Active Barriers to Reduce Phosphorus Release from Sediments: Effectiveness of Three Forms of CaCO$_3$

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Three forms of calcite—crushed limestone and two forms of precipitated calcite—were tested in laboratory bioreactors as possible active barriers to prevent phosphorus release from sediments, and therefore reduce the risks due to algal blooms (or eutrophication). The two precipitated calcite materials proved to be quite effective at reducing the release of phosphorus from Lake Carramar sediments under anaerobic conditions. Over a 20-day period, a 2% (1.1 kg (CaCO$_3$) m^{-2} layer of SoCal (a commercial product from Germany) reduced the amount of phosphorus released by almost 100 times over that occurring with no barrier. The Australian product (ESCal 2%), while not as effective as the SoCal, still reduced the phosphorus released by around 15 times that with no barrier. Limestone was ineffective in preventing the release of phosphorus. Mean phosphorus flux rates under anaerobic conditions were: control 66, SoCal 0.8, and ESCal 2.9 µmol (P) m^{-2} d^{-1}.

There is considerable scope to further optimize the conditions under which the ESCal calcite is formed to produce a product with smaller particle size and higher surface area than that tested here. Additionally, there is potential to precipitate the ESCal in situ and thus achieve even greater cost savings. Preliminary cost estimates are that it should be possible to dispense calcium hydroxide directly into the water column at around \$A 200 per tonne, and then use a CO$_2$ bubbler system to precipitate CaCO$_3$ directly in the water column.

Introduction

Many water bodies in Australia and elsewhere in the world experience algal blooms that can reduce the amenity value of the waterbody and can cause fish kills when the algae die and reduce the dissolved oxygen concentration. A number of factors are required for an algal bloom to occur,[1,2] with perhaps the most important being an excess of nutrients (particularly phosphorus and nitrogen). The main source of these nutrients is from the catchment or release within the waterbody from the sediments.

Management actions to reduce the incidence of algal blooms commonly focus on reducing nutrient inputs from the catchment, e.g., sewage discharges and diffuse runoff from agricultural land. But even in cases where this action has been quite successful, the recovery of the waterbody may still be very slow due to in situ release from the sediments.[1–4] Generally, it is only when the waterbody is stratified and the sediments become anaerobic that substantial amounts of nutrients (particularly filterable reactive phosphorus (FRP) and ammonium) are released.[5,6]

A number of methods have been used to reduce sediment release of nutrients, the most common being: nitrate addition, artificial destratification, oxygen injection, and dredging.[1]

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.[7] The concept of capping sediments in situ involves the placement of a cover over the sediment to seal it off and minimize release of contaminants to the water column. The cover material may simply provide a physical barrier over the sediment (e.g., sand and gravel), or may provide an active barrier. Active barrier systems are generally pervious geochemical materials capable of actively demobilizing contaminants in the pore water by the adsorption of precipitation processes.[8]

A number of active barrier materials have been tested, including calcite (CaCO$_3$), zeolites,[7] seawater-neutralized red mud,[9,10] and modified clays, such as Phoslock [11] and Kaolin Amorphous Derivative.[12]

This paper reports a study to assess the effectiveness of three calcite barrier materials (crushed limestone and two forms of precipitated calcite) in reducing the release of phosphorus from Lake Carramar sediments under both aerobic

and anaerobic conditions. Calcite was used as the active barrier material for two reasons. Firstly, a considerable amount of fundamental research on the effectiveness of calcite as an adsorbent has been reported[13–16] and, secondly, this material is likely to be more environmentally accepted than some of the other alternatives.

Our working hypothesis is that reducing the release of sediment-bound nutrients will have a beneficial effect on the waterbody in reducing the risk that cyanobacteria blooms will occur. However, it is also possible that the addition of an active barrier material to the sediments could result in adverse ecological effects. It is for this reason that we have developed an ecological risk assessment protocol specifically to assess the possible risk of adverse ecological effects from the use of active barrier materials.[17, 18]

Experimental

Lake Carramar is one of three interconnecting man-made lakes known as the Quiet Lakes, which form part of the Patterson Lakes system in Carrum Downs, a suburb of Melbourne (Fig. 1). Lake Carramar was chosen from the Quiet Lakes system because it has the most established history of significant algal blooms over recent years.[19] The lake is approximately one hectare in area, has gently sloping sides, a maximum depth of 2.5 m, and sandy sediments. The water is brackish with a salinity of approximately 4 parts per thousand. It also has characteristics likely to influence algal growth including: limited shading causing increased light and temperature levels; poor circulation allowing for stratification and long water residence time; low abundance of aquatic macrophytes thereby limiting competition for nutrients and light; limited habitat for zooplankton that consume algae; and highly nutrient-laden inflows such as urban stormwater and residential run-off.

Sediment cores were obtained by scuba divers in June 2000, and January, March, and November 2001.

Nutrient Release Experiments

A good knowledge of the factors controlling the storage and processing of nutrients (particularly phosphorus) in sediments was considered important, since conditions that released nutrients from inorganic or organic pools within the sediments will potentially lead to increased fluxes into the water column.

Our sediment-release model assumes that under short-term anaerobic conditions the pool of phosphorus associated with amorphous iron hydroxides would be released as filterable reactive phosphorus. Therefore, most of the core incubation experiments included either replicate or triplicate treatments under aerobic and anaerobic treatments to test this hypothesis.

Rates of aerobic respiration and photosynthetic production (where significant biomass of benthic algae was present) were measured in some experiments to provide estimates of the rates of remineralization and fixation of nutrients in the aerobic layer of the sediments.[20]

It was also possible to determine depth profiles of the nutrient concentrations in the pore water nutrient profiles by slicing cores under anaerobic conditions and obtaining pore water samples by centrifugation. This was done for a number of the sites prior to incubating the cores, and in some cases at the end of the incubation experiments.[20]

Bioreactor Experiments

Most of the nutrient flux experiments were performed using a core reactor system that allowed the regulation of gas exchange and the stirring rate of the water column. In addition, redox potential, pH, temperature, and oxygen concentration were continuously monitored using relevant probes controlled by an in-house software program.

