

PHOSLOCK[®]

PRODUCT OVERVIEW



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We are world leaders in water remediation and help to improve water quality in the face of environmental, economic and human health challenges relating to phosphorus pollution.



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Phoslock Environmental Technologies (PET) is a global leader in the treatment and remediation of freshwaters, particularly those impacted by excessive phosphorus concentrations.

Our flagship product, Phoslock®, is a unique lake management tool which improves ecological structure and function in waterbodies.

Phoslock®, was developed by the The Commonwealth Scientific Industrial Research Organisation (CSIRO) in the 1990s. Once applied to freshwaters, Phoslock binds available phosphorus and makes it inert within the system.

It has been extensively researched by independent experts as having distinct advantages over other competitive in-lake phosphorus control treatments.

What is Phoslock®?

Phoslock® is a modified clay product, consisting of lanthanum (5%) and bentonite (95%) (Figure 1) and was developed to improve water quality. Lanthanum is a rare-earth element which binds strongly to phosphate, making it a valuable tool in the control of phosphorus pollution in freshwaters.

It is manufactured through an ion exchange process, whereby lanthanum ions displace sodium and calcium ions within the bentonite matrix and are embedded within the clay layers. The binding of phosphate to lanthanum results in the formation of a naturally occurring mineral (Rhabdophane) that becomes an inert component of the sediments.

Phoslock significantly reduces available phosphorus concentrations in freshwaters and phosphorus released from sediment complexes; improving the water quality.



Figure 1. Phoslock® granules.

EXTENSIVELY TESTED BY REGULATORS AND SCIENTIFIC INSTITUTIONS WORLDWIDE

Phoslock has been extensively tested by regulators and scientific institutions worldwide and is produced according to strict water quality control guidelines, having attained National Sanitation Foundation certification (Figure 2) for use in potable water supplies, and the WQA Gold Seal to assure product quality and safety (Figure 2). Phoslock is also produced under the Quality Assurance Management System accredited to ISO 9001:2015 (Figure 2).

It has been applied to both heavily impacted recreational waterbodies as well as natural waterbodies with high conservation value which fall under the remit of legislation such as the European Water Framework Directive and the U.S. Clean Waters Act.



Figure 2. National Sanitation Foundation certification (ANSI/NSF 60), Water Quality Association Gold Seal and Quality Assurance Management System accreditation ISO 9001:2015

NUTRIENT POLLUTION: A GLOBAL CHALLENGE

Nutrient pollution is a widespread problem which impacts waterbodies worldwide. It is a natural phenomenon which usually occurs over centuries, as waterbodies fill with sediments. Human activity accelerates the rate at which nutrients (phosphorus and nitrogen) enter freshwaters. An excess of nutrients can lead to undesirable changes to lake ecosystems, which eventually leads to the deterioration in the structure and function of a waterbody, e.g. such as the loss of a biodiverse aquatic community.

Excess nutrients can enter waterbodies from external sources from surrounding catchments (Figure 3), which can include both diffuse sources such as, agricultural run-off and from point sources such as septic tanks. Climate change ((changes in precipitation (both frequency and amount), wind, rising temperatures and atmospheric pollution deposition)) and increased catchment loading from population growth and land-use change are the main external stressors that can increase the rate of external phosphorus loading to lakes.

Phosphorus can accumulate in lake sediments in large quantities following decades of nutrient pollution, only to be released when environmental conditions change. Lake ecosystems are able to buffer the effects of increased phosphorus inputs for a while, but eventually the system becomes overloaded. Even if catchment management reduces external sources of phosphorus entering lakes, it can take several decades, if at all, for a lake to begin to recover due to this legacy.

Over the past 20 years, Phoslock® has been applied to more than 300 waterbodies, including lakes, reservoirs, impounded rivers, ponds and brackish and saline waters and has been used in more than 20 countries.

