Phoslock Risk Assessment

An overview of risks to the aquatic environment associated with the use of Phoslock

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1 INTRODUCTION

Phoslock is a modified clay product that was developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia, to remove phosphorus from water bodies and eliminate the incidence of blue-green algal blooms. The use of Phoslock with its active ingredient lanthanum is a new but fast emerging effective P-inactivation and blue-green algae management tool. To assess and manage any possible adverse environmental side effects of a new product, it is crucial to understand the hazards and risks associated with its use, in this case to the aquatic ecosystem. The objective of this report is to outline existing information on the product and assess any risks it may pose to the aquatic environment.

1.1 WHAT IS PHOSLOCK ?

The raw materials of Phoslock consist of an inactive clay-based carrier (bentonite) which comprises 95% of the product by weight and the active ingredient lanthanum, which makes up 5% by weight. It is produced through an ion exchange process whereby lanthanum ions are exchanged with sodium ions from within the bentonite matrix. The lanthanum is bound to the surface of the clay where it retains its ability to react with phosphate. The development of Phoslock was specifically designed to fix lanthanum into a non-toxic carrier (bentonite) such that the lanthanum retains its capacity to bind phosphate but is rendered non-biologically available and therefore non-toxic.

1.2 WHAT IS LANTHANUM ?

Lanthanum is the 28th most abundant element, classed in a group of elements known as the “rare earth elements”. It has a concentration of about 18.3 ppm in the earth’s crust and is most commonly found in minerals such as bastnasite (Haghseresht 2006). Concentrations in lake sediments, measured by the Institute Dr Nowak in preliminary assessment work, i.e. prior to any Phoslock application, range from 8 to 37 mg/kg Dry Weight. Measurements of European rivers sediments show values of up to 44 mg / kg Dry Weight (Yasseri and Nowak, 2008).

Lanthanum is a strong binder of oxyanions like phosphate. Binding with phosphate forms a mineral called Rhabdophane (lanthanum phosphate) which is highly insoluble and stable across a wide range of pH and redox conditions, such as those found in lake water and sediment. This property makes it ideal as a phosphorus binding agent, which can be put to good use in lake restoration. It also makes it well suited as human medicine.

1.3 HAZARDS AND RISKS

Before discussing the hazards and risks associated with the use of Phoslock, it is worthwhile clarifying the use of these terms within this document.

Hazard: the inherent capacity of a chemical (or other substance, material or activity under consideration) to cause adverse effects under the conditions of exposure.

Risk: the probability of occurrence of an adverse effect resulting from a given exposure to the chemical (or substance, material or activity under consideration).

In the case of Phoslock, the main hazard is from Lanthanum which has been shown to cause toxic effects to some aquatic organisms, although it is used in much higher concentrations as a human medicine. However, the risks from Lanthanum through the use of Phoslock are strongly mitigated, reduced to a minimum by the chemical composition of Phoslock and its conditions of use.

Measures of the hazards to organisms associated with substances are usually assessed through tests known as toxicity or ecotoxicity assessments, whereby test organisms are exposed to a range of concentrations of the substance under controlled conditions over a range of time periods. At the end of the test, effects on the organisms are noted, such as death or signs of impact which do not result in death, e.g. impaired swimming ability, failure of eggs to hatch or the ability to reproduce. The notation used to describe the results is referred to as EC50 (Effective Concentration at which 50% of the test organisms show some, non-lethal impact) or NOEC (No Observable Effect Concentration). These values are statistically derived from the test data and define the concentration of the test substance at which the effects are seen.

Outcomes from toxicity assessments are influenced, amongst other things, by the concentrations of the test substance used, the duration of the exposure, the inherent sensitivity of the test organism to the substance and the medium in which the test substance is dissolved.

The following provides a review of the hazards to aquatic organisms from lanthanum and Phoslock, followed by the current state of knowledge of the risks posed by the use of Phoslock.

A note on bioavailability - this is an important concept in relation to understanding the risks posed by lanthanum in Phoslock. For a substance to be bioavailable it must have the ability to become integrated into an organism's metabolism. For lanthanum this happens when it is in the form of "free" ions. These are present when a lanthanum compound dissolves in an aqueous environment and the constituent atoms become dissociated. For example, lanthanum chloride will dissolve in water forming La and Cl ions. The lanthanum is readily bioavailable. However, if lanthanum is in the solid phase, i.e. tightly bound to another

chemical forming a substance which is insoluble, then it is not bioavailable, even if the particles of this substance are very small. Lanthanum binds to phosphate forming a highly insoluble compound, Rhabdophane, so is not bioavailable. Lanthanum in Phoslock is tightly bound within the highly insoluble Bentonite mineral matrix so is not bioavailable. In fact, lanthanum can only be extracted from these compounds in laboratory conditions using strong acids. So, while "free" lanthanum can be used in tests to assess the toxicity of lanthanum to organisms, lanthanum in Rhabdophane and Phoslock is not "free" and is unlikely to become so in the natural aquatic environment.