The bioreactors are based on the original design of Drs Rob Junk and David Jones (CSIRO), with some minor modifications (Fig. 2). They consisted of a central core sleeve of 143 mm internal diameter and length of 550 mm, with a total volume of approximately 9 L. Sediment samples of 200–300 mm length were collected leaving an overlying water volume of between 4–6 L. Each reactor was equipped with a sealed lid that housed a variable speed motor attached to a paddle suspended 100 mm below the top of the reactor sleeve. The bioreactor experiments were run in the dark.

Ports in the cap allowed the insertion of redox and pH probes as well as a thermocouple and sampling tube for removing sub-samples for oxygen measurement or nutrient analysis. Dissolved oxygen concentration was measured using a Clark-type oxygen electrode housed in a purpose-built sampling apparatus. Samples of 40–50 mL for oxygen measurement were pumped from each reactor in turn into the oxygen electrode manifold and then returned to the reactor. The electrode manifold was rinsed with deionized water between each measurement and kept under a nitrogen atmosphere by use of a glove bag, which minimized cross contamination between reactors and reduced the growth of biofilms on the electrode membrane.
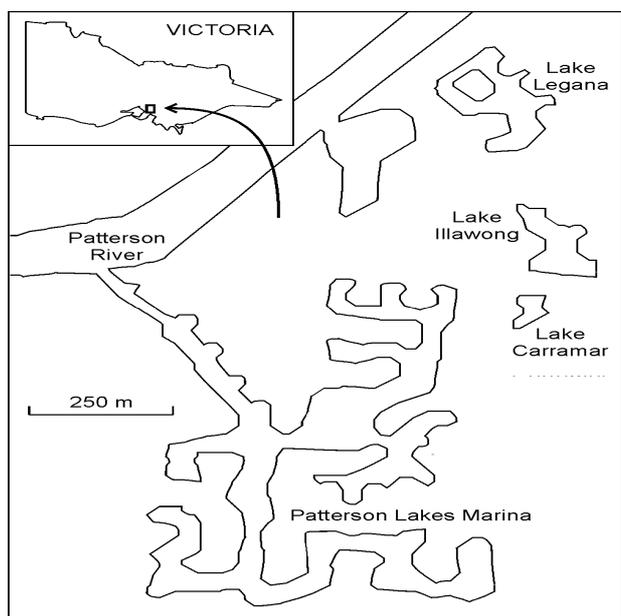
Fig. 1.   Diagram of Lake Carramar.

Fig. 2.   Diagram of the laboratory reactors used in the experiments.

Two sets of bioreactor experiments were undertaken using cores taken in June 2000 (Trip 1) and January 2001 (Trip 2).

Trip 1

Six cores were collected at a depth of 2 m on 29 June 2000, and were incubated in laboratory bioreactors for 7 d at 17–19°C. Three bioreactors were left open (aerobic) and three were bubbled with nitrogen (anaerobic).

Trip 2

Four cores were collected at a depth of 2.5 m on 24 January 2001, and were incubated in laboratory bioreactors for 8 d at 25°C. Two bioreactors were sealed for approximately 8 h per day to allow an estimate of respiration rates, and then bubbled with air for the remainder of the 24 h period (aerobic). The other two bioreactors were flushed continuously with nitrogen in the headspace over the water column (anaerobic).

Calcite Barrier Experiments

Three active barrier materials were tested.

Limestone (Lilydale). This material was obtained from a limestone quarry (Lilydale, Australia). The crushed and finely ground material had the following characteristics: surface area, 1.3 m^{2}g^{-1}; mean particle diameter, 3 500 μm.

SoCal. This material was obtained commercially from Solvay (Hannover, Germany) and is a precipitated calcite produce with very small particle size (mean particle diameter 33 μm) and large surface area (67 m^2 g^{-1}), making it an ideal phosphorus adsorbent.

ESCal. This material was obtained locally by precipitating CaCO$_3$ from Ca(OH)$_2$, a waste product from the production of acetylene. The product is very fine grained (mean particle diameter 600 μm), but slightly larger than the SoCal. Also the surface area is smaller than the SoCal (7.7 m^2 g^{-1}), but still considerably larger than the Lilydale calcite.

Two sets of barrier experiments were run under both aerobic and anaerobic conditions using sediment cores collected from Lake Carramar.

The laboratory reactors used for these barrier experiments were simplified versions of the bioreactors described above. They consisted of cylindrical polycarbonate tubes (93 mm internal diameter; 300 mm length), containing approximately 150 mm length of sediment and 100 mm of overlying water from the site. The bottom of each tube was sealed.

In each trial, duplicate cores for each treatment were run at 20–22°C under either aerobic or anaerobic conditions. Aerobic conditions were maintained by leaving the cores on the laboratory bench. In the first trial, the anaerobic cores were contained within a glove box with continuous flushing of pure nitrogen. This was modified in the second trial with the glove box flushed with mixture of nitrogen and 0.03% CO$_2$ (v/v) in order to maintain the carbonate balance in the overlying water. The overlying water of all cores was continuously bubbled with either room air or the anoxic N$_2$/CO$_2$ gas mix via a 0.5 mm (inside diameter) teflon tube.

Experiment 1

A total of 30 cores (96 mm diameter) were collected from Lake Carramar at a depth of 2.5 m on the 30 March 2001. Six cores were used in the bioreactors to determine the respiration and nutrient flux rates, and the other 24 cores were used for the barrier experiments.

Bioreactor experiments. These incubations were carried out at 17–18°C for 60 d, with three bioreactors bubbled with air (aerobic) and three bubbled with nitrogen (anaerobic).

Barrier experiments. The cores were incubated at room temperature (20–23°C) for 60 d. The aerobic reactors were bubbled with air and the anaerobic reactors with nitrogen gas. As an additional precaution, the anaerobic cores were contained within a glove box that was constantly flushed with nitrogen.

