A Novel Technique for Reducing Bioavailable Phosphorus in Water and Sediments

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A significant proportion of the research into and management of eutrophication in aquatic systems such as rivers, lakes and estuaries has focussed with varying success on reducing diffuse nutrient inputs from catchments. If new effective control strategies can be adopted to reduce the nutrient concentration in diffuse and point sources, natural resource managers will be equipped with a powerful complimentary management tool. A range of existing and novel sediment remediation materials were evaluated in terms of their effectiveness in reducing nutrient availability in a range of natural and wastewaters and from sediments. From this research a modified clay was developed which has been demonstrated to have considerable promise in reducing filterable reactive phosphorus (FRP) concentration in water in extensive batch test and core trials and a large-scale mesocosm trial. As a result of the success of the modified clay in both laboratory and field trials, both provisional national and international patent applications are pending. These provisional patents broadly cover the research and development and potential applications of the modified clay and related materials.

1. Introduction

Diffuse nutrient (nitrogen and phosphorus) pollution may occur via a multitude of mechanisms including direct runoff from urban and agricultural land, groundwater transport, and discharge and dilution from intensive agriculture. The very nature of diffuse nutrient pollution constrain remedial approaches that may be applied to reduce their flux and consequent effects on the environment. Remedial controls of diffuse nutrient pollution may also frequently be required to be applied on a range of scales *e.g.* in rivers, lakes or estuaries and in a variety of forms *e.g.* treating both soluble and solid (sediment-bound forms of nutrients). In addition, an over-riding requirement is that methods of diffuse nutrient control must, by virtue of their potentially widespread application, be environmentally harmonious.

Over the past four years the problems of nutrient pollution and natural inputs have been addressed by the CSIRO Land and Water and the Water and Rivers Commission in a joint project investigating methods of sediment remediation. The impetus for the sediment remediation project arose from a desire to redress the fluxes of nitrogen and phosphorus which were contributing to the occurrence of eutrophic conditions in the Swan River Estuary, Western Australia. These eutrophic conditions were manifested in the frequent and often large algal blooms that occurred in the late spring, summer and early autumn, particularly in the upper reaches of the Swan River Estuary system, particularly some 20-30km upstream from its discharge to the Indian Ocean. Specifically, the sediment remediation project at in Western Australia is addressing the biologically available phosphorus stored in sediments - one of the most common problems in controlling algal blooms in Australia's waterways.

Typically in the Swan River Estuary the nutrients which contribute to the occurrence of the algal blooms during the warmer months may emanate from nutrient enriched bottom sediments [1, 2]. The nutrient enrichment in these bottom sediments is derived from a combination of diffuse and point sources. The flux of nutrients into the estuary is also enhanced by local groundwater flow [3, 4]. In addition the nutrient flux to the estuary may be augmented by intermittent spring/summer rains which introduce from the catchment, an additional diffuse nutrient source.

2. Results and Discussion

At the commencement of the sediment remediation project a literature review was conducted which examined a range of existing and novel sediment remediation techniques [5]. The review included an evaluation of both physical (*e.g.* aeration, dredging) and chemical (*e.g.* alum, red mud) techniques and/or materials in terms of their potential or documented effectiveness in reducing nutrient (phosphorus and/or nitrogen) availability in aquatic environments.

It became apparent that no single technique was universally applicable to effectively reduce loading of P and/or N in the wide range of physico-chemical conditions commonly encountered in aquatic environments. In particular, there was a paucity of tools available to counter internal nutrient loadings in aquatic environments such as the Swan River Estuary as a consequence of nutrient regeneration processes from bottom sediments and in particular where the flux of these nutrients may also be enhanced by local groundwater flow.

A two-year series of laboratory and field trials of sediment remediation materials was conducted to identify materials that may have the potential to reduce the concentration of available nutrients in aquatic systems [6]. Specifically, the nutrient binding properties of 14 materials or derivatives identified in a review of potential sediment remediation materials were evaluated. Many of the natural materials, and in particular clays, did not perform well in reducing FRP concentrations during the batch test experiments. Few materials apart from some types of naturally occurring zeolites had, on the basis of the batch-test experiments, a demonstrated capacity to adsorb significant nitrogen (as ammonia) from solution. The disappointing results for natural clays led to research on clay derivatives and the development of a modified clay which had an increased phosphorus uptake capacity. Under batch-test conditions the modified clay could substantially reduce the concentration of FRP in solution.