2 WHAT ARE THE HAZARDS ASSOCIATED WITH PHOSLOCK AND HOW ARE THEY ASSESSED?

2.1 LANTHANUM TOXICITY – MEASURES OF THE HAZARDS FROM LANTHANUM

Lanthanum chloride has been used in a number of toxicity tests on aquatic organisms to assess the toxicity of lanthanum. In an aqueous medium, the lanthanum and chloride dissociate to their component ions. It is the "free" lanthanum ions which can be hazardous to aquatic organisms. In advance of reviewing the work to date it is important to consider the chemical nature of lanthanum ions which very readily bind to other ions. This means that in the presence of, for example, carbonate (which is found in hard water) or phosphate (which could be used as a nutrient source for a test organism), the lanthanum ions, will readily form new compounds which tend to be insoluble and therefore non-toxic. This means that test results can vary between hard and soft water and that the presence of phosphate in the test medium can remove many of the lanthanum ions from solution.

Groves (2010) reviews the results from a number of ecotoxicty tests using lanthanum chloride, carried out on a range of aquatic organisms. The reported EC50 values varied considerably, likely at least in part, to result from the use of different waters, e.g. natural hard water, nano-pure (artificially de-ionsed) water or artificially made lake water. Barry and Meehan (2000) reported EC50 values of 43 and 1180 µg/L lanthanum for Daphnia carinata over a 48 hour period of exposure in tap water (soft water) and artificial hard water respectively. In contrast, tests by Stauber and Binet (2000) using Ceriodaphnia dubia exposed to lanthanum chloride solutions for 48 hours produced an EC50 of 5000 µg/L lanthanum and there was No Observable Effect (NOEC) at a concentration of 2600 µg/L. Tests carried out at the Institute Dr Nowak produced an EC50 value of 23000µg/L using D.magna exposed to lanthanum chloride in synthetically produced soft water for 48 hours (Yasseri and Nowak 2008).

Over longer periods of exposure, days rather than hours, Stauber and Binet (2000) calculated an EC50 of 430 µg/L lanthanum for C. dubia in synthetic soft water with exposure over a 7 day period. This particular test looked at effects on reproduction in the species and they calculated a NOEC value of 50 µg/L lanthanum. Similar tests looking only at survival of the species produced an EC50 of 510 µg/L lanthanum.

More recent work by Lurling and Tolman (2010) produced an NOEC value of 100 µg/L for D.magna but stressed that this value was statistical and in fact their daphnia showed excellent growth rates and survival even at higher concentrations of lanthanum, including a nominal concentration of 1000 µg/L, the highest concentration in their study.

Information on the toxicity of lanthanum to other groups of aquatic organisms is less widely available. Stauber and Binet (2000) exposed the fish (Melanotaenia duboulayi) to lanthanum chloride in treated tap water over a 96 hour period giving an EC50 of <600µg/L lanthanum. Following applications of Phoslock to Lake Okareka in New Zealand, Landman et al (2007) showed accumulations of lanthanum in the liver and hepatopancreas of fish and crayfish collected from the lake but indicated that these concentrations reduced with time. They could find no evidence of physiological changes in these organisms which could be attributed to the lanthanum. Work carried out at the Institute Dr Nowak produced an EC50 for fish eggs of 150000 µg/L lanthanum in the presence of phosphate (Institute Dr Nowak, 2008)

2.2 LANTHANUM AS A MEDICINE FOR HUMANS

The ability of lanthanum to bind phosphate has led to its safe and effective use as a human medicine. Lanthanum carbonate, under the trade name Fosrenol®, is used to treat patients with end stage chronic renal disease. The process of drug development and clinical trials which led to its approval by the US-FDA has resulted in a significant volume of literature examining the toxicity of lanthanum carbonate in mammals (Asfar and Groves, 2009 and Haghseresht, 2006 and references therein). The bioavailability of lanthanum is very low, 0.00127% in humans (Pennick et al 2006). When ingested orally it is only minimally absorbed by the gut, most passing through the digestive tract and excreted as faeces. This is the mode of operation of Fosrenol® whereby the lanthanum carbonate dissociates in the acid environment of the gut, releasing lanthanum which binds phosphate. The insoluble lanthanum phosphate is eliminated as faeces when the kidneys are no longer able to carry out this function. As part of the process by which lanthanum removes phosphate from the body, it passes through the liver and bile system, so increased concentrations of lanthanum in the liver are to be expected. However, even after 4 years of lanthanum carbonate intake, clinical trials have shown no hepatotoxic effect in patients, neither is lanthanum present in the mitrochondria, nucleus or cytoplasm of liver cells (Persy et al 2006). Approved dose rates of Fosrenol® are from 750 to 3000 mg per day (http://www.fosrenol.com). Haghseresht (2006) provides a summary of lanthanum toxicity tests in mammals (mice, rats and dogs) which show that the doses of lanthanum carbonate prescribed for humans have little or no toxic effect in these mammals.