Sources of Phosphorus

- ➡ Sediment resuspension/nutrient release
- ➡ Redox reactions - most likely direction given conditions
- ⋯➡ Redox reactions - least likely direction given conditions



*Graphic not to scale

Figure 3. The main sources of phosphorus (P) to a eutrophic lake, with a focus on both external P sources and internal P load release mechanisms from chemical (redox related reactions during anoxic conditions), biological (bio-turbation - e.g. Chironomidae larvae) and physical (wind/wave action) release processes. The loss of P from a lake system include outflows, through groundwater exchange and sedimentation. P is tied in biomass in the lake (bacteria, phytoplankton, zooplankton, macrophytes, macro-invertebrates (not shown), fish and water birds) and passed through the keychain through predation/bacterivory or released back into the system through biomass degradation and excretion as organic matter (OM). The mineralisation of OM releases dissolved organic P (DOP), dissolved inorganic P (DIP) and particulate organic P (POP).

How does Phoslock® work?

The equation of phosphate binding with La:



Phoslock® uses the ability of lanthanum to bind with available phosphate in aquatic environments (Figure 4). One lanthanum ion will bind one phosphate ion in a molar binding ratio of 1:1. The lanthanum contained within Phoslock reacts with phosphate to form a strong, inert mineral known as Rhabdophane. This is a stable compound which does not dissociate under any of the water quality conditions found naturally in lakes (e.g. fluctuations in pH or anoxic conditions). Reaction rates between lanthanum and phosphate are rapid which results in the quick removal of excess phosphate and the prompt formation of Rhabdophane, which leads to improved water quality conditions (Figure 5).

This binding occurs over a wide pH range, however the most effective binding occurs between pH 5 – 9. Phosphate is still bound outside of this range but the binding efficiency is slowed if competing oxyanions and hydroxyl ions such as carbonate, hydroxide and humic substances are present. However, the bonds between these substances and lanthanum are weaker than those formed with phosphate, and over time, will dissociate and be replaced with Rhabdophane. Phoslock can be used in shallow aerobic waterbodies, but also in deep stratifying lakes where large amounts of phosphorus are often released from anoxic sediments during summer stratification.

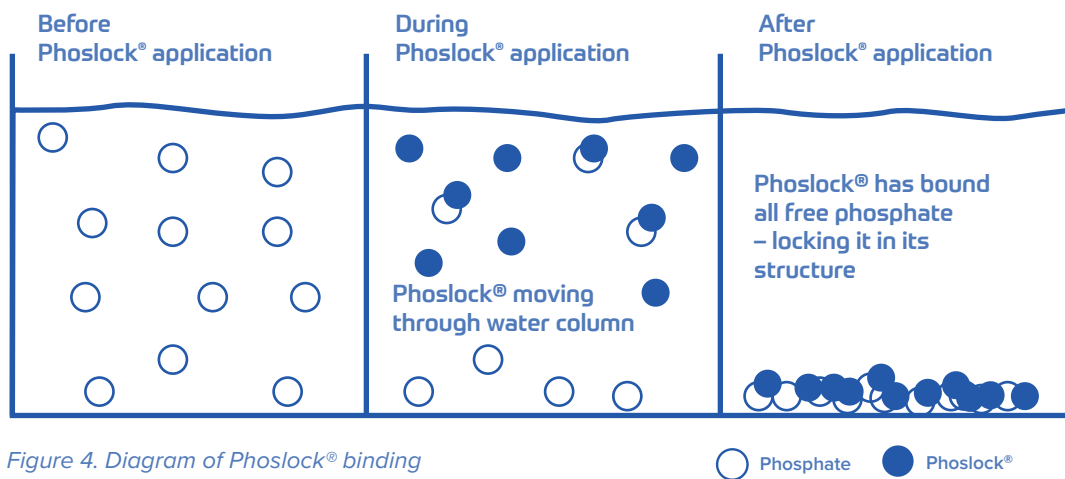


Figure 4. Diagram of Phoslock® binding the available phosphate



Figure 5. During the application of Phoslock® in Colorado Springs Colorado, USA.

On application to water bodies, Phoslock granules are applied by mixing with in-situ lake water to create a slurry, which is then sprayed over the water surface (Figure 6).

