., Webb, A. & Grace, M. (2002). *Risk assessment protocol for assessing ecological effects in using active barriers to prevent contaminant release from sediments*. Australian-German Alliance Project, WSC Report No 3, Water Studies Centre, Monash University, Melbourne, Australia, pp. (in press).
- House, W.A. (1990). *The prediction of phosphate co-precipitation with calcite in freshwaters*. *Water Res.* 24: 1017-1023.
- Jacobs, P.H. & Forstner, U. (1999). *Concept of sub aqueous capping of contaminated sediments with active barrier systems (ABS) using natural and modified zeolites*. *Water Res.* 33: 2083-2087.
- Mackinnon, I.D.R., Exelby, H.R.A., Page, B. & Singh, B. (1998). *Kaolin amorphous derivatives for the treatment of acid mine drainage*. Internal Report, UniQuest Ltd., University of Queensland, Brisbane.
- McConchie, D., Clark, M., Hanahan, C. & Davies-McConchie, F. (2000). *The use of seawater-neutralised bauxite refinery residues in the management of acid sulphate soils, sulphidic mine tailings and acid mine drainage*. Proceedings of the 3<sup>rd</sup> Queensland Environmental Conference, Brisbane, Australia.

## CONTACT

Jeff Taylor, Earth Systems Pty Ltd, Suite 507, 1 Princess Street, Kew, Australia, 3101. Ph: (61-3) 9205 9515. Fax: (61-3) 9205 9519. E-mail: [jeff.taylor@earthsystems.com.au](mailto:jeff.taylor@earthsystems.com.au)