2.3 PHOSLOCK TOXICITY – MEASURES OF THE HAZARDS FROM PHOSLOCK

Although Phoslock is a relatively new product, a wide range of toxicity tests using Phoslock have now been carried out by Phoslock Water Solutions (Australia) and independent

researchers (reviewed in Groves, 2010). The most recent studies have been carried out on a range of aquatic organisms using Phoslock granules dissolved into water (either tap, de-ionised, synthetic or lake water) at concentrations which would be representative of the conditions of use in a real lake environment.

As with toxicity tests undertaken on lanthanum chloride (described above), the results are influenced by, among other things, the duration of exposure, the medium in which the Phoslock is suspended, either hard or soft water and the maximum concentrations of Phoslock used. Where available, the assumed or measured lanthanum concentrations associated with the Phoslock in the tests are provided (but see note below). Tests on C. dubia gave EC50 results of >50mg/L Phoslock(>330 µg/L La) over a 48 hour exposure period, and >1mg/L Phoslock(>24 µg/L La) over a 7 day exposure period, the concentrations being the highest used in the test(Ecotox 2008). Where higher concentrations were used, EC50 values of 4900 mg/L (91183 µg/L La) and >6800 mg/L Phoslock(>14000 µg/L La) were obtained for D. magna in tap water and natural pond water respectively over 48 hours (Watson-Leung, 2008). Longer exposures carried out by Lurling et al (2008) and Lurling and Tolman (2010) produced LC50 values from 800 to 3130mg/L Phoslock depending on the measure of health used (length or weight) and medium (de-ionised water or artificial medium).

In studies prior to an application of Phoslock in Canada, work carried out by Watson-Leung (Watson-Leung 2008) gave the following results; EC50> 13600 mg/L Phoslock over 48 hours for the fish species Oncorhynchusmykiss, >3400 mg/L Phoslock for the amphipod Hyelellaasteca over 14 days, and >450 mg/L Phoslock for a mayfly, Hexagenia sp and the chironomid, chironomus zealandicus over 21 and 38 days respectively. It is worth noting that all these EC50 values are actually greater than the maximum concentrations used in the studies, so consequently these concentrations had no observable effect on the test organisms within each study.

Few toxicological studies have been carried out using species of algae (Groves 2010), but Lurling et al (2008) using a Phoslock solution produced an EC50 of 450mg/L Phoslock for Scenedesmus obliquus. However caution must be used when interpreting such results as algae need phosphate to grow and by definition, contact with Phoslock removes phosphate, so effects could be related as much to the reduced availability of phosphate as to Phoslock itself.

2.4 MEASURING "FREE" LANTHANUM IN PHOSLOCK TOXICITY TESTS

It is not straight forward to relate the Phoslock concentrations used in these experiments to actual concentrations of lanthanum ions to which the test organism may have been exposed. In theory there should be no dissociated, "free", lanthanum ions in a Phoslock solution but in practice, tiny quantities which are not bound within the mineral complex are present in the product. Some of the studies above have attempted to measure the lanthanum

concentrations in the test solutions. This is also not without difficulty as very small particles of bound lanthanum are thought to be able to pass through even the finest of filters. This makes a genuine assessment of dissociated lanthanum in solution difficult. It is also not relevant to measure or calculate the amount of total lanthanum in a test solution of Phoslock as virtually all of this will be contained within the Phoslock mineral complex.

3 PHOSLOCK – HOW THE HAZARD IS MITIGATED AND THE RISKS FROM ITS USE REDUCED

While there is evidence to suggest that "free" lanthanum ions are toxic to some aquatic organisms, even if the concentrations at which toxicity occurs appear somewhat variable, both the manufacture and properties of Phoslock reduce the hazards from lanthanum, resulting in the risks from lanthanum toxicity through the use of Phoslock being substantially lower than they would be were lanthanum used on its own. The following looks at the ways in which lanthanum toxicity is mitigated in Phoslock.

