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Application of Phoslock^{TM}, an innovative phosphorus binding clay, to two Western Australian waterways: preliminary findings

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Abstract

Phoslock^{TM} is a specially modified clay designed to permanently bind phosphorus in those situations where phosphorus (P) release from sediments is a main driver of algal bloom formation. Extensive laboratory and mesocosm trials have demonstrated the effectiveness of Phoslock^{TM} in binding sediment released P using less than a millimetre thickness of clay. Two full-scale applications were undertaken in the summer of 2001/2002 in the impounded riverine section of two estuaries along the coastal plain of south west Western Australia. Both rivers are subject to blue-green algal blooms in the summer months. Phoslock^{TM} applied in a slurry from a small boat reduced dissolved P in the water column to below detection limit in the few hours it took for the clay to settle and substantially reduced P efflux from the sediments during the course of the trial. The effect of P reduction on phytoplankton growth was clearly evident in the phytoplankton dominated Vasse River but was less clear in the alternating phytoplankton to aquatic plant dominated Canning River which is also subject to surface nutrient inputs.

Introduction

Eutrophication is a common feature of many Australian waterways – lakes, rivers, wetlands and estuaries – with a propensity to cyanobacterial blooms (Jones, 1994). The combination of high nutrient delivery from both urban and agricultural sources and impoundment in shallow water bodies during hot dry summers greatly exacerbate the symptoms of eutrophication.

A history of phytoplankton activity and organic matter accumulation ensures that internal nutrient loading is a significant source of nutrients to fuel subsequent phytoplankton activity in these impounded water bodies. In Western Australia, settlement of estuarine and riverine floodplains has required extensive drainage in some urban areas. In the agricultural catchments of these floodplains overclearing has led to rises in the groundwater table necessitating drainage back to the receiving water body which in the case of the two study areas is the impounded portion of an estuary. For many years the prevailing dogma in Australia has been that both freshwater and estuarine waterways were phosphorus limited with respect to phytoplankton (Harris, 1997), however recent studies (Thompson, 1998; Hart & Grace, 2000) have shown nitrogen limitation in almost all waterways in which phytoplankton bioassays have been conducted.

Given the recognized role of sediment nutrient supply in summer phytoplankton activity, the Water and Rivers Commission (WRC) and their research partner, the Commonwealth Scientific and Industrial Research Organization (CSIRO) developed a modified clay (Phoslock^{TM}), to work under a wide range of environmental conditions (pH ca. 5–10) including anoxia (Douglas, 1999).

This paper describes the preliminary results of full scale Phoslock^{TM} applications in two freshwater systems in Western Australia, both of which are riverine portions of estuaries impounded by wooden weirs to maintain a freshwater environment during the summer for mainly urban populations. As a consequence both are subjected to summer cyanobacterial blooms although the dynamics of the two systems are quite different. The Canning River alternates between the states discussed by Moss (1990), clear to turbid water macrophyte domination and turbid phytoplankton domination, whereas the Vasse River is at all times a turbid phytoplankton dominated system. In both water bodies concentrations of dissolved P ($PO^{3-}{}_4$) measured as filterable reactive phosphorus (FRP) and total phosphorus (TP) in bottom waters were higher than surface waters. Canning River data for the period 1994–1998 are shown in Fig. 2.

The objectives of the current study were to (1) determine application rates and timing with respect to summer rainfall and other variables; (2) evaluate use of Phoslock^{TM} in removing dissolved phosphorus (P) from the water column as well as to intercept sediment derived dissolved P; and (3) explore the effect of reduction of P availability on phytoplankton activity. The ability of Phoslock^{TM} to bind P has been well established through extensive laboratory and mesocosm trials (Douglas & Coad, 1997; Douglas, 1999); the challenge was to determine whether sufficient P could be removed to limit phytoplankton activity given that the surface and groundwater delivery of P were uncontrolled.