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%. 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 use of sand). The sand depth was set at 10 mm (approx. 400 g (dry weight) core^{-1}) and the reactive barrier material was added at two concentrations, 2 and 5% of the sand dry weight (2% = 8 g core^{-1}, 5% = 20 g core^{-1}). The loading rates of these materials are equivalent to 55.2 kg (dry sand) m^{-2} and 1.1 or 2.2 kg (dry CaCO$_3$) m^{-2} for the 2 and 5% treatments, respectively.

Experiment 2

A total of 22 cores (96 mm diameter) were collected from Lake Carramar at a depth of 2.5 m on 8 November 2001. These cores were incubated at room temperature (20–23°C) for 60 d. Aerobic cores were bubbled with air and the anaerobic cores with a nitrogen/0.03% CO$_2$ mixture. Again, the anaerobic cores were contained within a glove box that was constantly flushed with the N$_2$/CO$_2$ mix.

In total, four treatments were run with duplicate cores of each under both aerobic and anaerobic conditions. The treatments were: control (no barrier material added); ESCal 1%; ESCal 2%; and SoCal 2%. The barrier materials were applied as a slurry mixed with site water. Barrier material was added at two concentrations, 1 and 2% (1% = 4 g core^{-1}, 2% = 8 g core^{-1}). Loading rates for these materials are equivalent to 0.6 or 1.1 kg m^{-2} of dry reactive barrier material for the 1 and 2% treatments, respectively.

Pore Water Profiles

Sediment cores for pore water profiling were collected from the lake sampling site or from within the bioreactor at the end of a nutrient flux experiment. The cores used for pore water profiling were 96 mm internal diameter and at least 200 mm in length. The sediment dissection was performed under anaerobic conditions using a purpose-built hydraulic table and glove bag that allowed the sediment to be extruded from the core sleeve with a resolution of 5 mm.

Slices of sediment were transferred to nitrogen-purged capped centrifuge tubes and spun at 8 000 rpm for 10 min. Samples of the supernatant liquid were removed and acidified to pH < 2 using H$_2$SO$_4$. Ten core slices were collected to a total depth of 130 mm. Slices varied in depth from 5 to 30 mm with thicker slices collected at greater depth in the core, in order to define the transition of soluble nutrients in the aerobic/anaerobic interface.

Nutrient Analysis

All samples for 'soluble' nutrient analysis were filtered through 0.2 μm Nuclepore membrane filter at the time of collection unless otherwise noted. Samples were stored frozen at −20 or −70°C, with most of the samples acidified to pH 2 with H$_2$SO$_4$ at the time of collection.

Water samples from the anaerobic experiments were often found to release appreciable quantities of hydrogen sulfide upon acidification. It was important to remove this hydrogen sulfide from the sample as it can interfere with the spectrophotometric determination of filterable reactive phosphorus. An effective method to remove the hydrogen sulfide was to place the samples under vacuum prior to analysis.

Samples were analysed for ammonium (N as NH$_4$; NH$_4$-N), nitrate plus nitrite (N as NO$_x$; NO$_x$-N), and filterable reactive phosphorus (FRP) in the Water Studies Centre (WSC) analytical laboratory using a flow injection analyser (Lachat). The analytical methods and QC/QA procedures designated by the WSC laboratory were adopted.[21]

Results

Nutrient Release Experiments

Trip 1 (June 2000)

The average respiration rate, estimated from the first 2 days data, was around −10 (±5) mmol (O$_2$) m^{-2} d^{-1} for

Table 1. Flux rates from Lake Carramar sediments sampled June 2000
(positive flux = release; negative flux = uptake)

Reactor X	Treatment	NH_4 [mmol (N) m^{-2}d^{-1}]	NO_x [mmol (N) m^{-2}d^{-1}]	PO_4 [mmol (P) m^{-2}d^{-1}]	Respiration [mmol(O_2) m^{-2}d^{-1}]
RC1	unsealed	3.0	ns[A]	ns	−15
RC2	unsealed	2.8	0.03	ns	−5.7
RC3	unsealed	3.2	0.03	ns	−7.9
Mean (s.d.)		3.0 (0.2)	0.02 (0.02)	–	−9.6 (4.9)
RC4	N_2 bubbled	2.5	ns	ns	–
RC5	N_2 bubbled	1.9	ns	ns	–
RC6	N_2 bubbled	2.1	ns	ns	–
Mean (s.d.)		2.2 (0.3)	–	–	–

[A] ns = not significant (has been set as zero flux in statistical tests).

Table 2. Aerobic respiration rates for Lake Carramar sediments sampled January 2001
(positive flux = release; negative flux = uptake)

Day	Respiration rate [mmol (O_2) m^{-2}d^{-1}]	
	RC1	RC2
2	−37	−32
3	−40	−27
4	−31	−37
5	−35	−35
6	−31	−28
Mean (s.d.)	−35 (4)	−32 (4)

the open bioreactors (Table 1). This is probably an underestimate due to the gas exchange that would have occurred in these open reactors. Nutrient flux rates were calculated using data for the first 6 d of the incubation. No FRP was released from the Lake Carramar sediments under aerobic or anaerobic conditions. The flux of ammonium differed little between the aerobic (3.0 mmol (N) m^{-2} d^{-1}) and the anaerobic cores (2.2 mmol (N) m^{-2} d^{-1}). There was a slight increase in NO_x-N concentration in two of the aerobic cores, indicating that some nitrifying bacteria may be present.

Trip 2 (January 2001)

The respiration rates were estimated for the each of the aerobic cores daily using data for days 2 to 6. Aerobic respiration rates remained fairly constant for both cores at −35 and −32 mmol (O_2) m^{-2} d^{-1} for the two reactors, respectively (Table 2). There was no flux of FRP over the first four days of the experiment, with the FRP concentration at the limit of detection in all cores during this period. However, over the next 4 days some FRP was released, with FRP concentration reaching 9 μg (P) L^{-1} in the overlying water. The flux rates of ammonium and NO_x-N were calculated using data for the first seven days of the incubation. Ammonium flux in the aerobic cores was almost twice as high (7.1 mmol (N) m^{-2} d^{-1}) as in the anaerobic cores (3.3 mmol (N) m^{-2} d^{-2}; Table 3). It was not possible to say anything about NO_x-N, since there was essentially no NO_x-N present (maximum concentration detected was only 7 μg (N) L^{-1}).