3.1 MANUFACTURE

As previously mentioned, Phoslock uses a bentonite carrier which holds the lanthanum ions within the clay structure where they retain their ability to bind with other ions such as phosphate. The retention of the lanthanum within the bentonite complex ensures that it is non-toxic because it is in a particulate form and the lanthanum ions are not "free". The development of the product was specifically intended to remove toxicity associated with lanthanum.

During the manufacture of Phoslock, the ion exchange reaction is carried out in an aqueous environment after which the Phoslock is dewatered (dried) to form the final granular product. Very small quantities of residual lanthanum which are not part of the bentonite structure can potentially remain within the granules and be released when applied to a lake. However, strict manufacturing and quality control protocols ensure that the amount of residual lanthanum is minimised.

3.2 REACTION WITH OTHER CHEMICALS IN THE AQUEOUS ENVIRONMENT

Due to their chemical composition, lanthanum and phosphate react with each other very rapidly (within minutes, Haghseresht 2006a) when in solution together. As a consequence, lanthanum, when in the presence of phosphate will rapidly form the insoluble and stable Rhabdophane, rendering the lanthanum non-bioavailable and thus non-toxic. Phoslock is generally used in eutrophic water bodies, which by their very nature have high concentrations of phosphate, especially in the hypolimnion and in the sediment pore water. It follows that any free lanthanum which comes from the Phoslock granules will rapidly react with the phosphate and be rendered non-toxic.

Lanthanum can also react with carbonate which can achieve the same result as phosphate with regard to rendering free lanthanum non-toxic. However, the reaction with carbonate produces operational issues because the carbonate can compete with phosphate for the lanthanum binding sites. Ultimately this has less to do with toxicity and is of greater concern when determining the dosage for hard water lakes where a greater concentration of Phoslock may be necessary. However, it does explain why lanthanum appears less toxic in hard waters where the carbonate concentrations are high than in soft waters where they are very low.

That the toxicity of Phoslock is reduced by the presence of phosphate has been shown in toxicity studies by Martin and Hickey (2004) who demonstrated that the addition of phosphate to the highest concentrations of Phoslock leachate reduced impacts on fish fry. On the other hand the experiments of Lurling and Tolman (2010) showed unexpected results when phosphate was added to their daphnia toxicity tests. Instead the daphnia growth rates were lowered in the presence of phosphate. However, this was attributed to the very rapid precipitation of phosphate and lanthanum and the co-precipitation of algae, food for the daphnia. The animals were therefore starving rather than showing direct effects of lanthanum toxicity.

Under certain chemical conditions it is theoretically possible for lanthanum in the bentonite to exchange back into solution, thus reversing the process by which the Phoslock was created. This could occur if the Phoslock, once applied to water is exposed to very high concentrations of, for example, sodium, calcium or magnesium ions. However, the concentrations of these ions which are necessary to cause the reverse reaction are many hundred times higher than found in sea water, which of course are many times higher than those found in freshwater, so in practice this is a scenario not likely to be encountered in a freshwater lake environment (Haghseresht 2006). That said, in certain laboratory experimental conditions where the use of buffers are required to maintain a suitable pH, it is possible that sufficiently high concentrations of sodium could be present to cause some exchange with lanthanum from within Phoslock.

Very small amounts of lanthanum can potentially leach from Phoslock under other circumstances. It is thought this could happen in the presence of very soft water. However, where phosphate is present in high concentrations, such as those found in the hypolimnion of a highly eutrophic lake, or the sediment pore water, it effectively mitigates any harmful effects as it rapidly binds to the free lanthanum (Haghseresht, 2007).

Generally, Phoslock dose rates for lake restoration projects are not sufficient to bind all the available phosphorus in all the sediment of any one lake, therefore it is likely that there will always be phosphate present to bind any lanthanum which could leach from the product once on the sediment.

3.3 PRACTICAL APPROACHES TO MITIGATE ANY LANTHANUM TOXICITY FROM PHOSLOCK

With an understanding of how Phoslock works, it is possible to further reduce the likelihood of any toxic effects to aquatic organisms by, for example, choosing to apply Phoslock to a water body when the phosphate concentrations are at their highest, or directly to the hypolimnion of a stratified lake. In addition, applications which avoid the littoral zones are likely to reduce contact with the majority of the lakes flora and fauna, although this may not be practical or possible in very shallow lakes. Furthermore, Phoslock is intended for use as a tool to help reverse the effects of anthropogenic eutrophication, it therefore follows that any lakes where it is to be used will contain high concentrations of phosphate at certain times of the year or in certain parts of the water body, e.g. anoxic hypolimnion.