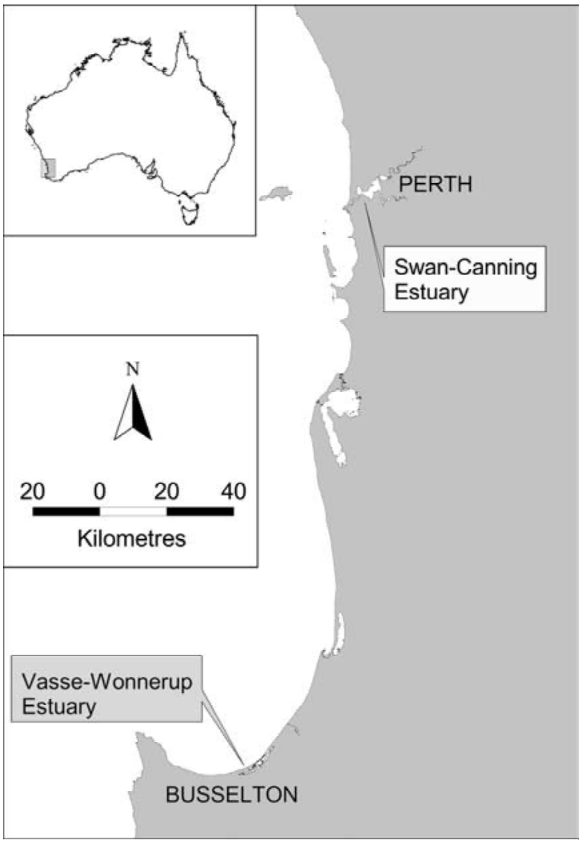

Figure 1. Both the Swan Canning and Vasse Wonnerup estuaries lie on the Swan Coastal Plain of Western Australia.

Methods

Study locations

The Canning River drains a rural to semi-rural upper catchment and an urban and industrial lower catchment to empty into the Swan–Canning Estuary in the city of Perth (see Fig. 1).

A water supply reservoir upstream and water abstraction by riparian water users results in little to no flow upstream of the weir during the period of impoundment (October–May). Water depths for 2 km behind the weir range from 1 to 3 m with one 5-m depression. Water is mainly fresh and summer water temperatures are high reaching 26 °C at the bottom and 29 °C at the surface. Thermal stratification leads to hypoxic and sometimes anoxic conditions.

Hypolimnetic oxygenation of the Canning River above the Kent St weir through subsurface diffusers has been successful over the last 3 years in reducing anoxia (especially in response to summer rain events), improving nitrification and denitrification efficiencies, and suppressing P efflux from the sediment (Greenop & Robb, 2001). Since previous trial applications of Phoslock^{TM} into the Canning River (Douglas & Adeney, 2001) indicated that Phoslock^{TM} was very effective when combined with oxygenated treatment, hypolimnetic oxygenation was continued throughout the current study.

The Vasse River flows through the town of Busselton to Geographe Bay through mixed farming and horticulture country (Fig. 1). Over 90% of the flow from the Vasse River catchment is now diverted directly into Geographe Bay and away from the lower Vasse River by the Vasse diversion drain to allow the town of Busselton to expand onto flood prone land. The net consequence is that the river is not subject to winter flushing flows resulting in substantial accumulation of fine sediment and organic matter. Water quality in the river is extremely poor with high nutrient concentrations in summer and autumn and cyanobacterial blooms sufficient to close the river to recreation through the summer. Mean TP concentrations have ranged from 170 μg l^{-1}during 1996–1998 to 330 μg l^{-1} during 1998–2000.

Phoslock^{TM} application and monitoring

Phoslock^{TM} is still in the pre commercial stage in which the clay is produced as a slurry which is then applied from a small boat through a spray manifold. The boat is resupplied from a shore-based tank. To both periodically remove P from the water column and to intercept sediment efflux an initial application of sufficient clay to produce a 0.5-mm thickness was applied, followed by additional applications through the water column in response to seasonal events. The intent was to apply a 1-mm thickness over the course of the summer. Areas to be treated were located adjacent to the weir boards in the historically worse area for blooms and control or untreated locations were selected upstream.

Extensive monitoring programs were established for the trials. Water samples were collected from surface and bottom waters for analysis of total nitrogen TN, dissolved inorganic nitrogen (DIN consisting of NO_x, NH_3), TP, silicate, dissolved organic carbon (DOC) and chlorophyll *a*. Samples for analysis of dissolved species were field filtered and shipped on ice along with the unfiltered samples under Chain of Custody to Australian Environmental Laboratories in Perth where analyses were performed according to American Public Health Association Standards (APHA, 1998). Measurements of physical variables such as temperature, conductivity, pH and dissolved oxygen (DO) were taken with Hydrolab multiprobe sondes on the Canning River and with a WTW (Wissenschaftlich Technische Werkstätten) multiprobe on the Vasse River. Phytoplankton samples were integrated over the water column consisting of three composites per site and enumerated for dominant species using a glass Sedgewick-Rafter chamber under $\times 400$ magnification.