In summary, Lake Carramar sediments had reasonably high aerobic respiration rates (−32 to −35 mmol (O_2) m^{-2} d^{-1}). Over the 7–8 day experimental period, these sediments released ammonium under both aerobic and anaerobic conditions, but little FRP was released under either condition. However, as is shown in the next section, appreciable FRP release only occurs after about 12 days of anaerobic conditions in this lake.

Active Barrier Experiments

SoCal and Limestone

Bioreactor control experiments. The nutrient flux rates in the bioreactors over the first ten days were consistent with previous short-term experiments. Ammonium flux rates (Table 4) were close to those measured for the cores sampled from this lake in June 2000 (Table 1), but were lower than the rates measured in January 2001 (Table 2). Rates were similar under aerobic and anaerobic conditions at 3.0 and 2.8 mmol (N) m^{-2} d^{-1}, respectively (Table 4).

There was no flux of FRP or NO_x-N from these Lake Carramar sediments over the first 10 days of the experiment (Table 4). However, FRP release commenced after about 12 days, and then continued at a fairly constant rate for the next 35 days (Fig. 3, control (anaer), no barrier, anaerobic conditions). The mean FRP flux rate was 16 μmol (P) m^{-2} d^{-1} under these conditions. Such rates of release would have little effect on the overall FRP concentration in a water column 2–3 m deep, even under prolonged anaerobic conditions.

Barrier experiments. Figure 3 shows the FRP concentrations with time for the three different treatments (sand, limestone, and SoCal) and control, under aerobic and anaerobic conditions. Table 5 records the mean FRP concentrations released from the anaerobic Lake Carramar sediment with (ESCal and SoCal) and without (control) a calcite barrier after 3, 13, and 20 days incubation.

The maximum rate of FRP release (16 μmol (P) m^{-2} d^{-1}) was measured under anaerobic conditions with no barrier material or sand present (Fig. 3). The 10 mm sand barrier reduced this rate by more than 50% to 6.1 μmol (P) m^{-2} d^{-1} over the 60 day experimental period. The FRP flux rates were very much smaller under aerobic conditions, reaching a maximum of only 3.4 μmol (P) m^{-2} d^{-1} with no barrier or sand, and less than 1 μmol (P) m^{-2} d^{-1} under all other treatments.

Under anaerobic conditions, the two barrier materials gave very different results. The SoCal kept the FRP flux

Table 3. Nutrient flux rates for Lake Carramar sediments sampled January 2001
(positive flux = release; negative flux = uptake)

Reactor X	Treatment	NH₄ [mmol (N) m⁻² d⁻¹]	NO$_x$ [mmol (N) m⁻² d⁻¹]	FRP[B] [mmol (P) m⁻² d⁻¹]
RC1	air bubbled	7.9	ns[A]	0.001
RC2	air bubbled	6.2	ns	ns
Mean (s.d.)		7.1 (1.2)	—	—
RC4	N₂ flushed	3.4	ns	0.003
RC6	N₂ flushed	3.2	ns	ns
Mean (s.d.)		3.3 (0.1)	—	—

[A] ns = not significant.   [B] For days 4 to 8.

Table 4. Flux rates from Lake Carramar sediments sampled March 2001 over a period of 10 days incubation
(positive flux = release; negative flux = uptake)

Reactor X	Treatment	NH₄ [mmol (N) m⁻² d⁻¹]	NO$_x$ [mmol (N) m⁻² d⁻¹]	PO₄[B] [mmol (P) m⁻² d⁻¹]
RC1	Air bubbled	3.4	ns[A]	ns
RC2	Air bubbled	2.5	ns	ns
RC3	Air bubbled	3.1	ns	ns
Mean (s.d.)		3.0 (0.5)	—	—
RC4	N₂ bubbled	2.5	ns	ns
RC5	N₂ bubbled	2.4	ns	ns
RC6	N₂ bubbled	3.4	ns	ns
Mean (s.d.)		2.8 (0.6)	—	—

[A] ns = not significant.   [B] For days 4 to 8.
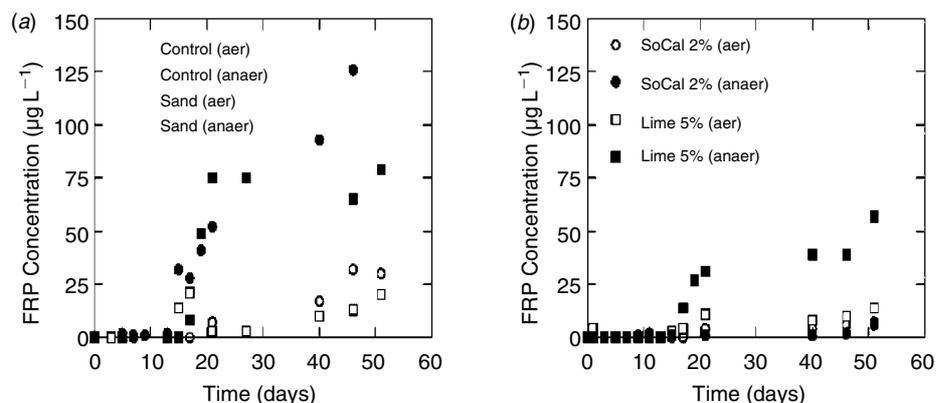
Fig. 3.   FRP concentrations [μg L⁻¹] in overlying water versus time [d] for Lake Carramar sediment sampled March 2001 under a range of different treatments. Control = sediment core with no barrier; sand = sand barrier; SoCal = precipitated calcite barrier; Lime = limestone barrier; aer = aerobic conditions; anaer = anaerobic conditions.

below 1 μmol (P) m⁻² d⁻¹ for both concentrations of barrier applied, while the limestone (at both 2 and 5%) appeared to have little effect on the FRP flux when compared with the sand layer (Fig. 3).