4 PHOSLOCK APPLICATIONS IN LAKES – ASSESSMENT OF RISK

The following provides information on the possible risks to and impacts on aquatic organisms from using Phoslock in natural lake environments. Overall, the design of Phoslock and its use in phosphate rich environments should virtually illuminate any risk to biota from lanthanum. It is also always important to balance any changes in the aquatic flora and fauna against the improvements to the lake as a result of a significant reduction in available phosphorus and it must also be considered that some changes could be a natural consequence of re-oligotrophication and not a result of toxicity from Phoslock.

4.1 LAKE WATER LANTHANUM CONCENTRATIONS FOLLOWING PHOSLOCK APPLICATIONS

The following graphs show the results of water sample analysis from four lakes treated with Phoslock. Analyses were carried out by the Institute Dr Nowak. They show the concentrations of lanthanum, either total or dissolved at a given number of days following the application, measured near the surface and from near the sediment at the deepest part of the lake. The Phoslock was applied to the surface water in each case. Total lanthanum includes the lanthanum bound tightly within Phoslock and any particulate Rhabdophane, formed if free lanthanum has reacted with phosphate. Dissolved lanthanum is measured in samples filtered through a 0.45µm filter and will include any free lanthanum but is also highly likely to include very small Rhabdophane particles which pass through the filter. Measurements of total lanthanum in the water column are seen as a tracer for the Phoslock.

The initial peaks correspond to samples taken shortly after a Phoslock application and are to be expected when the product is slowly settling through the water column. It is clear that the Phoslock usually settles out of the water column in less than 100 days. After this time occasional higher values, usually in the deep water are probably a result of sediment resuspension, lifting the Phoslock off the sediment into the water column. Otherwise the concentrations remain low, at around the limits of detection of the method, 0.01mg/L or,

more recently, 0.002mg/L as the analysis technique was improved. Apart from the initial few weeks following the application when the Phoslock is settling through the water column, it is clear that the surface water and deep water total lanthanum concentrations remain lower than the lowest EC50 value for lanthanum found in the toxicological studies.

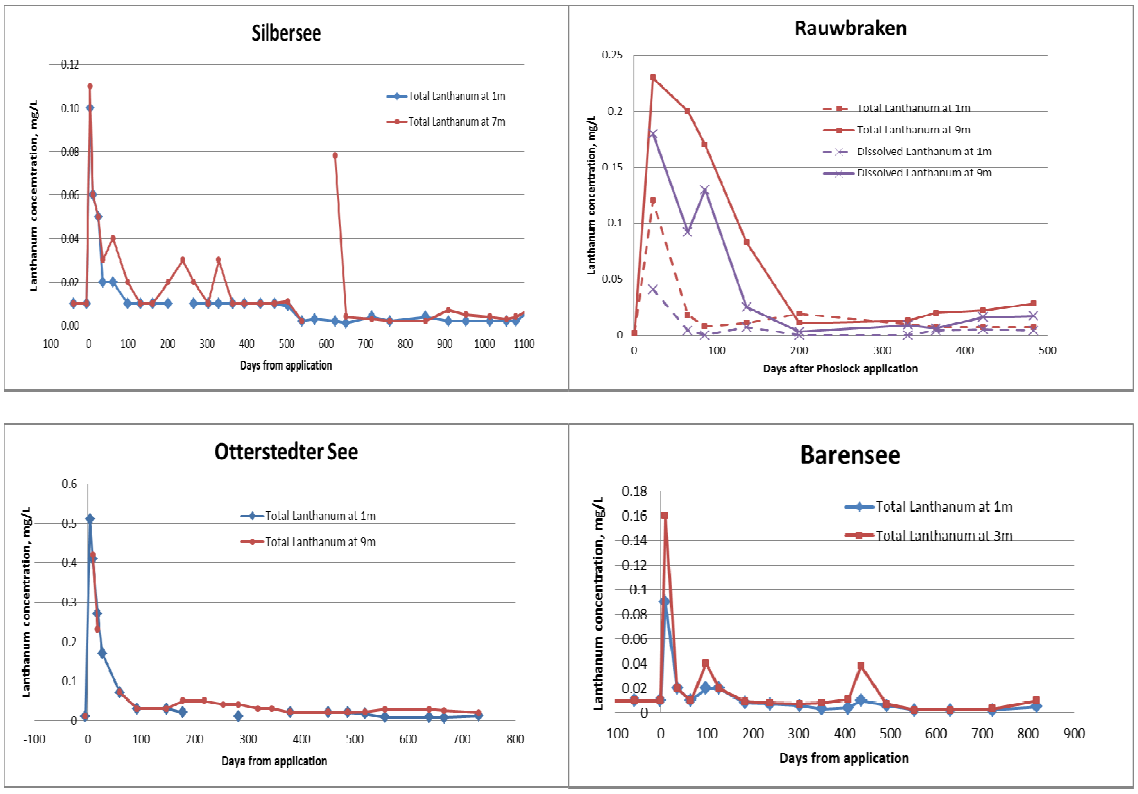

Figure 1: Lanthanum concentrations following the application of Phoslock to 4 lakes

