



The science behind the Swan-Canning Cleanup Program Issue 17, June 2001

# Phosphorus in the Canning– 1999-2000 Phoslock<sup>™</sup> trials

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Spraying Phoslock™ on the Canning River, January 2000

#### Overview

A large scale trial of Phoslock<sup>TM</sup> in the Canning River was implemented by the Swan River Trust, the Water and Rivers Commission and CSIRO Land and Water in January 2000 as part of the Swan-Canning Cleanup Program. The main objective of this trial was to determine whether the application of Phoslock<sup>TM</sup> could significantly reduce the bioavailability of phosphorus in the water column and in sediments of the Canning River.

### What is Phoslock<sup>™</sup>?

Phoslock<sup>TM</sup> is a modified clay that can reduce the dissolved phosphorus available to phytoplankton.

Extensive laboratory and mesocosm experiments, and a major field experiment, have demonstrated

that Phoslock<sup>TM</sup> is capable of reducing dissolved phosphorus concentrations under a wide range of pH and dissolved oxygen conditions. A distinguishing feature of Phoslock<sup>TM</sup> is its ability to bind dissolved phosphorus under the anoxic conditions experienced by many eutrophic waterways.

Phoslock<sup>™</sup> is applied as a slurry to surface waters and forms a reactive layer (typically 1 mm in thickness) on bottom sediments to bind dissolved phosphorus as it is released into the overlying water. Phoslock<sup>™</sup> also acts fast enough to bind dissolved phosphorus as it settles through the water column.





Application study area on the Canning River, Perth, Western Australia

### The Canning River

The Canning River is part of the Swan-Canning system, which is located on the Swan Coastal Plain in Western Australia. The Canning River is partially impounded by the Kent Street Weir during the summer months. As a result, water upstream of the weir remains fresh, and there is little flow during this time. The river sediments are the main source of nitrogen and phosphorus during the summer, and anoxia is common. Due to plentiful sunlight, little wind and high nutrient concentrations, the conditions of the Canning River are conducive to the prolific growth of phytoplankton, especially toxic blue-green algae (cyanobacteria).

### Trial details

This trial involved the application of 40 tonnes of Phoslock<sup>TM</sup> slurry to an 800 m section of the Canning, equating to a thickness of 1 mm on the river bed. Subsurface curtains were used to separate the trial area into three zones: Phoslock<sup>TM</sup> treated; Phoslock<sup>TM</sup> combined with oxygenation; and an untreated control zone.

The Phoslock<sup>TM</sup> was applied from 5 to 12 January 2000. A small aluminium boat was used to distribute the Phoslock<sup>TM</sup>, which was pumped from an onboard tank through a spray system mounted on the stern of the boat. Oxygenation did not commence in the oxygenated area until 15 February 2000.

An extensive sampling program was conducted to assess the effectiveness of Phoslock<sup>™</sup> in reducing phosphorus concentrations, and to assess if there were any wider environmental impacts.

### 1999/2000 — A summer of contrasts

In the month preceding the trial, Perth experienced its hottest December on record, with an average maximum temperature of  $32.4^{\circ}$ C. As a consequence the Canning River was almost stagnant and the warm conditions were creating the ideal environment for a phytoplankton bloom, which was just forming when the Phoslock<sup>TM</sup> was applied on 5 January 2000.

An unexpected event was the intrusion of saline water above the Kent Street Weir. Salt water was



Spraying Phoslock on the Canning River. The milky colour produced by the clay disappears after 1-2 days as the clay settles

detected in the usually fresh weir pool in December, as high water levels downstream of the Weir pushed water over the Weir boards. At the time of Phoslock<sup>TM</sup> application, bottom water salinity was 6–10 ppt throughout the Phoslock<sup>TM</sup> trial area. Surface water was still fresh, with a halocline at 1–1.5 m.

On 15 January 2000, the weather changed dramatically, with 13 mm rainfall followed by a downpour of 75 mm on 22–23 January 2000. Rainfall of 102 mm was recorded for the month, compared to the average of 9 mm, making January 2000 the wettest January on record. The rainfall resulted in the flushing of the Phoslock<sup>TM</sup> treated areas with more than 100 times the volume of the impounded water above Kent Street Weir.