Although the focus of these barrier experiments was on reducing FRP release, the barriers also affected ammonium release. Under anaerobic conditions and no barrier, ammonium was released at a rate of 2.8 mmol (N) m⁻² d⁻¹, which is more than 160 times greater than the maximum rate of FRP release (16 μmol (P) m⁻² d⁻¹). Additionally, the ratio of the nitrogen to phosphorus fluxes (expected to be about 16 : 1 (mol/mol) if the source is phytoplankton and 20 : 1 if the source is

seagrass[24] suggests that (a) phosphorus is being retained in the sediments naturally, (b) the source of nutrients to the lake is very high in nitrogen relative to phosphorus, or (c) previous aerobic/anaerobic cycles had substantially depleted the upper sediment layers of phosphorus.

Pore water profiles.   The FRP concentration was measured in pore water samples taken from two of the aerobic and two of the anaerobic bioreactor cores at the end of the 60 day incubation (Fig. 4). The shape of the FRP concentration profiles was that typically found, with lower concentrations in the surface sediment layers and much higher concentrations at greater depths. For example, in the aerobic cores the pore

Table 5. Mean FRP flux rates under controlled conditions

Treatment		Mean PO$_4$ flux [μmole m^{-2} d^{-1} ± s.d.]
control	oxic	3.4 ± 1.8
	anoxic	16.3 ± 2.5
sand	oxic	0.00 ± 0.00
	anoxic	6.1 ± 0.1
SoCal 2%	oxic	0.7 ± 1.0
	anoxic	0.26 ± 0.36
SoCal 5%	oxic	0.00 ± 0.00
	anoxic	0.77 ± 0.77
lime 2%	oxic	0.59 ± 0.35
	anoxic	5.6 ± 0.5
lime 5%	oxic	0.8 ± 1.2
	anoxic	3.7 ± 5.2

Fig. 4. Porewater FRP concentrations [μg L^{-1}] versus sediment depth [mm] for cores taken from Lake Carramar March 2001. Bioreactor cores under (*a*) aerobic conditions (●: RC1 oxic; ▼: RC2 oxic) and (*b*) anaerobic conditions (●: RC4 anoxic; ▼: RC6 anoxic).

Fig. 5. FRP concentrations [μg L^{-1}] in overlying water versus time [d] for Lake Carramar sediment under different treatments.

0.133 μmol (P) m^{-2} d^{-1} for the two replicates. These nutrient flux rates were calculated using data for the first 20 days of the experiment.

Both barrier materials significantly reduced the release of FRP from the anaerobic cores, with the effectiveness being SoCal > ESCal (Fig. 5). Each of the barrier materials released a small but detectable amount of FRP over the first seven days, and then maintained this concentration in the water column for the remainder of the experiment. A flux rate could not be calculated under these conditions because the sediment and the water column achieved equilibrium. Of course, under natural conditions, a continuous phosphorus flux could occur because there would be a larger volume of water per sediment surface area, and potential biological and abiotic sinks for phosphorus would be present in the system. This lack of data precludes an accurate estimation of the FRP flux rates with the calcite barriers, but it is possible to say that the rate is less than 0.01 μmol (P) m^{-2} d^{-1}.

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 μg (P) L^{-1}) with the ESCal-treated cores being around six times greater (24 μg (P) L^{-1}). However, both barriers released considerably less FRP than the control cores where the overlying water had an FRP concentration of 370 μg (P) L^{-1}. It is possible that some of the FRP was removed by biofilms growing on the sediment/barrier surface. However, we have no evidence that biofilms did form, and if they did, that they were more active on the calcite barriers compared with the control sediment without any barrier material.

Pore water profiles. Profiles obtained at the end of the 60 day experiment indicate that a significant amount of FRP was released under anaerobic conditions (Fig. 6), with high concentrations of FRP being generated in the first few centimeters of sediment in the control cores. A low concentration of FRP was maintained in the surface layers of the aerobic cores. Profiles for the 2% SoCal and 2% ESCal treatments are consistent with the hypothesis that these active barrier

water FRP concentration in the surface 20 mm was less than 50 μg (P) L^{-1}, increasing almost an order of magnitude to 500–600 μg (P) L^{-1} at around 100 mm depth (Fig. 4).

The FRP concentration in the surface layers of the anaerobic cores was around five times higher than those in the aerobic cores (Fig. 4). The FRP concentrations in the deeper sediment layers probably changed little during the experiments. Although it is expected that FRP would diffuse upwards from the deeper sediment layers, it appears much of this is retained in the top 20 mm through adsorption or biological activity. The higher FRP concentrations near the surface of the anaerobic cores may be due to release of adsorbed phosphorus from amorphous iron oxide complexes and/or a reduced biological demand.

SoCal and ESCal

Barrier experiments. There was no release of FRP from any of the aerobic cores over the 60 day duration of the experiment. However, under anaerobic conditions, FRP was released from the control after four days incubation and reached a maximum concentration at 20 days (Fig. 5). The FRP flux rates were relatively small, being 0.035 and

Fig. 6. FRP porewater profiles from Lake Carramar sediments under a range of different treatments: (*a*) aerobic control, (*b*) anaerobic control, (*c*) anaerobic 2% SoCal, (*d*) anaerobic 2% ESCal.

materials absorb the FRP released by the sediment under anoxic conditions, and achieve an equilibrium that is dependent on the binding capacity of the barrier material (Fig. 6). The results from the flux experiments suggest that the barrier materials reached equilibrium with the pore waters early in the experiment at around seven days. Thereafter, the barrier material adsorbed all further FRP generated in the sediment.