On the Vasse River weekly sampling at seven sites in both the treated and untreated areas commenced three weeks prior to treatment and increased to twice weekly in the week prior to treatment and the week immediately after treatment. During the Phoslock^{TM} applications, two to three sets of samples were taken at 2 h, 6 h and one day after application. Sampling continued for 29 weeks after the first application. Sampling in the Canning occurred at the same frequency over 27 weeks at 18 sites.

Additional water samples were collected for phytoplankton bioassays using the all but one nutrient addition technique of Thompson (1998) wherein leaving out one nutrient from a full media recipe (Fe, N , P, Si) gives a measure of how much of the missing nutrient was available. Previous bioassay work on the Canning (Thompson et al, in press) showed that trace metals and vitamins were never limiting. Samples were collected at one treated and one untreated site in both the Vasse and Canning Rivers at 2-weekly intervals.

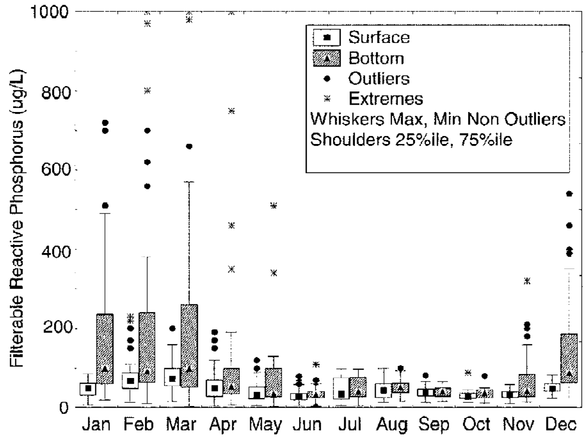

Figure 2. Median concentrations of FRP in both surface and bottom waters of the Canning River in the period 1994–1998.

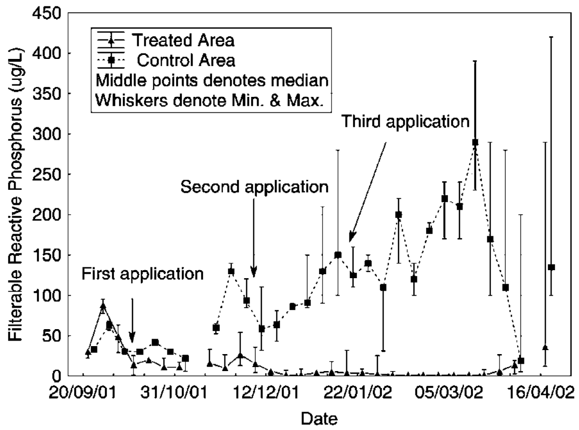

Figure 3. Bottom water median concentrations of FRP at both treated and untreated sites in the Vasse River.

Results

Vasse River

An initial application of 20 tonnes (dry weight equivalent) Phoslock^{TM} (specific gravity=2.2) was made to a 650-m section of the Vasse River during October 2001, with two subsequent applications of 10 tonnes each in December 2001 and January 2002.

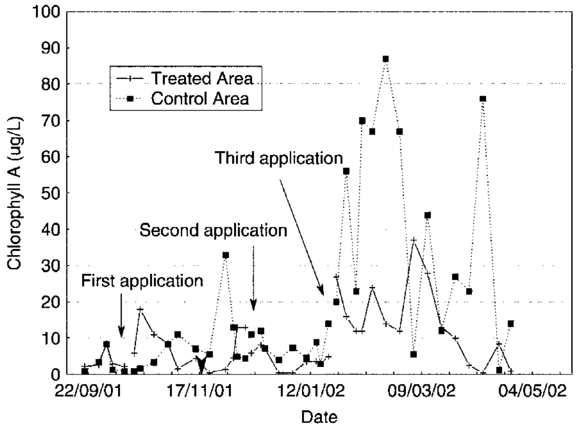

Figure 4. Chlorophyll *a* concentrations at both treated and untreated sites in the Vasse River.

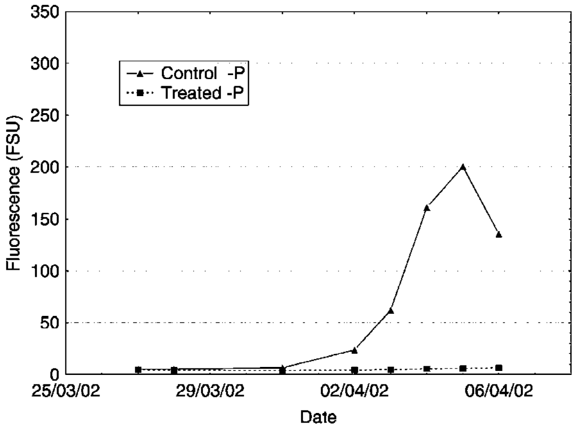

Figure 6. Phytoplankton bioassay results for the treated site showing P limitation as compared to the untreated site.