Further investigation of the modified clay, clearly the most promising sediment remediation material, involved a rigorous assessment of its physico-chemical properties. The modified clay was tested under a wide range of simulated environmental conditions using small-scale batch tests to determine their robustness in the adsorption of phosphorus in response to variation of a combination of environmental factors (pH, salinity, dissolved organic carbon and dissolved oxygen). The most outstanding properties of the modified clay were its ability to remove FRP under anoxic conditions and over a wide range of pH.

In our laboratory tests it was demonstrated that modified clay was able to reduce the concentration of FRP in samples by more than 90% under a range of physico-chemical conditions. As a result of the success in the batch-test experiments, it was decided to concentrate on further research and development of the modified clay. In particular, the performance of the modified clay was evaluated using a series of natural water/wastewaters (Tables 1, 2). These results clearly demonstrate that for a variety of natural and wastewaters with a wide range of matrices and bottom sediments suspended in water there is a substantial reduction of FRP concentration over the period of the batch test.

Table 1. Removal of filterable reactive phosphorus (FRP) from trials with sediments (7 day batch tests) and natural waters (48 hour batch tests) over a range of salinities.

Sample type (salinity)	***PO_4-P (µg/L - no treatment)***	***PO_4-P (µg/L – modified clay)***	***PO_4-P reduction***
Sediments			
Swan R (0 ppth)	120	<5	>98%
Swan R (5 ppth)	120	<5	>98%
Swan R (30 ppth)	130	<5	>98%
Waters			
Ellen Brook (0 ppth)	450	9	98%
Avon River (4 ppth)	20	<5	>87%
Swan R (30 ppth)	35	<5	>93%

Table 2. Removal of filterable reactive phosphorus (FRP) from wastewaters (48 hour batch tests)

Effluent type	***PO_4-P (µg/L - no treatment)***	***PO_4-P (µg/L – modified clay)***	***PO_4-P reduction***
Subiaco STP	1130	<5	>99%
Denmark STP	3490	<5	>99%
Northam STP	2410	5	>99%
Piggery Abattior	5320	8	>99%
Piggery manure	1910	12*	>99%

*pre-treated with lime, pH adjustment required

An additional series of laboratory trials conducted over periods of one to three weeks using cores of sediment collected from the Swan and Canning Rivers and Lake Monger also demonstrated the effectiveness of the modified clay in reducing the diffuse flux of FRP from bottom sediments. Treatment of the cores involved the application of thin veneer of a powdered form of the modified clay. Results of a core trial using sediment cores from the Canning River are shown in Figure 1. A large reduction in the FRP concentration to less than 5µg/L occurred within two hours after the application of the modified clay and this was sustained for the remaining 460 hous of the core trial. In contrast, FRP concentrations in the control cores increased for approximately 200 hours and thereafter began to decline due to assimilation by an algal bloom. An additional graphic example of the effectiveness of the modified clay in reducing the diffuse nutrient flux and as a consequence a reduction in algal growth in water overlying sediment cores collected from the upper Swan River Estuary is shown in Figure 2. Concentrations of chlorophyll-a were reduced by up to *ca.* 95% in the cores treated with the modified clay over a three week period.