These results also show that the activity of the barrier material is not confined to simply intercepting FRP diffusing up from below. It also acts as a sink that reduces the accumulation of FRP up to 15 mm deep. A secondary effect of the barriers may be that by reducing the accumulation of high FRP concentrations in the surficial sediment, 'pulsed' releases of FRP during sediment resuspension events would also be reduced.

Discussion

Nutrient Release from Sediments

Key Processes

The processes involved in the uptake and release of nutrients from sediments have been well studied.[5] A simple conceptual model summarizing the main processes operative under three common conditions—aerobic, anaerobic, and with the presence of an active layer of calcite—is provided in Figure 7. This model assumes the major source of nutrients (P, N) is sediment organic matter, which is broken down by bacteria under either aerobic (oxic) or anaerobic (anoxic) conditions. In most lakes, this sediment organic matter would consist of dead phytoplankton and perhaps also macrophytes
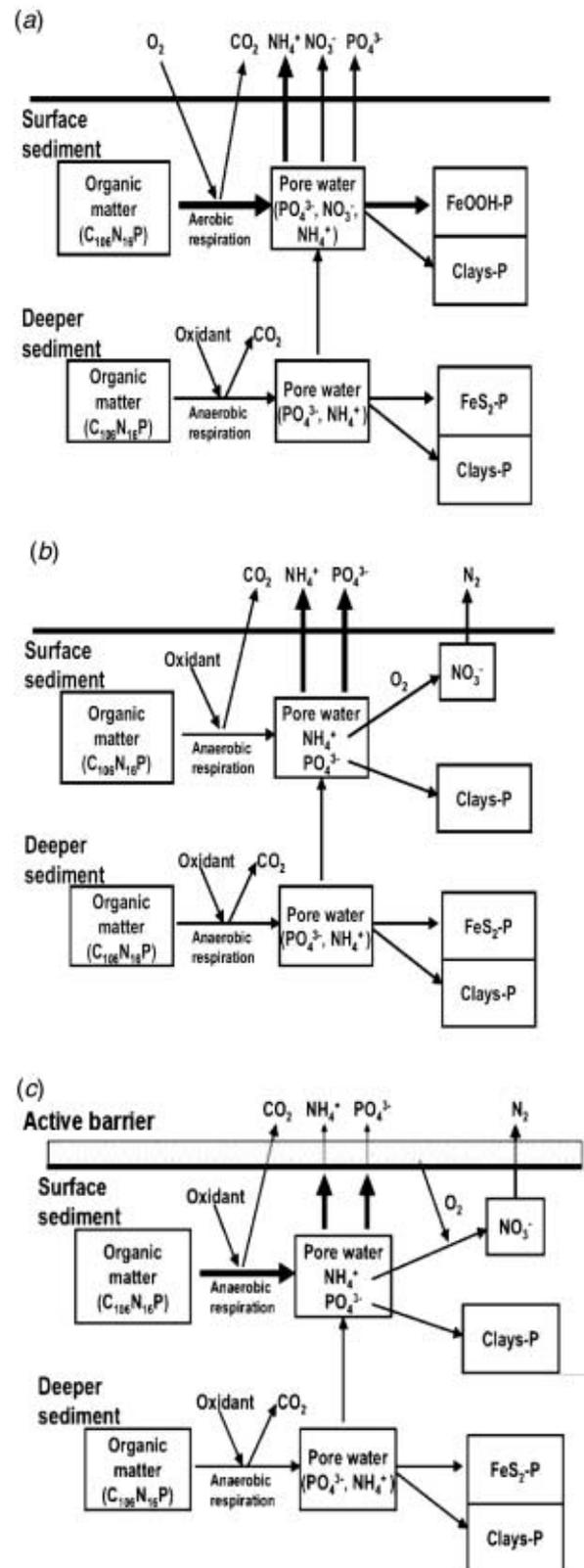
Fig. 7. Conceptual model of the processes occurring within the sediments resulting in release of phosphorus and nitrogen: (*a*) aerobic conditions, (*b*) anaerobic conditions, and (*c*) anaerobic conditions but with active barrier material on the sediment surface. The model assumes the main source of phosphorus is from organic matter. Box marked 'Clays-P' represents all clay-like surfaces that can interact with orthophosphate.

that have settled to the bottom, with an approximate molar ratio of the major elements $C : N : P$ being $106 : 16 : 1$ (Redfield ratio). In some systems it is also possible that substantial amounts of phosphorus could be added to the sediments via suspended particulate matter transported from the catchment.

Aerobic breakdown (respiration) requires oxygen as the oxidant, with the metabolizable organic matter being converted to CO_2, orthophosphate (PO_4^{3-}), ammonium (NH_4^+), and nitrate (NO_3^-). The relative balance between ammonium and nitrate will depend upon the actual redox conditions. Anaerobic respiration also involves the oxidation of organic matter to CO_2, but under these conditions oxidants other than oxygen is involved (these include NO_3^-, Fe^{III}, and Mn^{IV}).

Aerobic conditions.   The processes occurring under conditions where the water column is aerobic can be divided into those occurring in the sediments close to the sediment/water interface and those occurring in the deeper sediments. Under these conditions, organic matter in the surface sediments is broken down by aerobic bacteria, with the release of orthophosphate, ammonium, and nitrate to the pore waters. In most sediments, FeOOH and clays will adsorb much of the orthophosphate. Aerobic sediments would then release ammonium, nitrate, and possibly a very small amount of orthophosphate.

It is unlikely that O_2 can diffuse from the surface to depths greater than around 10 cm in these sediments, such that at depths greater than 10 cm, sediments are likely to be anaerobic. In these deeper sediments, anaerobic breakdown of organic matter can occur, again releasing FRP and ammonium to the pore waters. These deeper sediment pore waters generally contain very high concentrations of ammonium and high concentrations of FRP. The concentration of FRP will be dependent upon the presence of adsorbing surfaces, such as FeS, FeS_2, and clay–FeOOH. The presence of iron sulfides will depend upon the amount of sulfate present.