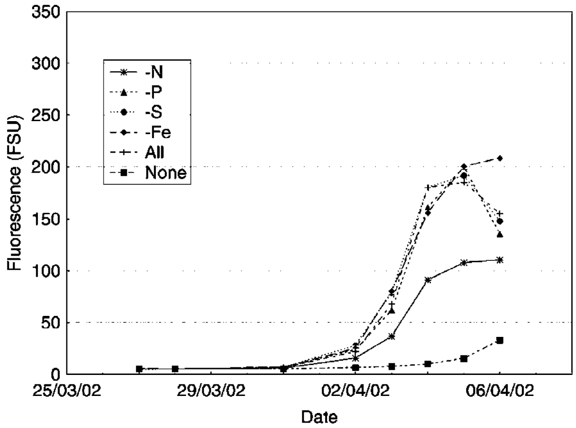

Figure 5. Phytoplankton bioassay results using the all but one technique for the untreated site showing N limitation and P availability.

Prior to the first application of Phoslock^{TM} concentrations of FRP in the surface and bottom waters in both the treated and control areas were of a similar magnitude (Fig. 3). Throughout the experiment the similar magnitude of surface and bottom water concentrations of FRP and physical parameters at all sites indicated a well mixed river. A decrease of FRP in the treated area from about 50 μg l^{-1}to about 20 μg l^{-1}was observed after the first application. More significantly, as FRP concentrations in the untreated areas increased to concentrations approaching 200 μg l^{-1}, concentrations in the treated area remained low and reached the detection limit of 5 μg l^{-1}after the second treatment. In the treated area FRP concentrations were lower compared to the untreated area for 194 days.

Phytoplankton growth as measured by Chl *a* did not show such a clear trend (Fig. 4). Concentrations in both the treated and untreated areas fluctuated around 10 μg l^{-1}Chl *a* until the summer heat increased growth rates to visible bloom activity. Chl *a* in the treated areas fluctuated around 30 μg l^{-1}and reached a maximum of 80 μg l^{-1}.

Phytoplankton blooms did develop late in the summer showing higher total counts in the untreated area compared to the treated but the species mix was quite different between the two areas. In the untreated area nitrogen fixing cyanobacteria predominated (*Anabaena* circinalis) and in the treated area non nitrogen fixing cyanobacteria were common.

Phytoplankton bioassay results for the untreated area (Fig. 5) showed nitrogen limitation as indicated by no growth in the 'none' treatment and no growth in the all but nitrogen treatment. Strong growth without any additional phosphorus indicated abundant available phosphorus. In the treated area, the all but phosphorus treatment was virtually the same as the none and the all but nitrogen treatments, indicating a reduction in bioavailable phosphorus of ca 96%: nitrogen and phosphorus were co-limiting (see Fig. 6).

Canning River

An initial application of 30 tonnes of Phoslock^{TM} was made to a 1.5-km section in November 2001, after the weir boards were in place and flow had diminished. Application was interrupted for 2 weeks due to light rain which increased flow over the weir. A subsequent application of 15 tonnes was made in January 2002 at the onset of hot weather. A third application of 15 tonnes was held in abeyance with the intention of dosing the river following a summer rain event, which did not occur. The entire treated area was oxygenated via

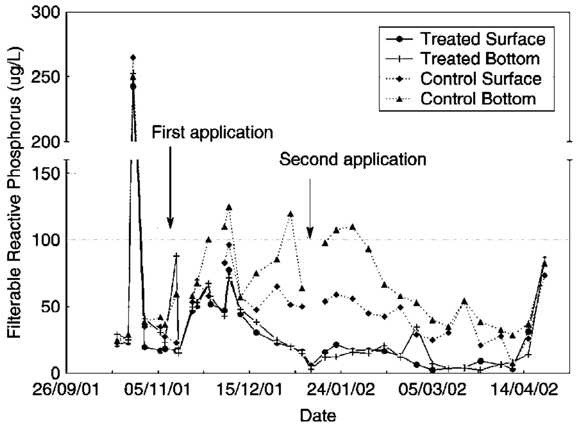

Figure 7. FRP concentrations in the Canning River untreated and treated sites for surface and bottom waters.

