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**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION  
AND ASSESSMENT SCHEME**

**FULL PUBLIC REPORT**

**Lanthanum Modified Clay**

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## **FULL PUBLIC REPORT**

### **Lanthanum Modified Clay**

#### **1. APPLICANT**

CSIRO Land and Water of Underwood Avenue FLOREAT WA 6014 and Integrated Mineral Technology Ltd of 24 Eagleview Place EAGLE FARM QLD 4009 have submitted a standard notification statement in support of their application for an assessment certificate for Lanthanum Modified Clay (Phoslock<sup>TM</sup>).

#### **2. IDENTITY OF THE CHEMICAL**

The molecular and structural formulae, impurities and details of exact manufacture volume have been exempted from publication in the Full Public Report and the Summary Report.

**Chemical Name:** Reaction product of bentonite or equivalent clay and lanthanum chloride, in a substitution process in which most of the sodium in the bentonite is replaced by lanthanum, with variable substitution at other sites for elements such as calcium and magnesium.

**Chemical Abstracts Service (CAS) Registry No.:** 302346-65-2

**Other Names:** Lanthanum-modified bentonite;  
Lanthanum-modified clay (LMC);  
Rare earth-modified clay.

**Marketing Name:** Phoslock<sup>TM</sup>.

**Molecular Weight:** Varies according to the size of clay particles in the end-use product.

**Method of Detection and Determination:** X-ray fluorescence (XRF) and X-ray diffraction (XRD).

**Spectral Data:** Not provided.

#### **3. PHYSICAL AND CHEMICAL PROPERTIES**

Unless otherwise indicated the physico-chemical properties listed below and discussed later relate to Phoslock™, a 30% dispersion of the modified clay in water.

<b>Appearance at 20°C &amp; 101.3 kPa:</b>	Odourless off-white cloudy aqueous suspension (Solid is cream to pale brown).
<b>Boiling Point:</b>	Not determined.
<b>Specific Gravity:</b>	2 000-2 500 kg/m <sup>3</sup> and will vary with the degree of hydration of the clay.
<b>Vapour Pressure:</b>	Not determined.
<b>Water Solubility:</b>	Expected to be insoluble (see comments below).
<b>Partition Co-efficient (n-octanol/water):</b>	Not determined (see comments below).
<b>Hydrolysis as a Function of pH:</b>	Not determined.
<b>Adsorption/Desorption:</b>	Having ability to adsorb organics (see comments below).
<b>Dissociation Constant:</b>	Not determined.
<b>Particle Size:</b>	Not determined, Phoslock™ is formulated as an aqueous suspension.
<b>Flash Point:</b>	Not determined.
<b>Flammability Limits:</b>	Not determined.
<b>Autoignition Temperature:</b>	Not likely at temperatures <2 000°C
<b>Explosive Properties:</b>	None known or expected.
<b>Reactivity/Stability:</b>	The chemical is non-reactive, but is designed to adsorb oxyanions.

### 3.1 Comments on Physico-Chemical Properties

Clay minerals are highly insoluble in water, and this will also apply to the notified material. However, there is the possibility that under saline conditions the lanthanum may be exchanged for ions such as sodium which could lead to elevated lanthanum levels in the water (see Section 8.2). However, specific formulations of Phoslock™ are used under estuarine/saline conditions to minimise lanthanum release.

Partition coefficient and adsorption/desorption data are not applicable for a mineral. The notified chemical has no affinity for either the aqueous or the organic phase.

#### 4. PURITY OF THE CHEMICAL

**Degree of Purity:** 100%

**Hazardous Impurities:** The notified chemical is manufactured to ensure that trace elements and radioactivity are at levels that are similar to those found in normal clay or clay products.

**Non-hazardous Impurities (> 1% by weight):** Normal clay constituents including trace organic materials.

**Additives/Adjuvants:** None.

#### 5. USE, VOLUME AND FORMULATION

Phoslock™ containing 10-30% (w/w) notified chemical is used to control soluble phosphate concentrations in rivers, lakes and other water bodies. It can also remove a range of oxyanions such as arsenate in natural and artificial environments.

Phoslock™ will be manufactured in Australia. Phoslock™ is formulated as a fine particulate aqueous suspension or slurry at 10-30% solid (w/w). It will be packaged in approved sealed road tankers. The notifiers indicate that depending on its use, the notified chemical can be manufactured into other formulations, such as:

- Sandwiched between materials (e.g. between geotextile layers);
- Incorporated into other substrates; or
- Pelletised or granulated into a variety of size.