The slurry disperses through the water column, binding phosphate as it slowly sinks, before settling on the sediments, where Phoslock binds phosphate as it is released from the sediments until all lanthanum binding sites are saturated with phosphate. Settling rates vary according to the chemical composition of the receiving waters but all Phoslock particles typically reach the bed sediments in days.

Phoslock does not form an impenetrable physical barrier once it ‘caps’ the sediments and overtime this layer is worked into the sediment profile through bioturbation by benthic organisms such as chironomid larvae. Rhabdophane remains in-situ and becomes part of the sediment profile which can help consolidate fine and fluid sediments.



Figure 6. Phoslock® application process, with granules (left) being mixed with lake water (middle) and then applied to the surface of a waterbody (right).

Dosage Calculation

Phoslock® dose rates are tailored for each waterbody but are generally based on total phosphorus concentrations in the water column and the amount of ‘potentially releasable phosphorus’ (PRP) in the sediment (Figure 7). Not all PRP will be released from sediments within a few years as phosphorus contained in deeper sediments may take a few years to diffuse into the overlying water column and organic phosphorus may only become bio-available within one, two or even three years through microbial degradation processes.

A variety of methods can be used to assess the PRP, however the most common method is based on the results of a fractionation procedure (Psenner, 1988; Hupfer, 1995) and the dry weight analysis. Once the percentage of bio-available phosphorus in the sediment has been assessed through Psenner fractionation, an estimation as to which depth of sediment will interact with the overlying water column should also be made to determine a suitable sediment capping dose.

Many authors have considered this issue of sediment depth interaction and various estimates have been made. Cooke et al., (2005) estimate that most phosphorus release occurs within the top 4 cm while other studies have suggested that a sediment depth of up to 10 cm should be taken into account (Bostrom et al., 1982). Dosage calculations for most of the projects that have been undertaken with Phoslock worldwide in recent years have been based on the top 4 or 5 cm of sediments. However, in very shallow lakes and lakes with relatively fluid sediments, sediment depths of up to 10 cm have been considered.

Reset dosage can be applied for multi year longevity and efficacy

WCL + PRP x lake volume = lake phosphorus load (kg)

WCL = water column total phosphorus load

PRP = phosphorus load potentially released from sediments (usually the top 5cm)

Lake phosphorus load (kg) x 100 = Phoslock® dose (tons) recommended for a reset.

Without knowing the specific phosphorus concentrations of a water body, as an estimate, for every acre, approximately 1 ton of Phoslock is applied for a reset. Please also refer to the Tech Sheet for alternative methods to make smaller lake and ponds more manageable and predictable each year.

Application Strategy

Each application of Phoslock® is different and tailored to the characteristics of the water body. GPS tracking and depth detection systems are always used. Phoslock can be applied through two different approaches:

(1) A one-off application - enough Phoslock should be added to bind the phosphorus in the water column and the potentially releasable phosphorus from the active sediment depth.

(2) A staged approach – an initial dose to remove phosphorus from the water column and the top 4 cm of sediment and the adoption of a monitoring programme to indicate when the next dose is required. Subsequent applications tend to be significantly smaller than initial ones.

Phoslock can be applied over the surface of the water body or directly into the hypolimnion. This is recommended when most of the potentially releasable phosphorus is located in the sediment of the hypolimnion.



Figure 7. Phoslock® application process, broad-casted from the shoreline.



Fig 8. Phoslock® 55lb bags.

Phoslock® is a safe choice

Phoslock® has been comprehensively researched within the scientific community over the past 25 years. During this period, a large number of research projects have been undertaken investigating the potential toxicity of Phoslock to both aquatic life and human health. These studies have been conducted across a full range of scales, from laboratory and mesocosm experiments to whole lake studies and have conclusively shown that the use of Phoslock poses negligible risk to aquatic biota. Toxicology is the study of how chemicals interfere with the normal function of a biological system and toxicological assessments of adverse effects are generally based on the use of defined dose descriptors such as EC50 (an ecotoxicity dose descriptor defined by the lowest concentration where 50% of test subject species show an effect).