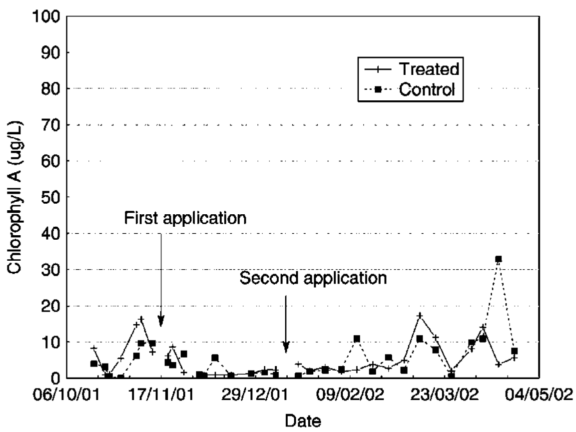

Figure 8. Chlorophyll *a* concentrations at both treated and untreated sites in the Canning River.

the hypolimnetic diffusers during the trial period and bottom water oxygen concentrations were maintained at 5 mg l^{-1}.

Reductions in concentrations of FRP after Phoslock^{TM} application were less clear in the Canning than in the Vasse although reductions in both surface and bottom FRP did occur. Average concentrations in the untreated area (across all sites) for both surface and bottom waters are shown in Fig. 7. Bottom water FRP concentrations in the untreated area (across all sites) were higher than the surface throughout most of the trial, becoming low in both and surface and bottom waters towards the end of the trial.

In the treated area (see Fig. 7), average FRP concentrations (across all sites) dropped in both surface and bottom waters after Phoslock^{TM} application but remained above the detection limit of 5 μg l^{-1} until the end of the trial. Chlorophyll *a* concentrations (Fig. 8) fluctuated in both treated and untreated sites with no discernible difference between the two areas. Phytoplankton bioassay results for two dates at treated and untreated sites showed N to be the most limiting nutrient, generally an order of magnitude more limiting than P which was most available at the untreated site.

Discussion

Although these data are preliminary it would appear that a substantial shift in phosphorus availability was affected at both Vasse and Canning trial sites with clear results from the Vasse and at first examination, less clear results from the Canning. As noted in previous trials, Phoslock^{TM} application reduced not only bottom water but also surface water P concentrations. There is some evidence that FRP was progressively removed from water as the slow flow of the Canning River and wind movement brought elevated FRP water from the control areas through the treated area.

For both trial areas Phoslock^{TM} was applied in the historically worse area for blooms adjacent to the weir boards and the untreated areas selected upstream of the treated areas historically showed less bloom activity as measured by phytoplankton cell counts. In the Vasse River it was clear from the nutrient chemistry, phytoplankton bioassay, and phytoplankton taxonomic results that the application of Phoslock^{TM} had changed the system. Most striking was the lower chlorophyll *a* concentrations in the treated areas with respect to the control and the shorter duration of the bloom activity. The Vasse River appeared relatively unaffected by surface drainage during the course of the trial. Although a phytoplankton bloom discoloured the water in the treatment site potentially toxic species were in low concentrations compared to the untreated site. Additional analysis of the extensive data set is required to determine the significance of this species shift.

In the Canning River the emergent macrophyte *Potamogeton* crispus grew prolifically in the early part of the summer throughout the treated area and part of the untreated area but died off in the hot temperatures of January and February. Competition for nutrients between aquatic plants and phytoplankton appears to determine (Vincent, 2001) whether this linear lake is either dominated by the semi-emergent macrophytes *Potamogeton* crispus, *Hydrilla* verticillata and floating plants such as *Azolla* and *Lemna* or is a turbid phytoplankton (*Anabaena, Anabaenopsis*) dominated system during the hotter summer months. Populations of large *Ceriodaphnia* spp noticed in phytoplankton samples collected in the river in reaches colonized by *Potamogeton* disappeared as the *Potamogeton* collapsed. The clear water was quickly dominated by phytoplankton and floating plants such as *Azolla* sp. and *Lemna* sp. which were moved back and forth within the weir pool by prevailing winds.