It is anticipated that a significant percentage of the chemical will be used for large-scale field trials or treatment of waterways and lakes during the first year of introduction. Proposed manufacture volumes of Phoslock™ in the first 5 years will be up to 5 000 tonnes per year with greater quantities to be produced as required for trials and/or application in export markets.

#### 6. OCCUPATIONAL EXPOSURE

The notifiers indicated that initially only a small number of manufacturing operators, transportation and store workers, laboratory staff and field personnel will potentially contact the notified chemical.

##### *Manufacture site*

Phoslock™ will be manufactured by 2-10 operators at up to three sites in Australia. Manufacturing processes consist of receiving containers, transferring the constituents to a

holding tank, calibrating the mixing machine by pouring and weighing of constituent chemicals, and controlling the mechanical mixing of Phoslock™. After the suspension has settled to the desired slurry density, it is pumped to a holding tank by direct pour or slurry pumping. When a batch of the slurry is required for treatment of a waterbody, it is transferred using slurry pumping or pouring directly from the holding tank to the tanker trucks used for transport. Alternatively, the slurry may also be transferred using slurry pumping or pouring directly from the holding tank to other vessels prior to dewatering.

Dry lanthanum chloride powder is received in bags of 20 kg to 1 tonne. It is transferred by a combination of manual and mechanical lifting. The 1 tonne bags of dry bentonite powder are moved mechanically to the mixing tank inlet, where the corner of each bag is cut, pouring bentonite directly into the mixing tank. The tank contains water below the inlet and is fitted with an agitation paddle to minimise the dust level during the operation.

Workers may inhale lanthanum chloride and bentonite as both are in powder form. In addition, a low level of aerosols may be generated during the mixing process. Dermal contamination will be the main route of occupational exposure to Phoslock™. Mixing will take place in water. Other engineering controls including adequate ventilation and local exhaust are equipped at the manufacturing site. Workers will wear facemasks, eye protection, chemically impermeable gloves and work clothing (long sleeves and long trousers).

#### *Storage and analysis*

There will be 10 storage and laboratory staff. Storage workers will receive and store the shipping containers. Laboratory workers will take samples during the manufacturing process and analyse production batches for quality control. Laboratory workers will handle only small quantities of the chemical. The existing analysis facility is expected to be equipped with adequate industrial controls and provide personal protective equipment for laboratory staff.

Storage workers are unlikely to be exposed to the notified chemical unless the containers breached.

#### *Transport*

There will be 10-20 transport workers transferring Phoslock™ from the manufacturing site to the field. The notifiers indicated that these transport workers are probably contract haulage staff. Phoslock™ is packaged in registered sealed tankers. Exposure to the notified chemical is possible if the sealed tankers are broken.

#### *Field workers*

Phoslock™ will be pumped from the tanker trucks to tanks in boats fitted with spray guns. Field workers will spray Phoslock™ evenly over the surface of the water. As Phoslock™ is manufactured as a slurry, the principal exposure pathways for field workers are likely to be by skin, with potential for inhalation of aerosols. There will be 20-30 field staff. The notifiers did not specify the protective equipment for field workers. However, the Material Safety Data Sheet (MSDS) for Phoslock™ stated that protective equipment including eyewear, chemically impermeable gloves, work clothing to cover arms, legs and torso and facemask should be used. The notifiers also suggested that during fieldwork, exposure to aerosols will be limited by the benefit of forced draught ventilation e.g. movement of workboat on river.

#### *Exposure of manufacturing and using other formulations*

The notifiers indicated that there could be several additional formulations of Phoslock™. No details of these formulations and occupational exposure data have been provided in the submission.

## **7. PUBLIC EXPOSURE**

The notified chemical will be marketed predominantly for commercial use. However, exposure of the public to the notified chemical may occur in the event of an accidental spill during transport of the formulated products. According to the MSDS provided for formulated products containing the notified chemical, a spill should be contained with dikes or absorbents to prevent contamination of sewers or streams.