## Significant reductions in phosphorus were achieved

When Phoslock<sup>TM</sup> was applied, initially to the Phoslock<sup>TM</sup> only area, concentrations of filterable reactive phosphorus (FRP) declined rapidly, falling below detection limits. This represented the removal of at least 95% of the FRP present in the water

column. FRP is the fraction of phosphorus in water that is immediately available to algae. At this stage there was no oxygenation treatment, so the two trial areas were identically treated. The FRP concentrations in the Phoslock<sup>TM</sup> and oxygenation treatment area declined in a similar manner to the Phoslock<sup>TM</sup> only area after the application of Phoslock<sup>TM</sup> approximately one week later. The low FRP concentrations in the Phoslock<sup>TM</sup> treated areas were maintained from the start of the application until runoff from surrounding areas following rain on 15 January 2000 began to affect water quality. With this rainfall FRP concentrations rose rapidly and then decreased as the first flush of nutrients was washed through by runoff from sustained rainfall.

The monitoring of an untreated control area allowed the Phoslock<sup>TM</sup> treated areas to be compared with ambient conditions. In the initial period before the rain events, FRP concentrations in the control area also fell slightly, but were still an order of magnitude greater than those in the Phoslock<sup>TM</sup> only area. Spraying Phoslock on the colour produced by the clay as the clay settles.



Figure showing changes in FRP concentrations with time. The grey shaded area shows relative flow rates in the Canning River. Point 1 is the application of Phoslock on 5 January 2000. Point 2 is the first rainfall and first flush of nutrients. At point 3 high flow rates flush the trial area. At point 4 FRP concentrations in the bottom water of Phoslock treated areas are consistently less than those of the control area.



Phoslock<sup>TM</sup> forms a reactive layer on the sediment that binds phosphorus as it is released from the decomposition of organic matter, or transported into the water body from the catchment. This reduces

The size and duration of the FRP reductions after the rain events are promising because they imply that Phoslock<sup>TM</sup> was still binding FRP being released from the sediment, and thus significantly reducing FRP concentrations in the water column. This is despite the water initially treated with Phoslock<sup>TM</sup> being flushed out of the trial area, additional nutrients being imported from upstream, the probable loss of some Phoslock<sup>TM</sup>, and its mixing and burial in the sediments. Other factors that affected FRP concentrations are discussed below:

#### Dissolved oxygen concentrations

In the presence of high dissolved oxygen concentrations, dissolved phosphates (of which FRP is a direct measure) may bind with iron oxy-hydroxides. Under anoxic conditions iron oxy-hydroxides may dissolve, releasing the phosphorus bound to them. However, phosphorus bound to Phoslock<sup>TM</sup> stays bound under anoxic conditions.

Throughout the trial a number of factors affected the dissolved oxygen status of the water column. Firstly, the presence of a saline bottom layer limited mixing of the water column, resulting in low oxygen conditions until the treatment areas were flushed with fresh water.

The oxygenation plant commenced operation on 15 February 2000. The median bottom dissolved oxygen concentration in the Phoslock<sup>TM</sup> and oxygenation area for the remainder of the monitoring period was 5 mg/L, compared to 1 mg/L prior to oxygenation. The first substantial divergence between FRP concentrations in the Phoslock<sup>TM</sup> and oxygenation area relative to the Phoslock<sup>TM</sup> only area was noted after the commencement of oxygenation.

### Progressive reduction through treatment area

After the flow event, it became apparent that FRP concentrations in the Phoslock<sup>TM</sup> and oxygenation area were substantially lower than in the Phoslock<sup>TM</sup> only area. This was probably because the water, which was moving very slowly downstream, had already been treated in the Phoslock<sup>TM</sup> only area, prior to further FRP reduction in the Phoslock<sup>TM</sup> and oxygenation area. Additional FRP reduction may have occurred due to active oxygenation after 15 February 2000.

### Phosphorus uptake by phytoplankton

Phytoplankton use phosphorus as they grow. Thus, an absence of FRP may mean very clean water, or it may indicate a raging phytoplankton bloom! However, during the Canning River trial increases in phytoplankton biomass were not responsible for reduced FRP concentrations in the Phoslock<sup>TM</sup> treated areas. Prior to the rainfall events, FRP concentrations were still high with phytoplankton present, but following the application of Phoslock<sup>TM</sup> were reduced by more than 95%. After the rainfall phytoplankton concentrations remained low.

#### Aquatic plant growth

At various times during the summer in the Kent Street Weir pool, it is usual for dense beds of the rooted aquatic plant *Potomogeten crispus* to appear, proliferate, and then die out. As *Potomogeten* grows it draws phosphorus from the sediment and so, like Phoslock<sup>™</sup>, prevents phosphorus in the sediment from being released into the water. When the *Potomogeten* dies the nutrients it contains may be released as it decomposes.