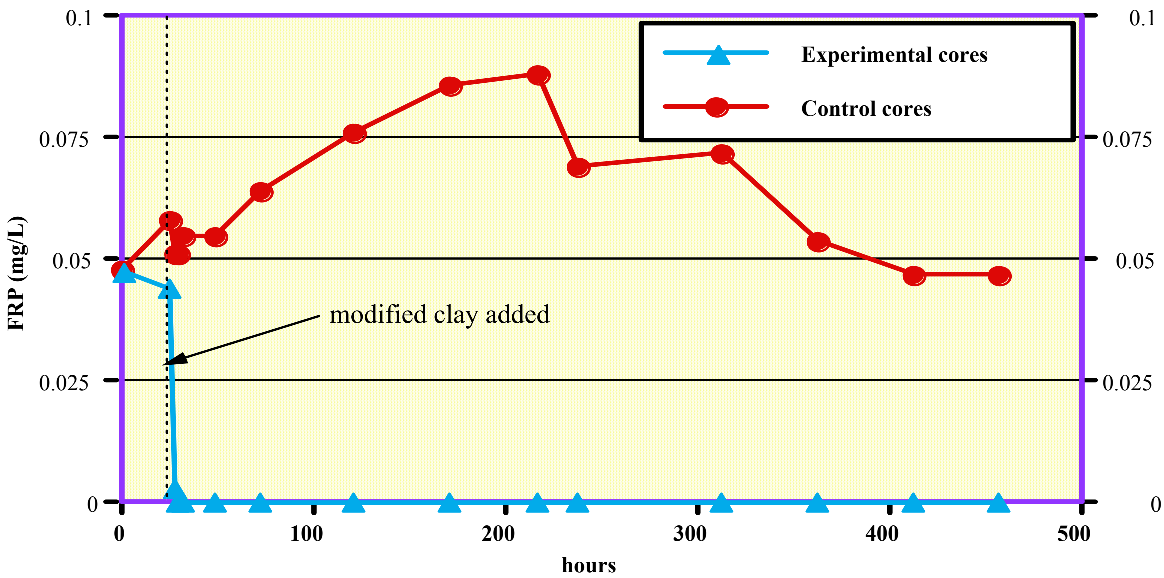

Figure 1. Reduction in filterable reactive phosphorus (FRP) in experimental cores from the Canning River due to the application of a modified clay.

Figure 2. Effect of modified clay in reducing filterable reactive phosphorus (FRP) and consequent algal growth in a sediment core from the Swan River Estuary. Note the partially oxidized surface layer of the sediment and the extensive worm burrows in both cores.

As a result of the promising performance of the modified clay in reducing FRP in a variety of trials in the laboratory a number of small field trials were conducted. These trials centered on the use of small mesocosms (*ca.* 1m in diameter) in the Swan and Canning Rivers and Lake Monger. These trials demonstrated that FRP could be reduced in the water column within the mesocosm by up to *ca.* 90% in periods up to seven weeks [7].

In late 1997 and early 1998, a major trial of the modified clay was undertaken, using two *ca.* 5m diameter mesocosms (Figure 3). The trials were undertaken in Lake Monger, a large suburban lake in Perth subject to extensive point and diffuse nutrient inputs and with a long history of persistent algal blooms over the spring/summer months.

Modified clay was added to the experimental mesocosm six days after the commencement of the trial and this resulted in a large and rapid reduction in the overlying water of the filterable reactive phosphorus (FRP) concentration within the first 24 hours (Figure 4). This initial reduction was primarily due to the removal of FRP from the water column during the settling of the modified clay. Thereafter the modified clay formed a thin adsorptive ('reactive') capping on the Lake Monger sediments.

The reduction of the FRP concentration was sustained in the experimental mesocosm up to day 73. In contrast, FRP concentrations within the control mesocosm exceeded 3.5 mg/L by day 73. It appears that a driving force behind the flux of nutrients into the water column may have been the small, positive groundwater flux measured in Lake Monger.

A measure of the absolute reduction in both FRP and total phosphorus (TP) in the experimental relative to the control mesocosm is given in Figure 5. The absolute reduction of phosphorus species in the experimental mesocosms due to the application of the modified clay in the period day 6 to day 73 was *ca.* 94-100% for FRP and 83-96% for TP of that in the control mesocosm. Significantly, there was little or no change in the concentration of other nutrients of major water quality parameters. Thus, apart from the desired reduction in FRP, little other perturbation to the water quality occurred [7].

As a consequence of the substantial reduction in FRP, there was a major change in the total inorganic nitrogen (TIN) to filterable reactive phosphorus (FRP) molar ratios (TIN/FRP) within the mesocosms (Figure 6). In addition to the probable change from nitrogen to phosphorus limitation of algal growth that occurred due to the reduction in phosphorus, the major change in TIN/FRP molar ratios present a possible shift in prevailing algal species away from blue-green algal blooms. These possible changes in nutrient limitation and species of algae are of major ecological significance.