The notified chemical is to be applied to natural aquatic systems including lakes, rivers, estuaries, dams, ornamental ponds and natural wetlands, as well as artificial environments including waste effluents. The usual application rate will result in a layer of less than 1 mm thickness on top of existing sediments, and is primarily intended for the removal of phosphates from the environment. The notifiers do not intend that there will be environmental release to drinking water from groundwater or surface water contamination, or that the chemical will leach to recreational water, but the submission does not indicate how this will be prevented. The chemical is likely to be used in situations where the aquatic systems are degraded by toxic algal blooms. Public contact with the chemical may occur where the chemical has been spread over publicly accessible water bodies. The notifiers intend that the public would be excluded from the aquatic area during the period of application, and the mixing of the chemical with naturally occurring sediments should result in its presence at low residual concentrations. The submission states that should contamination of drinking water occur, normal treatment processes should remove any of the remaining notified chemical. Therefore the risk of exposure of the general public to the notified polymer is considered low.

## **8. ENVIRONMENTAL EXPOSURE**

### **8.1 Release**

A small amount of the modified clay may be released during manufacture and transfer of the clay slurry to tanker trucks. However, it was indicated that these spills would be contained by bunding, and would be probably returned to the mixing vessels used in preparing the slurry.

The notified chemical is intended as a treatment chemical for water bodies which are susceptible to blooms of algae, and as such all will be introduced into a variety of water bodies including rivers, lakes, dams and streams. It is possible that up to 5 000 tonnes of the modified clay may be produced and used each year. A surface application rate sufficient to give approximately 1 mm of clay coverage of the bottom sediment would be sufficient to treat approximately 2 500 hectares of water, and this usage rate indicates that a significant quantity of lanthanum could be applied to aquatic environments each year. However, the lanthanum will be strongly associated with the bentonite clay and would not be released as soluble lanthanum into the water. Over time it is expected that some of the applied clay would be lost from the treated systems (eg. dams, lakes and rivers), particularly during periods of high flow where substantial mobilisation of sediments may occur.

## 8.2 Fate

Clay minerals are very stable in the environment and once released the clay is expected to persist within aquatic sediments. The clay is expected to become “loaded” with lanthanum phosphate which is highly insoluble except at extremely high or low pH. The notifier indicated that Phoslock™ is stable in the pH region 5-11 which is applicable to the pH of most environmental waters likely to be treated with the new clay, and consequently re-release of phosphorus and/or lanthanum is not expected.

Since  $\text{La}^{3+}$  ions are toxic to some aquatic organisms (see Section 10), the potential release of free lanthanum from the clay to the water column would appear to be of most significance for the purposes of assessing environmental hazard associated with use of the new clay. In low ionic strength water, the lanthanum remains strongly bound to the clay silicate plates, but under saline conditions (high ionic strength) there is the possibility for a re-exchange of the bound  $\text{La}^{3+}$  for ambient  $\text{Na}^+$  (or  $\text{Ca}^{2+}$ ) ions. In reality, the conditions which would enable this to take place would not be realised in bodies of fresh water, although it remains a possibility in brackish water – eg. river estuaries. However, any  $\text{La}^{3+}$  released in this manner is not expected to remain free, since it is expected to become strongly associated with natural humic material in the water and sediments through interaction with carboxylate groups in humic and fulvic acid (Torres and Choppin, 1984; Geng et al., 1998; Dupre et al., 1999). As stated previously, further modifications of Phoslock™ are likely to limit the release of lanthanum, if any, under brackish conditions.

Although the clay is chemically very stable, flood events would be likely to redistribute the material, and it is expected that it will eventually become distributed in the river sediments. Over time it is probable that the modified clay could be mobilised and carried appreciable distances down stream in a river system. However, remobilisation would not be likely if the clay were applied to static water bodies such as ponds and lakes.

## 9. EVALUATION OF TOXICOLOGICAL DATA

There is no toxicological data for the notified chemical. The notifiers provided copies of published scientific literature on the constituent chemicals of lanthanum chloride and bentonite, as surrogate data. Mammalian toxicological data on lanthanum chloride and bentonite were supplied in form of an extensive literature review.

### 9.1 Lanthanum chloride

Lanthanum chloride (CAS No. 10099-58-8), as one of the rare earth chloride salts, may have anticoagulative effects (Beaser, 1942; Dycheroff & Gruenewald, 1943). Lanthanum competes with calcium in a large range of biomolecules and biomolecular processes. A review by Das et al., (1988) reported that  $\text{La}^{3+}$  reacts *in vitro* with various tissue components, eg proteins, enzymes and phosphates. By displacing and replacing calcium ions in certain selected cell systems,  $\text{La}^{3+}$  inhibits the significant role of calcium in the various cellular processes. For example,  $\text{La}^{3+}$  inhibits the calcium pump of red blood cells and, in animal studies,  $\text{La}^{3+}$  has been shown to inhibit muscle activity by blocking calcium-activated enzymes.