The active element in Phoslock, lanthanum, binds very strongly to available phosphorus but could be potentially toxic to some aquatic organisms if it were present in water in its dissolved form (La^{3+} (free lanthanum)).

The incorporation of lanthanum into a bentonite carrier overcomes this and prevents any negative impact when lanthanum is applied in the form of Phoslock to freshwaters. Bentonite acts as a lanthanum carrier and has a naturally low toxicity.

Once Phoslock is applied to freshwaters, it forms very small particles and the lanthanum in the water column is analytically determined as total lanthanum (TLa) and filterable lanthanum (FLa). Especially in soft water lakes Phoslock disperses, resulting in very fine non-toxic lanthanum containing particles that can pass through various filter sizes Reitzel et al., (2017). Reitzel et al., (2017) point out that much of the FLa measured, even after 30 minutes of ultracentrifugation, were still very fine colloids and not truly dissolved lanthanum. Only in lake water, with a combination of very low alkalinity, low phosphate and very high dissolved organic carbon, is the FLa concentration measured in the filtrate after ultracentrifugation probably considered in its dissolved form. Ultracentrifugation is time consuming and costly and the use of lanthanum speciation modelling has been used in many scientific publications to accurately assess if La^{3+} ions could be released from Phoslock following an application. This chemical equilibrium modelling enables lanthanum speciation to be determined prior to Phoslock treatment under the specific physio-chemical conditions of the waterbody. This allows an accurate estimation of dissolved lanthanum cations in the water with respect to the specific water chemistry of the waterbody.

This is of particular importance in very soft water lakes with low phosphate and high humic substance concentrations as these are the only conditions when ionic lanthanum could potentially occur following a treatment. However, when Phoslock is applied to lakes with at least moderately low alkalinity, concentrations of dissolved lanthanum can be expected to be very low. It is also important to know that unreacted lanthanum remains within the clay matrix and is not expected to easily diffuse out of the carrier material (Dithmer et al., 2015). In addition to phosphate, lanthanum also binds other oxyanions (e.g. carbonate). Soft water lakes have lower concentrations of these oxyanions and therefore, if the concentration of phosphate in the water is low, less lanthanum binding activity occurs. Consequently, in low alkalinity, soft water lakes with a high humic substance content in the water, Phoslock dosages should be calculated with care and chemical equilibrium modelling is a suitable tool to ensure that sufficient concentrations of phosphate are present in order to bind any lanthanum cations that could potentially be released from Phoslock under these particular conditions.

TOXICITY

Toxicity studies of lanthanum to freshwater biota have been conducted using different forms of lanthanum, including lanthanum chloride, lanthanum nitrate and lanthanum-modified bentonite (Phoslock). These studies have covered a wide range of aquatic biota such as zooplankton, macroinvertebrates, fish, nematodes and macrophytes, but results have varied according to the test stressor used. This variability is the result of the different chemical properties of soluble lanthanum salts compared to Phoslock and it is therefore important for ecotoxicological assays to reflect realistic conditions of an application scenario. Consequently, tests should be conducted with Phoslock itself rather than surrogate substances in order to fully understand toxicity impacts.

Measuring TLa concentrations in the water column is a good way to assess if Phoslock is present post-treatment. Lanthanum is usually bound very quickly to available phosphate and so TLa concentrations decrease in a waterbody over time. The EC50 concentrations of the studies that have used Phoslock as the stressor for assessing toxicity amongst aquatic groups are considerably higher than those ever recorded in systems where Phoslock has been applied.

Lanthanum can bioaccumulate in fish, crayfish, chironomids, macrophytes and waterbirds following applications. In some cases, lanthanum has accumulated for up to five years following a treatment. However, no adverse effects have been reported in any of the peer-reviewed studies that have investigated this.