Anaerobic conditions.   Under anaerobic conditions, the surface pore waters contain high concentrations of ammonium and FRP. The FRP can be produced both by anaerobic decomposition of organic matter and release from FeOOH surfaces (FeOOH dissolves under anaerobic conditions). Additionally, denitrification may occur under these conditions, where part of the ammonium is converted to nitrate, which is subsequently reduced to nitrogen gas. Nitrification is normally aerobic, although there is now evidence suggesting NO_3 production can occur under anaerobic conditions through the reduction of manganese.[22] Significant denitrification would need an aerobic/anaerobic mix in the sediment that is more likely to occur in aerobic cores. The processes occurring in the deeper sediments have been discussed above.

Nutrient Fluxes under Anaerobic Conditions

FRP was not released from Lake Carramar sediments under aerobic conditions. Apparently, there is enough FeOOH in these sediments to prevent phosphorus release. This was not the case for ammonium, which was released from these sediments even under aerobic conditions. However, since the work undertaken in this study was focused on the application

of active barriers to reduce the release of phosphorus, we discuss below only the situation for anaerobic conditions when the most FRP release occurs.

The anaerobic release of FRP from Lake Carramar sediments sampled in both March 2001 and November 2001, took some time to commence, and even when it did occur the fluxes were relatively low. FRP release commenced from the March 2001 samples after about 12 days delay, with the mean FRP flux rate measured as $16 \, \mu mol \, (P) \, m^{-2} \, d^{-1}$. The November 2001 samples released FRP after four days of anaerobic conditions, but the release rates were almost insignificant (ca. $0.08 \, \mu mol \, (P) \, m^{-2} \, d^{-1}$). These very small release rates would have little effect on the overall FRP concentration in a water column 2–3 m deep, even under prolonged anaerobic conditions.

The delay in release of FRP is consistent with a slow dissolution of FeOOH complexes in the sediments under anaerobic conditions. The source of the dissolved phosphorus could be from these complexes, and also from the mineralization of organic phosphorus compounds in the top layer of the sediment. This is consistent with the measured concentrations of phosphorus in the surface sediment pore waters of the bioreactors at the completion of the experiment.

Calcite Barrier Materials

How Effective are the Calcite Forms Tested?

Two of the calcite ($CaCO_3$) active barrier materials tested in laboratory bioreactors proved to be quite effective at reducing the anaerobic release of phosphorus from Lake Carramar sediments. The most effective materials were fine, precipitated $CaCO_3$, in which the SoCal was the most effective. Over the 60 day experimental period, a layer of SoCal (2%) reduced the amount of phosphorus released by almost 100 times that occurring with no barrier. ESCal (2%), 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.

It seems the particle size, and hence surface area, of the calcite is very important in determining the amount of phosphorus uptake. For example, the most effective barrier material SoCal had the smallest particle size ($33 \, \mu m$) and the largest surface area ($67 \, m^2 \, g^{-1}$). Presumably, the large surface area resulted in a greater number of surface adsorption sites available to the adsorbing orthophosphate. The ESCal had a surface area around eight times smaller than the SoCal, surprisingly close to the difference in effectiveness between these two barrier materials in reducing phosphorus release.

With hindsight, Lake Carramar was not a particularly good case study. While these sediments released FRP, this only occurred after a considerable period of anoxia (4–12 days). Thus, the importance of sediment nutrients in stimulating algal blooms in this lake is questionable, given that it is unlikely that this system would experience periods exceeding 10–20 days when persistent stratification of the water column would occur. Additionally, even after phosphorus release commenced, the flux was small and would contribute little to

stimulate the algal blooms known to occur. For example, if it is assumed that half of the bottom sediment area (i.e., 3500 m^2) contributes FRP at a rate of 0.1 mmol (P) m^{-2} d^{-1} for period of 10 d into the water column (average deep 2 m, water column volume ca. 14 000 m^3). We calculate the increase in FRP concentration would be only 8 µg L^{-1}.

How does Phosphorus Interact with Calcite?

The interaction of phosphorus with calcite has been well studied. It is a common observation in many hardwater lakes that calcite precipitates during summer, when the higher metabolic activity of algae or macrophytes can use dissolved CO$_2$ and result in supersaturation of calcite. This precipitation of calcite can also scavenge phosphorus from the water column.[13]

The coprecipitation of calcite and orthophosphate has been studied by House and colleagues.[16,23] They suggest the mechanism involves initial interaction between orthophosphate and the calcite surface during crystal growth, followed by incorporation of some surface-associated phosphorus into the crystal structure as growth occurs. House[23] found that the phosphorus coprecipitation rate was linearly related to calcite precipitation rate in many systems.

The situation is somewhat different with calcite already present as an active barrier rather than being precipitated in situ. In this case, the mechanism probably involves very rapid adsorption of orthophosphate onto the calcite surface (this adsorption is indistinguishable from surface precipitation), followed by the slow incorporation of the calcium phosphate into the calcite crystal matrix. Suzuli et al.[15] have shown that when orthophosphate is added to calcite, most of the phosphorus very rapidly (< 30 s) becomes associated with the calcite, although it can take up to an hour before equilibrium is achieved.

The final product of this adsorption/coprecipitation process will be a complicated mixture of CaCO$_3$ and forms of calcium phosphate. The dominant form, in most cases, is likely to be hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH), HAP), which has a very low solubility product ($K_s = 3.2 \times 10^{-59}$ M^9 at 20°C). This compares with the solubility product for calcite of 4.2×10^{-9} M^2 at 20°C.

How Long will the Calcite Barrier Remain Effective?

Three factors would be expected to influence the long-term effectiveness of calcite active barriers:

(a) Stability of the barrier material (will it dissolve?). Calcite barriers will dissolve if placed in systems where the water is undersaturated with respect to CaCO$_3$, i.e., if the calcite saturation index (SI$_{calcite} = $ [Ca^{2+}]·[CO$_3^{2-}$]) is negative. On the other hand, if the SI$_{calcite}$ is positive, further precipitation of calcite will occur.

