PHOSLOCK®
Phosphorus Locking Technology

An Overview of Phoslock and Use in Aquatic Environments

What is Phoslock?

Phoslock is a patented phosphorus locking technology containing lanthanum (5%), a naturally occurring earth element, embedded inside a clay matrix (~95%). Phoslock was developed by the Australian national science agency, Commonwealth Scientific and Industrial Research Organization (CSIRO), to remove phosphorus from water bodies and restore water quality. Phoslock is produced through a patented ion exchange process whereby lanthanum ions displace sodium ions within the clay matrix. The formulation process of Phoslock absorbs lanthanum into a non-toxic carrier such that the lanthanum retains its capacity to bind phosphate when applied to aquatic environments and results in a non-toxic mineral that becomes an inert component of the sediments.

For over ten years, Phoslock has been successfully used in water resource restoration programs around the world to remove free reactive phosphorus and restore water quality. Although Phoslock is a new technology to the United States (2010), it is rapidly emerging as the most effective phosphorus inactivation and water quality restoration solution for ponds, lakes and reservoirs.

How does Phoslock work?

Following an application of Phoslock, the lanthanum ions sorbed to the clay matrix react preferentially with free phosphate compounds in water (removing free reactive phosphorus) and rapidly form a highly stable insoluble mineral. The resulting mineral complex becomes integrated as an inert component into the natural sediments of the waterbody and is not bio-available. Due to the specificity of Phoslock to phosphate, as long as binding sites are available, it will continually bind new incoming phosphorus from internal and external sources.

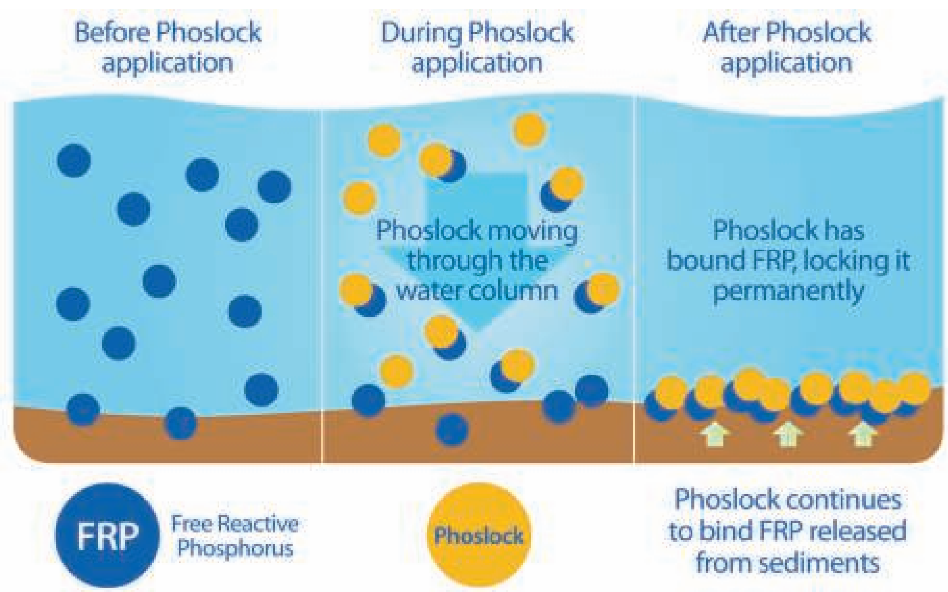

Figure 1. *Illustration of the binding of Phoslock with Free Reactive Phosphorus (via phosphate bond) in water and as it is released from sediments.*

[†]Throughout this document, we use the phrase negligible risk. Risk is the probability of occurrence of an adverse effect from a given exposure to a substance. All substances have an inherent hazard (capacity to cause adverse effects). However, the risk of a potential adverse effect is managed by the product formulation, use directions, application rates and exposure. Phoslock at appropriate uses and dosing will result in negligible or insignificant risk.