Humans can also theoretically be exposed to Phoslock through using recreational waterbodies following a Phoslock application (e.g. a recreational waterbody such as the Kralingse Plas (Figure 10)). Exposure pathways are most likely through ingestion and dermal contact, caused by swimming or watersport activities and from fish consumption. It should be noted however, that lanthanum carbonate is used for medicinal purposes to treat patients suffering from hyperphosphatemia. Sold under the trade name, Fosrenol®, lanthanum carbonate is typically administered at doses of between 375 and 3,000 mg/day of elemental lanthanum, usually over many years. Based on an average prescribed dose of 1,500 mg/day (~900 mg lanthanum/day), users of recreational water bodies treated with Phoslock would need to consume at least 380 L of water per day in order to ingest the same quantity of elemental lanthanum as an average Fosrenol® dose. This large volume of water is impossible to consume by a person in a day and therefore, an application of Phoslock would never deliver as much lanthanum as a single Fosrenol® tablet. The long-term consumption of lanthanum carbonate (10+ years) has shown no adverse safety outcomes amongst patients. Similarly, consumers would need to ingest vast amounts of fish; more than 1,000 kg per day based on the highest flesh lanthanum concentrations recorded in fish to reach the nominally safe recommended therapeutic dose in adults.

In summary, based on the responses of a range of aquatic organisms, the risk of toxicity to aquatic life is low following a Phoslock application to a waterbody. The ingestion of Phoslock treated water directly after an application would pose no risk to human health and similarly eating fish that have accumulated lanthanum would also not pose a risk.



Figure 9. Kralingse Plas lake, The Netherlands, 11 months after treatment

Phoslock® versus other chemical measures

Different approaches can be adopted to tackle phosphorus pollution. Some measures, such as algaecides and biological control measures, are aimed at directly controlling the symptoms of nutrient pollution rather than the underlying problem. Other measures, such as dredging and chemical phosphorus inactivation, aim to reduce nutrient concentrations to levels which are more typical of unimpacted aquatic systems.

Phoslock® is an in-lake solution that specifically targets phosphorus pollution and controls internal phosphorus load.

More than 140 materials able to bind phosphorus have been identified in the scientific literature. However, the vast majority of these have only been tested in the laboratory and there is a lack of published information about their toxicity, efficiency under differing environmental conditions, longevity, and costs. Additionally, many of the materials are not manufactured or produced in commercial quantities.

Commercially available phosphorus-binders include: Phoslock, aluminium sulphate and polyaluminium chloride, ferric chloride, various calcium-based compounds and several natural clays and soils. Phoslock has several advantages over them (Table 1).

- Unlike iron and aluminium salts, Phoslock does not impact the pH or conductivity of the water in which it is used. This avoids the need to add chemicals to the water (e. g. to buffer the pH) and eliminates any stress to aquatic organisms caused through pH changes.
- Phoslock binds phosphorus under a wide pH range, under anoxic conditions, in the presence of humic substances and in saline waters.
- Once Phoslock binds to phosphate, the phosphate it has adsorbed will not be released under anoxic conditions or when the pH of the water changes.
- Phoslock does not crystalize.
- Phoslock will not lose its binding capacity over time and has the capacity to increase sediment stability. Phosphate bound to lanthanum cannot be released because of resuspension events caused by wind, waves or bioturbation.

Table 1. The advantages of using Phoslock® over other phosphorus binding commercial products.

PHOSLOCK®	ALUMINIUM SALTS	IRON SALTS
Effective between pH 5 and 9	Effective between pH 6 and 8	Effective between pH 5 and 8 (depending on the salt used)
Effective under anoxic conditions	Effective under anoxic conditions	Not effective under anoxic conditions
Does not affect water pH and conductivity	Affects water pH and conductivity	Affects water pH and conductivity
Increases sediment stability	Does not affect the sediment stability and can easily resuspend	No studies have been done on the effect of sediment stability
No need to be applied with a buffer	Might need to be applied with a buffer	Might need to be applied with a buffer
Phosphate adsorbed will not be released under anoxic conditions or within pH 4-12	Phosphate adsorbed will not be released under anoxic conditions or within pH 6 - 9	Phosphate adsorbed will be released under anoxic conditions
Binding capacity does not decrease with time	Binding capacity decreases with time	Binding capacity may decrease with time
Does not have coagulant properties	Has coagulant properties	Has coagulant properties

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