The computer program PHREEQC was used to compute the saturation indices for calcite and hydroxyapatite under different conditions in Lake Carraram (Table 6). These data show that temperature and pH are particularly important. In Lake Carramar, temperature varies from around 10–12°C in winter to as high as 22–25°C in summer. During the time we have been studying this lake, the pH has been consistently

Table 6. Saturation indices for calcite and hydroxyapatite as function of temperature and pH for Lake Carramar water
Assumes FRP concentration of 5 µg L^{-1}

Temperature [°C]	pH	SI (calcite)	SI (HAP)
15	7.0	−0.86	−3.16
	7.5	−0.19	−0.86
	8.0	0.30	1.16
20	7.0	−0.61	−2.89
	7.5	−0.12	−0.61
	8.0	0.37	1.39
25	7.0	−0.54	−2.62
	7.5	−0.05	−0.36
	8.0	0.44	1.62

around 7.5, but can go as high as 8.5 in summer when algal productivity is high.

During the summer/autumn period when most algal blooms occur in this lake, the pH is around 7.5 and temperature around 20°C. For these conditions of temperature and pH, the solution is slightly undersaturated, suggesting the calcite is finely balanced between precipitation and solubilization (Table 6). If the above conditions hold for this system, it is likely that a calcite barrier would remain in place for a considerable time and would not dissolve. Additionally, if the water column orthophosphate concentration in this lake was around 5 µg L^{-1}, we predict the solution is slightly undersaturated with respect to hydroxyapatite.

The above solubility calculations assume close to ideal conditions and therefore represent the lowest limit of solubility. The calculations assume (a) no interacting or inhibiting species or alternative reactions such as vivianite formation, (b) all FRP is as orthophosphate (unlikely), and (c) there is no inhibition of surface nucleation and precipitation of hydroxyapatite by other species (e.g., humics). Practically, the free orthophosphate ion concentration is likely to be much lower than we have assumed, and saturation conditions may not be occurring.

(b) Sorption capacity of the calcite barrier (will it become saturated with phosphorus?). Laboratory tests of phosphorus sorption capacities of ESCal and SoCal were run in distilled water at concentrations ranging from 14 to 140 mg (P) L^{-1}. The results indicated that SoCal had a maximal sorption capacity of two to three times ESCal at all concentrations. Both products showed lower binding capacities at lower phosphorus concentrations. The maximal binding capacity for SoCal and ESCal were 3 and 1% (by weight), respectively, at high external phosphorus concentrations. Estimates of binding capacity at concentrations closer to those found in the water column of Lake Carramar were an order of magnitude smaller (0.1–0.2% by mass).

Anaerobic phosphorus flux rates for a number of lake sediments we have tested ranged from 0.01 to 1 mmol (P) m^{-2} d^{-1}.[17] Assuming the highest phosphorus flux rate, the 2% ESCal treatment of approximately 1 kg m^{-2} dry weight would have sufficient sorption capacity to trap all of the released phosphorus for close to one year. Even if the maximal sorption capacity was not attained, the calcite barriers would probably remain effective for several years since anaerobic

conditions, the times when phosphorus would be released, would be unlikely to last more than a few months per year. Given that more typical anaerobic phosphorus flux rates are likely to be less than that used above, and closer to 0.1 mmol (P) m^{-2} d^{-1}, calcite barrier material would be expected to remain effective for some years.

(C) Will the barrier become ineffective by other processes? It is possible that the barrier material could be buried either by mixing within the sediment or by being covered with suspended material washed into the lake. If this happened it would certainly reduce the capacity to adsorb phosphorus from the water column. However, it is unlikely that the capacity to trap phosphorus fluxing up through the sediments would be much reduced.

Application of Calcite Barriers in Australia

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 $A 3800 per tonne. However, although the ESCal is slightly less effective in retaining phosphorus, its potential application cost, estimated at $A 2000 per tonne, makes it a more attractive option.

To date there has been little investigation of the method used to prepare the ESCal calcite. There is considerable scope to further optimize the conditions under which the ESCal calcite is formed to produce a product with smaller particle size and higher surface area than that tested here. Additionally, we believe there is potential to precipitate the ESCal in situ and thus achieve even greater cost savings. For example, our preliminary cost estimates are that it should be possible to dispense calcium hydroxide directly into the water column at around $A 200 per tonne, and then use a CO_2 bubbler system to precipitate $CaCO_3$ directly in the water column. Obviously, more work is needed to firm up the feasibility of both these options

Conclusions

Three forms of calcite as possible active barrier materials were tested in laboratory bioreactors. The two precipitated forms of calcite (SoCal and ESCal) proved to be effective at reducing the release of phosphorus from Lake Carramar sediments under anaerobic conditions. Over a 20 day period, a 2% layer of SoCal reduced the amount of phosphorus released by almost 100 times that occurring with no barrier. ESCal (2%), while not as effective as SoCal, still reduced the phosphorus released by around 15 times that with no barrier.

The uptake mechanism seems to involve rapid adsorption of the orthophosphate to the calcite surface, followed by further reaction with Ca^{2+} ions to form a highly insoluble form of calcium phosphate (hydroxyapatite). The long-term stability of the calcite (i.e., will it all dissolve?) can be determined by calculating the calcite saturation index, using information on the composition of the overlying water ($[Ca^{2+}]$, $[Mg^{2+}]$, alkalinity, pH, temperature, etc.). The prevailing conditions of temperature and pH in Lake Carramar, suggest that the water column is slightly undersaturated, with calcite finely balanced between precipitation and solubilization. It is likely

that a calcite barrier would remain in place for a considerable time and would not dissolve.

On the basis of the promising results reported here, we intend to undertake further testing of ESCal and other substitutes, but probably in another urban lake system where sediment nutrient release makes a greater contribution to algal problems. These further investigations will include: long-term laboratory studies to further test the effectiveness of ESCal, further investigations to optimize the preparation of the suitable calcite material, studies to optimize the 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.[17,18]

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