Ecological Assessment

To assess and manage possible environmental impacts of a product, it is important to understand the potential risks associated with its use. The objective of the following information is to describe existing toxicity data on the product and assess any potential risks to the aquatic environment. Typical Phoslock application rates are < 150 mg/L. Phoslock applications may occur as a single event or over several days and also may be split over a season or multiple seasons depending on the site and management objective.

Evaluation of Lanthanum Toxicity

Lanthanum is a naturally occurring earth element. Lanthanum can occur in many forms. One such form, lanthanum chloride ($LaCl_3$) can be potentially toxic to aquatic organisms due to the dissolution of high levels of free lanthanum into water after application. This prohibits the use of $LaCl_3$ as an environmentally compatible phosphorus mitigation solution. However, when lanthanum is applied to surface waters in the form of Phoslock, the risk of potential lanthanum toxicity to aquatic organisms is negligible due to the unique formulation of Phoslock (absorbed to the clay matrix) and a limited potential for exposure to free lanthanum. When Phoslock is applied to water, lanthanum associated with the clay in Phoslock preferentially and rapidly binds with phosphate (PO_4), forming a highly stable mineral called rhabdophane ($LaPO_4$). This resulting rhabdophane complex has a very low solubility ($K_{sp} < 10^{-27}$) and is not influenced by changes in pH and redox reactions in waterbody sediments, thus is not bio-available. Lanthanum can only be extracted from rhabdophane in the laboratory using strong acid extraction methods.

Laboratory studies with Phoslock demonstrated that no lanthanum released within 24 hours when granular Phoslock (10 mg/L) was dissolved in de-ionized water; and only a small concentration of lanthanum (~0.016 mg/L or 3% of the total lanthanum in Phoslock) was released from the 10 mg/L concentration of Phoslock when dissolved in low alkalinity natural water or synthetic soft water (*Yasseri and Nowak 2008*).

Even if the total amount of lanthanum applied to a system following a Phoslock application became readily available in water (which it does not due to the Phoslock formulation and the fact that lanthanum binds to phosphates in water), the margin of safety associated with lanthanum toxicity is very high. For example, free lanthanum levels following an application dose of 75 mg/L Phoslock in Barensee Lake, Germany resulted in a peak level of 0.130 mg La^{+3}/L shortly after application and <0.02 mg/L one month later. Toxicity tests from this Barensee Lake project revealed an EC_{50} of 103 mg La^{+3}/L zooplankton (*Daphnia magna*) and EC_{50} of 150 mg La^{+3}/L for fish eggs (*Danio rerio*). The peak level of La^{+3} detected in the lake following application was approximately 800 and 1,150 times lower than the EC_{50} concentrations for zooplankton and fish eggs respectively.

The main potential for free lanthanum in water following a Phoslock application is in waters that have a very low alkalinity (< 20 mg/L) and low phosphate concentration (<0.005 mg/L). Typical Phoslock applications are not conducted in waters with low alkalinity and low phosphate levels. Even in these low alkalinity aquatic environments, the concentration of dissolved lanthanum associated with the product is very low and below predicted toxicity thresholds. In these systems, risks can be further mitigated by several other assessment and management strategies such as conducting pre-application laboratory "jar tests" using lake water and lowering and/or splitting the Phoslock dose over time through a series of applications. Due to the ability of organisms to readily process lanthanum (through the liver) and the low level of free lanthanum that potentially becomes available for a short period of time following Phoslock applications, the aquatic toxicity risk and hazard to aquatic organisms is negligible.[†] While free lanthanum can be used in tests to assess the toxicity to organisms, lanthanum in Phoslock, or bound as rhabdophane, is not free and unlikely to become available or achieve concentrations of toxicological concern in the natural aquatic environment.