4.2 LANTHANUM ON THE SEDIMENT

Formation of the new mineral Rhabdophane, either within the lanthanum-bentonite complex of Phoslock or from the binding of free lanthanum with phosphate is considered to render bound phosphate and lanthanum inert within the sediment. Its stability in the physical and chemical conditions found on and within the sediments ensures that neither lanthanum nor phosphate will be re-released. Effectively Rhabdophane becomes part of the inert sediment where it stays and is worked into the sediment through bioturbation and/or buried by new sediment formation. Consequently lanthanum-bound phosphate is not thought to pose any risk to biota and there is no risk that lanthanum can be released from the complex.

4.3 EFFECTS ON THE BIOTA

This section looks at the ways in which the biota could be influenced by Phoslock.

4.3.1 ALGAE

One of the main measures of success of Phoslock is to limit the availability of phosphate which lowers the phytoplankton biomass or alters its composition. Therefore is virtually impossible to separate any directly toxic effect of Phoslock from the beneficial effects of phosphate reduction. Overall, Phoslock Europe does not think there are non-target impacts on phytoplankton and it is worth noting that in lakes where the Phoslock has become saturated and phosphorus release from the sediment resumes, or where external phosphorus sources have not been eliminated, phytoplankton communities can return to a state resembling the pre-application condition.

Benthic or epiphytic algae could be subjected to longer exposures of Phoslock, if the application occurs in water shallow enough for their growth. There has been no work done on toxicity to such taxa so impacts are unknown. However, they will also be influenced by a reduction in available phosphate independently of any other impacts.

4.3.2 MACROPHYTES

Macrophytes are often absent or the species composition and distribution impacted in highly eutrophic lakes. Due to poor water clarity colonisation is only likely in the most shallow water areas and will consist mainly of one or a few tolerant taxa. Unless the water body is very shallow, it is likely that any macrophytes present will be restricted to the lake margins, therefore it is unlikely that they will be exposed to Phoslock, which is usually applied to the deeper areas of lakes. In theory smothering by Phoslock could be a problem if it were applied over macrophyte beds, due to a reduced light availability, but generally this is avoided as applications tend to take place in the late autumn, winter or early spring when most macrophytes, if present, will already have died back naturally. There is currently no evidence to suggest toxic impacts to macrophytes from Phoslock but some evidence to show that an application of Phoslock is in fact beneficial to the macrophyte community as a consequence of clearer water and improved light penetration (Meis 2011).

4.3.3 CLADOCERANS

Toxicological studies have shown low levels of toxicity to species of daphnia from Phoslock (Ecotox 2008). However, it is possible that the feeding mechanisms of some taxa could be disrupted by the presence of the Phoslock particles in the water column. Exposure of most planktonic cladocerans will probably be restricted to the period between the Phoslock application and the time it takes to sink from the water column. Generally, Phoslock is not applied to the entire surface of a water body so it is likely that even if there is some mortality to individuals in the path of the application, numbers may build again from areas around the margins of the lake where no Phoslock was applied. Taxa which are not planktonic may be more prone to impacts from Phoslock if it is applied to sediment where they occur. There have been no reports of the total disappearance of cladocerans following

Phoslock applications. However, you might expect to see changes in the species composition as a result of the lowering of phytoplankton biomass and changes to its composition. This would seem to be a natural consequence of reducing the phosphate load to the water column.

4.3.4 INVERTEBRATES

Invertebrate fauna ranges from profundal communities of chironomid larvae and oligochaetes to a much wider range of taxa living in the littoral zones, either as larvae or permanently. Those living in the profundal zone are most likely to be exposed to long-term exposure of Phoslock, living in the sediments onto which Phoslock settles. The work of Watson-Leung (2008) showed no toxicological impacts to chironomids over several weeks at Phoslock concentrations of 450 mg/L. Furthermore the presence of high concentrations of phosphate in the sediment pore water should minimise any toxicity from lanthanum. Sediments from Clatto Reservoir in Scotland showed an apparently thriving profundal invertebrate community three months after a Phoslock application (Spears et al 2010).