The loss of grazers and the rapid recycling of nutrients from the collapsing aquatic plants may partly explain the phytoplankton growth in the treated areas. Nutrient delivery from drainage waters entering into the treated area were the suspected cause of higher P and N concentrations at one of the treated sampling sites. From previous studies (WRC, unpublished) there appears to be rapid conversion of FRP to organic P (as seen in the increase of TP) as a result of biological uptake. During short periods of anoxia (during shutdown of the hypolimnetic oxygenation) elevated P concentrations in bottom water were not observed in contrast to previous years when bottom water P peaks corresponded to the onset of anoxia.

Consideration of the sediment distribution and the pattern of Phoslock^{TM} application suggest an additional possibility. The thickest accumulation of P and organic rich sediment in the treated areas was seen, in previous studies, to be at the margins of the channel. To provide refuge for the Swan River Goby and to avoid smothering of the emergent aquatic plants, Phoslock^{TM} was not applied close to the emergent leaves along significant portions of the banks. It is thus possible that insufficient sediment coverage was achieved with the Phoslock^{TM} application, explaining the slow drop off of FRP when compared to the rapid response observed in the Vasse River.

The higher flow and lower dosing rates in the Canning may also explain the difference between the two areas. In the Vasse the theoretical 1 mm dry equivalent of Phoslock^{TM} was achieved, whereas in the Canning less than 0.5 mm dry equivalent was applied.

Summary

In phytoplankton dominated waters such as the Vasse River, reducing the efflux of P from the sediments can alter the overall P availability, reduce phytoplankton biomass and cause a change in phytoplankton species composition. The significance of these changes has yet to be examined. In macrophyte dominated systems, interception of sediment derived P is more complex requiring good ecosystem understanding to guide the timing and quantity of Phoslock^{TM} application.

Phoslock^{TM} is effective in intercepting P released from the sediments and can strip dissolved P from the water column when applied as a slurry. Applying successive treatments throughout the summer with the first application prior to bloom formation appears to be an effective strategy in managing P concentrations in the water column. Retaining Phoslock^{TM} for treatment after summer rain also appears to be sound strategy and aiming for 1mm dry equivalent Phoslock^{TM} to bottom sediment is advised.

From this and previous studies, however, it is clear that this technique will only be effective in controlling algal blooms in combination with source control and sensible catchment management. Future work will explore the use of Phoslock^{TM} in the treatment of waste streams such as urban and rural drains, and agricultural sources as an adjunct to improved site management practices.

References

Douglas, G. B. & J. A. Adeney, 2001. 2000 Canning River Phoslock^{TM} trial. Confidential report prepared for Water and Rivers Commission. CSIRO Land and Water Report January, 2001: 75 pp.

Douglas, G. B. & D. N. Coad, 1997. Review of estuarine sediment remediation techniques. Confidential Report prepared for Water and Rivers Commission. CSIRO Division of Water Resources Report (96–11). 81 pp. Revised October, 1997: 96 pp.

Douglas, G. B., J. A. Adeney & M. S. Robb, (1999). A novel technique for reducing bioavailable phosphorus in water and sediments. International Association Water Quality Conference on Diffuse Pollution: 517–523.

Greenop B., K. Lovatt & M. Robb, 2001. The use of artificial oxygenation to reduce nutrient availability in the Canning River, Western Australia. Wat. Sci. Technol. 43(9): 133–144.

Harris, G. P., 1997. Algal biomass and biogeochemistry in catchments and aquatic ecosystems: scaling of processes, models and empirical tests. Hydrobiologia 349: 19–26.

Hart, B. & M. Grace, 2000. Nitrogen Workshop 2000: Sources, transformations, effects and management of nitrogen in freshwater ecosystems. CSIRO Land and Water Australia. Occasional Paper 10/00.

Jones, G. J., 1994. Bloom forming Blue Green Algae (Cyanobacteria). In Sainty, G. & S. Jacobs (eds), Aquatic Plants of Australia. Sainty and Associates, Sydney NSW: 264–285.

Moss, B., 1990. Engineering and biological approaches to the restoration from eutrophication of shallow lakes in which aquatic plant communities are important components. Hydrobiologia 200/201: 367–377.

Thompson, P. A., 1998. Spatial and temporal factors influencing phytoplankton in a salt wedge estuary, the Swan River, Western Australia. Estuaries 21: 801–887.

Thompson. P. A., A. Waite & K. McMahon, Dynamics of a cyanobacterial bloom in a hypereutrophic, stratified weir pool. Mar. Freshwat. Res. (in press).

Vincent, W. J., 2001. Nutrent partitioning in the upper Canning River, Western Australia, and implications for the control of cyanobacterial blooms using salinity. Ecol. Eng. 16: 359–371.