Exposure to water column biota

The phosphorus removal capacity of Phoslock does not change drastically under different chemical or environmental conditions. From a water chemistry standpoint, the binding and removal of Phoslock is a straight forward process. Phoslock binds to phosphates over a pH range of 4 to 11, and binds to phosphates under aerobic and anaerobic conditions. Water analysis during and after application reveals no significant change in pH and no need to buffer treated waters during or after a Phoslock application. A pH change in the water column, sediment water interface and bottom sediments will not result in a release of lanthanum from Phoslock and phosphorus bound as rhabdophane. Since Phoslock rapidly settles to the sediments, the potential exposure duration to organisms in the water column is relatively short. Also, due to the unique formulation of Phoslock, the lanthanum remains sorbed to the clay until it is displaced by phosphates, and subsequently only disassociates a minimal amount of free lanthanum to the water.

Invertebrates

Data were compiled from numerous different testing agencies on a range of sentinel water column invertebrates. Responses of these zooplankton species, including both mortality and reproduction, were evaluated throughout Phoslock exposures. The data show a wide margin of safety associated with Phoslock (*Table 1*) applications at predicted use rates and environmentally relevant concentrations.

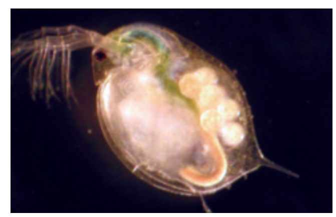

Table 1. Description of Phoslock toxicity experiments with sentinel zooplankton species.

Species	Endpoint	Test Duration	Lowest Observed Effect Concentration (LOEC)*	Water	Reference
Ceriodaphnia dubia	Mortality	48 hours	> 50mg/L Phoslock	Field water	Ecotox 2008
Ceriodaphnia dubia	Reproduction	7 days	> 1mg/L Phoslock	Field water	Ecotox 2008
Ceriodaphnia dubia	Mortality	7 days	> 1mg/L Phoslock	Field water	Ecotox 2008
Ceriodaphnia dubia	Mortality	48 hours	> 12,500 mg/L Phoslock	Synthetic soft	Stauber, 2000
Daphnia magna	Mortality	48 hours	> 50,000 mg/L Phoslock	Synthetic soft	Martin & Hickey, 2004

** Due to the amount of Phoslock needed to result in impacts to biota, many studies did not test concentrations high enough to result in significant impacts, thus toxicity endpoints are reported as greater than the highest concentration tested and does not indicate the actual lowest observed effect levels.*

Fish

The responses of numerous fish species to Phoslock exposures has been evaluated to determine potential risks following application. No mortality or adverse impacts to fish have been observed in field applications in the United States or internationally. Based on data generated for several different fish species (*Table 2*), there is minimal risks to fish expected with applications of Phoslock at standard dose rates in aquatic environments.

Table 2. Description of Phoslock toxicity experiments with sentinel fish species.

Species	Endpoint	Test Duration	Lowest Observed Effect Concentration (LOEC)*	Water	Reference
Melanotaenia duboulayi	Mortality	96 hours	> 50,000 mg/L Phoslock	Synthetic soft	Ecotox 2006a
Oncorhynchus mykiss	Mortality	96 hours	> 3,125 mg/L Phoslock	Synthetic soft	Martin & Hickey, 2004
Oncorhynchus mykiss	Mortality	48 hours	> 13,000 mg/L Phoslock	Natural pond-field	Watson-Leung 2008

** Due to the amount of Phoslock needed to see impacts to biota, many studies did not test concentrations high enough to result in significant results, thus toxicity endpoints are reported as greater than the highest concentration tested and does not indicate the actual lowest observed effect levels.*