Figure 3. Large (*ca.* 5m diameter) mesocosms being placed into Lake Monger

3. Patenting, Intellectual Property and Commercilization

Provisional patents have been lodged both nationally and internationally which broadly cover the research, development and potential applications of the modified clay and related mineral-based materials jointly developed by CSIRO Land and Water and the Water and Rivers Commission/Swan River Trust. Commercial partners have been sought to assist in the manufacture and/or marketing of the modified clay. The commercialization process is on-going, commencing in late 1998.

4. Conclusions

A modified clay has been developed that has been demonstrated to be able to substantially reduce the concentration of FRP in a variety of natural and wastewaters under batch-test conditions. Laboratory-based sediment core trials also indicate that the modified clay can reduce the concentration of FRP in waters overlying the sediment for periods of up to 19 days. A large-scale mesocosm trial indicated that the modified clay was able to reduce FRP (and TP) concentrations in the experimental mesocosm by approximately 90%. Further large-scale field trials will be conducted to validate the performance of the modified clay in typical field conditions in sites impacted by diffuse and/or point sources of nutrient pollution. These trials are likely to be conducted in late 1999/early 2000. In addition, research will also be conducted into methods of preparation and delivery the modified clay.

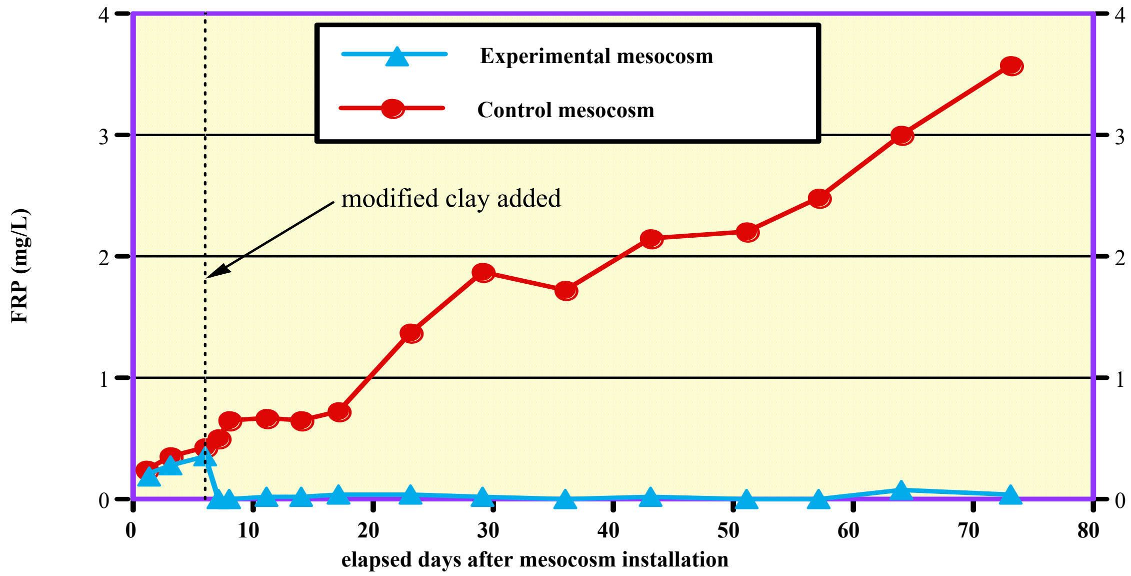

Figure 4. Mean filterable reactive phosphorus concentration (FRP) in the control and experimental mesocosms in the Lake Monger large-scale mesocosm trial.