Before the Phoslock<sup>TM</sup> trials commenced, dense beds of *Potomogeten* present in both the Phoslock treatment area and the control area were beginning to die back, and by 10 March all had disappeared. However, by 31 March the *Potomogeten* had regrown and once again covered most of the treated and control areas. Since the *Potomogeten* was similarly abundant in both control and Phoslock<sup>TM</sup> areas, and because it was dying back when Phoslock<sup>TM</sup> was applied, its presence was not likely to impact on the overall results of the trial.

## Transformation to organic or particulate phosphorus

FRP is not the only form of phosphorus present in the environment. Phosphorus may also be bound to particles or contained in organic matter, including that already present within phytoplankton cells. A potential exists for all of this phosphorus to become bio-available over time. Total phosphorus (TP) measurements were used to determine the total of the different forms of phosphorus present in a water sample.

After the Phoslock<sup>TM</sup> was applied, there were significant reductions in TP (see Table 1). Following the rainfall events, TP concentrations in the Phoslock<sup>TM</sup> treated areas again declined to levels that were significantly lower than those in the control area. The significant reduction in total phosphorus concentrations is further evidence that FRP in the water had been bound to Phoslock<sup>TM</sup> and buried in the sediment. If the FRP had, for example, just been incorporated into phytoplankton biomass, there would have been no reduction in total phosphorus concentrations.

**Table 1:** Average reduction in FRP (+/- 1 std dev) in Phoslock<sup>™</sup> treated areas compared to control section

Phoslock™	Bottom FRP	Bottom TP	Surface FRP	Surface TP
	Percentage reduction – first period – pre-flood			
Phoslock <sup>™</sup> only	56 ± 49	21±53	55 ± 34	-
Phoslock™ + oxygen	52 ± 34	43 ± 28	63 ± 28	19 ± 20
	Percentage reduction – second period – post-flood			
Phoslock <sup>™</sup> only	36 ± 32	-	24 ± 29	20 ± 32
Phoslock™ + oxygen	63 ± 19	44 ± 17	48 ± 23	29 ± 29



Figure illustrating the length of time for which there were significant reductions in FRP in the Phoslock treated area compared to control area. The grey shaded area indicates relative flow through the trial area.

## Effect of Phoslock<sup>™</sup> on phytoplankton growth

The major objective of applying Phoslock<sup>TM</sup> to the Canning River was to reduce the phosphorus available to phytoplankton, in order to limit their growth. Laboratory and mesocosm experiments have shown that Phoslock<sup>TM</sup> can do this, but the complexity and scale of even a small river such as the Canning brings many other variables into play.

Before Phoslock<sup>TM</sup> was applied, a phytoplankton bloom consisting mainly of blue-green algae had developed from Kent Street Weir to Nicholson Road bridge. This bloom was flushed from the treatment area by the rain events. The application of the Phoslock<sup>TM</sup> did not have a discernible impact on the bloom before it was flushed away by the rainfall, even though FRP concentrations were reduced to below detection limits. Why is this? The most probable cause is a mechanism that some phytoplankton (particularly cyanobacteria) employ, known as 'luxury uptake of phosphorus'. This simply means that when phosphorus is plentiful, phytoplankton will absorb more than their immediate needs require, as insurance against future scarcity. Researchers have shown that cyanobacteria can increase their biomass 4-32 fold using only their internal phosphorus stores. This means that some time lag between the application of Phoslock<sup>TM</sup> and response by phytoplankton, especially cyanobacteria, can be expected. The lack of phytoplankton response to the application of Phoslock<sup>TM</sup> in the 10 days before the rainfall started implies that the phytoplankton were surviving on their phosphorus reserves. Alternatively, there may have still been enough FRP available to sustain the phytoplankton in the short term.

After the rain event there were substantially more nutrients available than after the Phoslock<sup>TM</sup> was applied and conditions appeared favourable for growth, yet no blooms appeared. The blue-green algae present before the rain did not re-establish themselves. However, blue-green algae are often relatively slow growing and require stable conditions to form blooms. Other phytoplankton, such as certain species of green algae, respond much more opportunistically to a favourable change in conditions. There was evidence of localised phytoplankton growth in both the treated and control areas after the river flow subsided. These incidents were confined mainly to the Phoslock<sup>TM</sup> and oxygenation area, between 1–22 February. However,

densities of phytoplankton were generally low after the rainfall. Organisms that consume phytoplankton, such as zooplankton, may have been partly responsible for limiting phytoplankton densities during this time.

However, the atypical rainfall and flow during the trial period confounded the interpretation of the algal response to the application of Phoslock<sup>TM</sup>.