Exposure to benthic organisms

When Phoslock settles at the sediment-water interface it forms a thin (< 2 mm) permeable layer that continues to actively bind phosphate released from the sediments or that from inflow. Due to the fine particulate nature of Phoslock, it does not produce a thick flocculent layer at the sediment-water interface. When the lanthanum in Phoslock binds to phosphate, the resulting mineral complex $LaPO_4$ is formed. This stable mineral has a very low water solubility co-efficient ($K_{sp} < 10^{-27}$) and is not bio-available to benthic organisms. Lanthanum is a naturally occurring earth element found in soils throughout the United States (Shacklette H.T, Boerngen J.G, 1984). A soil study conducted by the University of California detected lanthanum at an average background level of 20.3 mg La/kg in soil samples collected throughout California (Kearney, 1996). Concentrations in waterbody sediments, prior to any Phoslock application, have been measured from 8 to 37 mg/kg dry weight on average and many European river sediments have up to 44 mg/kg dry weight (Yasseri and Nowak, 2008). Background levels of lanthanum (bound in forms with chlorides, carbonates and phosphates) in water bodies sediments tested globally (US, Europe and Australia) have typically ranged from 12 - 36 mg La/kg, with occasional extreme exceptions high and low (Phoslock Water Solutions, 2011).

During and after Phoslock application, the additional lanthanum to the waterbody's sediment is negligible. As a result of typical variation in background sediment concentrations, Phoslock applications are not expected to provide a significant or quantifiable change in total Lanthanum concentration in the bottom sediments of treated waterbodies.

Table 3. Description of Phoslock toxicity experiments with benthic invertebrates.

Species	Endpoint	Test Duration	Lowest Observed Effect Concentration (LOEC)*	Water	Reference
Chironomus zealandicus	Mortality & emergence & sex ratio	38 days	All > 400mg/L Phoslock	Lake water	Clearwater 2004
Chironomus dilutus	Mortality	10 days	> 3,400mg/L Phoslock	Pond water	Watson-Leung, 2009
Polypedilum parvidum	Mortality	10 days	> 400mg/L Phoslock	Field water	Clearwater & Hickey 2004
Hyalella azteca	Survival and growth	14 days	> 450mg/L Phoslock	Pond water	Watson-Leung, 2009
***Hexagenia* sp.**	Survival and growth	21 days	> 450mg/L Phoslock	Pond water	Watson-Leung, 2009
***Macrobrachium* sp. (shrimp)**	Mortality	96 hours	> 50,000 mg/L Phoslock	Synthetic soft water	Ecotox, 2006b
***Macrobrachium* sp.**	Mortality	7 days	> 800 mg/L Phoslock	Synthetic soft water	Ecotox, 2006b
***Macrobrachium* sp.**	Mortality	14 days	> 800 mg/L Phoslock	Synthetic soft water	Ecotox, 2006b

** Due to the amount of Phoslock needed to result in impact biota, many studies did not test concentrations high enough to significant impacts, thus toxicity endpoints are reported in the greater than the highest concentration tested and does not indicate the actual lowest observed effect levels.*

A variety of different benthic invertebrates have been evaluated in toxicity experiments to determine potential risks associated with Phoslock applications. Responses variables in these studies included survival, emergence time, growth and sex ratio at emergence. Even with long exposure durations and high Phoslock concentrations, no significant impacts were observed with benthic organisms at and above predicted use rates. The predicted risk is negligible and no field toxicity has been observed.

Phoslock and Human Health

There is a very low potential exposure to lanthanum in Phoslock after being applied due to the minimal bio-availability. Even if an exposure occurs, lanthanum is readily processed by the liver and excreted with no negative impacts observed. Lanthanum is used in a prescription drug called Fosrenol® to decrease blood phosphate levels in humans. The Food and Drug Administration approved human dose rate for Fosrenol is 750 to 3,000 mg/day.

Exposure via Ingestion of Treated Water

In case of lanthanum ingestion via drinking even a large volume of Phoslock treated reservoir water, there is negligible risk to human health. Applying Phoslock on a reservoir at the dose rate of 50 ppm (a typical dose rate of Phoslock in a waterbody with an average concentration of phosphorus and alkalinity) and assuming that 100% of La (5% La in Phoslock) was released out of the product (which does not happen because alkalinity and PO4 will bind the "free" La in surface waters), the person would need to drink 80 gallons of reservoir water per day to ingest the minimum dose that corresponds to the lowest Fosrenol daily intake. Drinking 2 gallons of water daily under these artificial conditions would result in consuming La levels 40 times lower than the minimum daily dose of Fosrenol. The maximum dose of Fosrenol is 3,000 mg/day; the average person would need to drink 317 gallons of reservoir water per day to receive the maximum dose of La that is the Fosrenol daily intake. These large volumes of water could not be consumed by a person per day. Drinking Phoslock treated water directly after an application would pose negligible risk to human health.