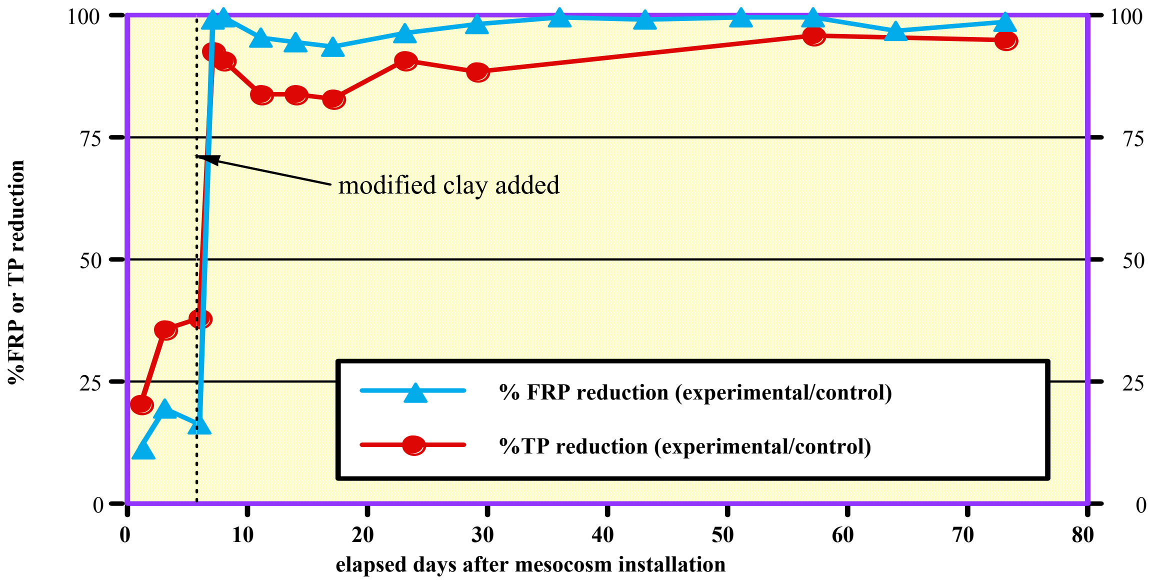

Figure 5. Percentage reduction in mean filterable reactive phosphorus (FRP) and total phosphorus (TP) concentration in the experimental relative to the control mesocosm in the Lake Monger large-scale mesocosm trial.

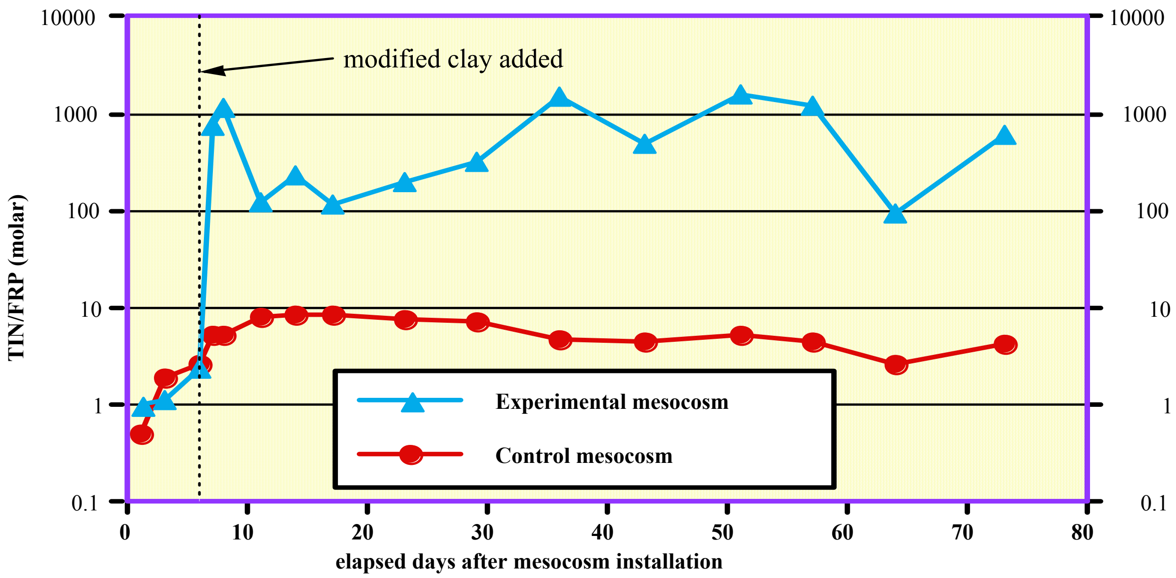

Figure 6. Mean total inorganic nitrogen (TIN) to filterable reactive phosphorus (FRP) molar ratio (TIN/FRP) in the experimental and control mesocosms in Lake Monger mesocosm trial.

5. References

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