### Impact assessment shows Phoslock<sup>™</sup> benign

A comprehensive suite of indicators of environmental impacts, including fish, waterbirds, macro-invertebrates and periphyton, was measured before and after application of the Phoslock<sup>TM</sup>. Interpretation of the data collected was affected by a number of events including heavy rains, and a fuel spill upstream of the trial area soon after the application. However results showed that the application of Phoslock<sup>TM</sup> did not adversely affect populations of macro-invertebrates, freshwater shrimps or periphyton. In addition, this study also provided a guide for modifications to the application process, ensuring future applications are efficient and impact free.

### Microbial activity continues

Sampling of both total heterotrophic bacteria (bacteria that use organic material as a source of carbon and energy) and denitrifying bacteria (bacteria that gain energy from the transformation of nitrate to nitrogen gas) was undertaken to determine the response of the microbial community to the application of Phoslock<sup>TM</sup>. Results suggest that even with the application of the Phoslock<sup>TM</sup> there was sufficient phosphorus for microbial communities in both the water and sediment to function.



Above: Warning sign for phytoplankton bloom. On the Canning River these signs normally indicate the presence of cyanobacteria (blue green algae) in concentrations greater than 20 000 cells/mL





Anabaena scum on the Canning River, 1994. Severe algal blooms were experienced in the Canning River upstream of the Kent Street Weir in 1992, 1994 and 1997. These blooms result in the production of odours and the closure of the river to recreational use. The cyclical 'boom and bust' nature of phytoplankton blooms impacts on other aquatic flora and fauna, and results in a continuing deterioration of the health of the system. The small picture on the left shows a sample of the cyanobacteria Anabaena species under a scanning electron microscope.

### Negligible toxicity from Phoslock<sup>™</sup>

The development of Phoslock<sup>TM</sup> has included extensive pre-trial laboratory testing on a range of test species using United States Environmental Protection Authority toxicity testing criteria. This study showed there to be negligible toxicity to the test species.

The trial monitoring program also included a range of whole effluent toxicity tests designed to assess potential effects of the Phoslock<sup>TM</sup> on aquatic life. These tests performed by the CSIRO Centre for Advanced Analytical Chemistry assessed acute and chronic toxicity on the cladoceran Ceriodaphnia dubia, green alga Selanastrum capricornatum and juvenile eastern rainbow fish *Melanotaenia duboulayi*. No significant toxicity effects were observed in these test species.









### Conclusions

The January 2000 Canning River trial demonstrated, for the first time on a large scale, that Phoslock<sup>TM</sup> was effective at removing FRP released from the sediments, and was also effective at removing FRP from the water column as it settled.

FRP concentrations were reduced by at least 95% in the Phoslock<sup>TM</sup> treated areas until unseasonal rain events flushed the area.

Phoslock actively removed FRP after the normal flow conditions returned.

Extensive ecotoxicity studies showed Phoslock<sup>TM</sup> was not significantly toxic to test species.

### Future work

The results of this trial highlight the potential of Phoslock<sup>TM</sup> to substantially reduce FRP in aquatic systems. Theoretically, removing phosphorus so effectively from a eutrophic waterway should result in a decreased abundance of phytoplankton. However, as this trial has shown, the complexities of a natural system do not always allow a smooth transition from theory to practice. Further large scale trials, with the aim of establishing a link between the application of Phoslock<sup>TM</sup> and decreased phytoplankton abundance, are therefore a priority. The focus of further trials will be to apply Phoslock<sup>TM</sup> prior to the onset of a bloom with subsequent smaller applications to maintain low FRP concentrations.

The lack of alternative products with the capabilities of Phoslock<sup>TM</sup> means there are widespread potential applications in the fields of natural resource management and wastewater treatment. Potential uses that future work will examine are:

Drains, compensating basins, nutrient stripping basins and constructed wetlands. Drains are a major source of fresh nutrients for water bodies such as the Canning River, especially during summer. Compensating basins, nutrient stripping basins and constructed wetlands are often used as temporary storages for drainage water. Originally the intention was to prevent flooding, but they are increasingly being used to improve water quality before the drainage water enters major rivers or sensitive ecosystems. Phoslock<sup>TM</sup>, if applied appropriately, may improve the phosphorus removal capacity of these systems. A major challenge is designing and managing application techniques that create sufficient contact between the Phoslock<sup>TM</sup> and influent water for phosphorus to be removed.

*Treatment of waste from intensive agriculture and aquaculture.* Intensive agriculture can, if not properly managed, be a major point source of nutrients in the catchment. The closer to the source that these problems are dealt with, the better. Phoslock<sup>TM</sup> may offer a cost-effective treatment to effluent from dairies, piggeries, poultry farms and aquaculture. Development work in this field will continue with CSIRO Land and Water and industry partners.

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### For more information

More information on the Swan barge Project and the Swan-Canning Cleanup Program is available from the Swan River Trust.

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