There are likely to be many more species of chironomid present than those used in the toxicology studies making generalisation about toxic effects difficult, but assuming all profundal chironomids are physiologically similar, it is likely that the results from the toxicological studies can be applied more generally. No studies have been carried out using oligochaetes therefore it is not possible to say what impact Phoslock might have on them.

As with macrophytes, the invertebrate fauna living in the littoral zone of the lake is unlikely to come into direct contact with Phoslock unless the entire lake is very shallow (effectively entirely littoral). In waterbodies where they have been surveyed, such as the Torrens River in Australia and Clatto Reservoir in Scotland, no adverse effects on the macroinvertebrate fauna have been found (AWQC 2007, Meis et al 2010).

4.3.5 FISH

Risks to fish will depend partly on the life stage and partly on the mode of feeding. Fish eggs and larvae are thought to be more sensitive to toxicity than the adults but as reported above, those studied do not seem particularly sensitive to lanthanum or Phoslock. Fish which feed in the sediment are probably exposed to higher levels of Phoslock than those which feed on plankton or other fish. However, as with humans, the results of the few studies published, seem to suggest elevated concentrations of lanthanum in the liver, which is consistent with its excretory path in humans but low concentrations in other tissues such as muscles (Landman et al 2007). Elevated concentrations on skin tissue may be expected for animals which are frequently in contact with the sediment. Whilst it is hard to draw firm conclusions from the limited data, it seems unlikely that fish will suffer from lanthanum toxicity caused by Phoslock. See also section below on Bioaccumulation.

4.3.6 BIRDS AND MAMMALS

Impacts on these groups could be the direct result of short-term localised disturbance caused by the application machinery, although this will be limited to a small area at any one time, leaving the remainder of the lake undisturbed. Timing of applications should be such that they avoid disturbance to breeding species, or overwintering bird species if present. Exposure to Phoslock is likely to be restricted to consumption of other organisms living in or on the sediments, from macrophytes to invertebrates and fish. However, as with humans it is most likely that in these higher animals, lanthanum will pass through the organism rather than being accumulated. For this reason it seems unlikely that they will suffer any toxicity caused by Phoslock. See also section below on Bioaccumulation.

4.3.7 BIOACCUMULATION

There is little information available in the scientific literature on the bioaccumulation of lanthanum in the environment, although Persy et al (2006) found that lanthanum is excreted in humans and does not bio-accumulate.

The most reliable eco-toxicological study of the potential for lanthanum bio-accumulation conducted so far compared fish and crayfish from two lakes in New Zealand - one to which Phoslock had been applied in three successive years and one in which no Phoslock application had taken place. Landman et al (2007) were able to measure an accumulation of lanthanum in the liver and hepatopancreatic tissue of these organisms but stated that the concentrations decreased with time, dropping back to low levels between each Phoslock application. The presence of lanthanum in the liver is also to be expected given the nature of the excretory route of the element. They could find no evidence of physiological responses which could be linked to the lanthanum. This conclusion is consistent with Persy et al (2006) who reported no hepatotoxic effect in patients undergoing long-term treatment with Fosrenol®.

Studies on macrophytes in the Torrens River following Phoslock applications showed increased concentrations of lanthanum in the roots of the macrophyte species examined, but no suggestions were given as to the possible implications of this (AWQC 2008).

For certain organisms, for example Daphnia, it is not very clear as to the route of exposure to Phoslock, for example, whether it is entirely ingested or whether it is also absorbed through the body. However, where the product is ingested, it seems unlikely that accumulation through the food chain will be a significant problem given the fact that lanthanum is not absorbed through the gut, the very property which makes it a suitable medicine for humans.

A further possible route of lanthanum accumulation is through the emergence of chironomids into their adult, flying stage. Having lived in a lanthanum-rich environment for some time they could present a possible source of lanthanum to insect feeding birds,

although, as mentioned, absorption through the gut is very low so this is probably not a cause for concern.

4.4 PHYSICAL IMPACTS FROM PHOSLOCK

There is the possibility of some risk to aquatic organisms from the increased sediment load in the water column during and for some days following the application. Fish are likely to be able to avoid the most turbid areas but planktonic animals may be affected.

The thin layer of Phoslock on the sediment surface could alter the physical properties of the sediment and impact on the biota. The work on Clatto Reservoir (Scotland) by the Centre for Ecology and Hydrology (Meis et al 2010, Spears et al 2010) has shown that under the conditions present in that waterbody, the profundal organisms seemed unaffected by the presence of the Phoslock and in fact their activities rapidly move the product through the surface few centimeters of sediment. Phoslock applications are generally not of a sufficiently high concentration to form a layer of more than a few millimetres over the sediment, so it is probable that any physical effects will not impact upon the profundal community. Eventually, the Phoslock will be dispersed through the sediment, through bioturbation and buried as new sediment forms above.