Exposure via Fish Consumption

The risk via consuming Phoslock/lanthanum in fish harvested from Phoslock treated water after application was negligible as shown in a fish health investigation, after three successive applications of Phoslock in Lake Okareka, New Zealand. The Lake Okareka fish health monitoring report (*Landman et al., 2007*) demonstrated that trout and koura accumulated lanthanum only in the liver and hepatopancreas tissues, not in the flesh/muscle following the application of Phoslock. It was also demonstrated that lanthanum was removed from the fish liver and hepatopancreas tissues within a few months and the concentrations of lanthanum returned to baseline before another Phoslock application one year later, suggesting a biological capacity to depurate lanthanum (*Landman et al., 2007*). This is also consistent with the findings that the main excretion route for absorbed lanthanum in humans or animals is via the liver into bile (*Damment & Pennick, 2007*). The highest concentration of lanthanum measured in the liver of male and female trout in Lake Okareka after one and two months of Phoslock application was 1.2 and 0.8 mg/kg. Similarly, the highest concentration of lanthanum in the hepatopancreas tissues of male and female trout was 0.8 and 1.0 mg/kg respectively (*Landman et al., 2007*). Therefore, in total the highest concentration of lanthanum in one trout was 2.0 mg/kg. Thus, a person would need to consume 826 pounds of fish per day to ingest the minimum dose of La that corresponds to the lowest Fosrenol daily intake. The average person would need to consume 3,306 pounds of fish per day to consume the maximum daily dose of La from Fosrenol. These large quantities of fish would not be consumed by a person per day. If a person consumed 2 pounds of fish this would result in consuming La levels 400 times lower than the minimum daily dose of Fosrenol. Moreover, fish liver and hepatopancreas tissues are not generally consumed by humans. Even consumption of large quantities of fish liver and hepatopancreas tissues harvested from Phoslock treated waterbody would pose negligible risk to human health.

Lanthanum is not a Hazardous Substance

Phoslock is not considered hazardous by the Occupational Health and Safety Administration (OSHA) Hazard Communication Standard (*29 CFF 12910.1200*). Lanthanum and the clay used in the formulation are not listed on the USEPA Toxic Substances Control Act inventory list. Lanthanum is not on the Australian National Occupational Health and Safety Commission (OHSC) List of Designated Hazardous Substances (*NOHSC, 1999a*).

No risk has been associated with contact of Phoslock. The main potential for human exposure to Phoslock is during the application process. Due to some small particulates in the formulation, there could be some potential eye irritation and inhalation for applicators and handlers associated with an application. Applicators and handlers should follow suggested personal protective equipment guidelines found on the package label and material safety data sheet.

Summary

Phoslock is patented phosphorus locking technology that has been specifically formulated to decrease potential exposure to aquatic biota. Phoslock poses a negligible to very low risk to the aquatic environment while providing a high affinity to bind and remove phosphorus that results in improvements to water quality. A review of toxicity data has shown a large margin of safety to aquatic organisms and humans that may be exposed to Phoslock treated water during and following application.

Phoslock phosphorus locking technology is NSF/ANSI Standard 60 certified for use in drinking water. This certification ensures that Phoslock applications, at the maximum use rate specified on the product label, does not contribute contaminants that could cause adverse human health effects. NSF/ANSI Standard 60 is the nationally recognized health effects standard for products which are used to treat drinking water.
In addition, this certification requires annual product testing, facility inspections, quality assurance, good manufacturing practices, and product stock inspections. The United States Environmental Protection Agency and all states rely on and accept ANSI accreditations by authorized independent third party accreditation agencies, such as Water Quality Association (WQA).

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