4.5 EFFECTS ON HUMANS

Toxicity to humans through the handling and application procedure can be minimised by use of appropriate personal protective equipment and restricting access to fully trained staff. Drinking water to which Phoslock has been recently applied (before it has settled) could result in ingestion of the product, although the concentrations would be many times lower than the dose prescribed for patients taking the lanthanum-based medication, Fosrenol®. Uptake via consumption of fish is another possible route by which humans could consume Phoslock. However, the work of Landman et al (2007) showed no accumulation of lanthanum in the muscles of the fish, that part usually eaten, and that the concentrations in the liver and pancreatic system reduced after a few months. Furthermore, very large quantities of fish would need to be consumed to approach the minimum lanthanum dose of Fosrenol® (Asfar and Groves 2009).

5 OTHER POTENTIAL HAZARDS ASSOCIATED WITH PHOSLOCK

5.1 BENTONITE

Bentonite is not considered toxic to humans or the environment. It is an approved food additive and used in a wide range of food and drink manufacturing processes, in animal feeds and pharmaceutical products (Asfar and Groves, 2009 and references therein).

5.2 TRACE METALS

Strict quality control protocols ensure that the concentrations of trace metals in Phoslock are below limits which could cause toxic effects. A very pure grade of lanthanum chloride is used during the production of Phoslock and all raw materials are sourced from ISO accredited factories.

Lurling and Tolman (2010) measured trace metal concentrations in leachates from Phoslock and found low concentrations. They concluded that no environmental risks are expected from metals leaching from Phoslock during an application.

The following table shows the concentrations of trace elements in Phoslock against those from a European lake sediment which has been subject to long-term sewage effluent loading. Whilst some of the more common elements found in sediments, such as iron, aluminium, magnesium and sodium are in higher concentrations within Phoslock than in these particular sediments, they are contained within the Bentonite matrix and therefore simply add to the mineral component of the sediment. It is noteworthy that the more harmful metals are in much lower concentrations in the product than the sediments. It must also be considered that once applied, the absolute amount of Phoslock is very small compared to the amount of sediment, therefore, total quantities of trace elements added (with the exception of Lanthanum) will be considerably lower than already occur in the sediments.

	Phoslock concentrations: mg/kg	**First 3 cm of Lake Sediment concentrations: mg/kg**
Al	58000	23333
Ca	910	172667
Cd	<1	1
Cr	13	57
Cu	6	59
Fe	22000	17367
Hg	<0,1	0,100
K	1400	5667
La	50000	13
Mg	14000	7400
Mn	180	1053
Na	4500	457
Ni	<1	39
P	220	893
Pb	25	51
Zn	56	157

6 CASE STUDY – LOCH FLEMINGTON

Loch Flemington is a high alkalinity, very-shallow (mean depth 0.75 m; maximum depth 2.35 m) eutrophic loch of glacial origin situated in northern Scotland. Significant hydrological modifications were made to the loch during the 19th century whereby the water levels and loch size were increased. It is designated a Special Protection Area (SPA) under the Habitats and Birds Directive for breeding Slavonian grebe (Podicepsauritus). The loch has suffered many years of cultural eutrophication leading to internal sediment P release and high concentrations in the water column. This in turn has led to nuisance blue-green algal blooms, deterioration of the macrophyte community and loss of the Slavonian grebe as a breeding species. The loch is now considered to be in unfavourable condition under all conservation targets (national and European), particularly macrophyte community and suitability for breeding Slavonian grebe.

Phoslock has been applied as part of the restoration strategy for this loch but of particular interest is the fact that the effects of the application have been the subject of study by a PhD student, Sebastian Meis, working under the supervision of the Centre for Ecology and Hydrology (CEH) in Edinburgh. Consequently, a broad range of before and after parameters have been measured, including the biota. The study and thesis are not yet complete but preliminary results are available from the CEH website (http://www.ceh.ac.uk/sci_programmes/water/LochFlemingtonPublications.html). The results presented so far show no apparent adverse effects to the biota and in fact after only one year the macrophyte community is showing a positive response to the clearer water. It seems clear from this work that of these biotic parameters measured there appears to be no short-term (1-year) negative impacts as a result of the use of Phoslock in this lake (Meis 2011).

7 CONCLUSION

It is the opinion of Phoslock Europe that the structure, design and application strategies of Phoslock mitigate the hazards from lanthanum toxicity. The result is a product which presents a very low risk to the aquatic environment whilst at the same time resulting in significant improvements to water quality and biota by phosphate reduction.

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