The acute oral toxicity of lanthanum chloride in rats ( $\text{LD}_{50}$  2 370-4 184 mg/kg) is very low (Cochran, 1950, Sax, 1984, RTECS, 2000). When giving subcutaneous injections, the  $\text{LD}_{50}$



was determined to be >1 000, 3 500 and >500 mg/kg in frogs, mice and rats, respectively (Sax, 1984). Information from toxicity studies has indicated that the liver is the target organ (Das et al., 1988).

Lanthanum chloride was non-mutagenic in a bacterial mutagenicity assay (EPA GeneTox Program, 1988). However, intraperitoneal injection of lanthanum chloride caused an increase in the mitotic index and the nuclear volume of liver cells, and an immediate decrease in the mitotic index of rat and mouse bone marrow cells (De and Sharma, 1981; Das et al., 1983). In the review by Das et al. (1983) chromosomal changes have been observed in a number of studies. Dose-related binding to DNA has also been observed.

In the reproductive and developmental toxicity studies, lanthanum chloride caused sperm morphological changes, and reduction of sperm motility and sperm count in goats (RTECS, 2000). A single injection of 44 mg La/kg into pregnant mice reduced the number of successful pregnancies and average litter size (Abramczuk, 1985).

A few studies indicate that rare earth compounds contribute to the risk of pneumoconiosis and chronic pulmonary reactions in workers. However, no direct evidence with lanthanum chloride has been found in workers. In a comparative *in vitro* toxicity study in a pulmonary alveolar macrophage culture, lanthanum chloride gave an LC<sub>50</sub> of 52 µM, comparable to cadmium (28 µM), suggesting that exposure to lanthanum may be harmful.

Lanthanum and lanthanum salts are not on the NOHSC *List of Designated Hazardous Substances* (NOHSC, 1999a). Based on the available information, they are unlikely to be classified as hazardous substances in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b).

## 9.2 Bentonite

Bentonite (CAS No. 1302-78-9) consists of a group of clays formed by crystallisation of vitreous volcanic ashes that were deposited in water. It has been used as a filler in crayons, a lubricant in oil well drilling, a base in cosmetics and in the manufacture of concrete. Bentonite has been approved as a food additive in Australia.

The expected acute oral toxicity of bentonite in humans is very low (LD<sub>50</sub>>15 g/kg) (HSDB, 2000). However, severe anterior segment inflammation, uveitis and retrocorneal abscess from eye exposure were reported when bentonite had been used as a prophypaste (Austin & Doughman, 1980).

In a 33 day dietary (2 and 6%) and a 90 day dietary (1, 3 and 5%) studies in chickens, no changes in behaviour, overall state, clinical and biochemical parameters and electrolytic composition of the blood. Repeat dietary administration of bentonite did not affect calcium or phosphorus metabolism. However, larger amounts caused decreased growth, muscle weakness, and death with marked changes in both calcium and phosphorus metabolism.

Bentonite did not cause fibrosis after 1 year exposure of 60 mg dust (<5 µm) in a rat study (Tatrai, 1985). However, in a second rat study, where 5 µm particles were intratracheally instilled at 5, 15 and 45 mg/rat, dose-related fibrosis was observed. Bentonite clay dust is

believed to be responsible for bronchial asthma in workers at a processing plant in USA (Browning, 1969).

Ingestion of bentonite without adequate liquids may result in intestinal obstruction in humans. Hypokalemia and microcytic iron-deficiency anaemia may occur in patients after repeat doses of clay. Chronic ingestion has been reported to cause myositis (HSDB, 2000).

Bentonite is not on the NOHSC *List of Designated Hazardous Substances* (NOHSC, 1999a). Based on the available information, it is unlikely to be classified as a hazardous substance in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b).

### 9.3 Lanthanum modified clay (Phoslock™)

No toxicological data were provided for the notified chemical.

The notified chemical is a bentonite clay partially substituted with lanthanum. CSIRO unpublished data indicate that Phoslock™ closely resembles bentonite in its physical properties with a single exception; Phoslock™ does not appreciably swell on absorption of water. In addition, free lanthanum ions are not dissociated from Phoslock™ when the latter is placed in an aqueous environment. Phoslock™ is a colloidal hydrated aluminium silicate which will form highly viscous suspensions or gels in water. These colloidal particles are unlikely to cross the biological barriers.

Phoslock™ is expected to have a LD<sub>50</sub> >15 g/kg in humans with adequate water intake. The MSDS for Phoslock™ states that eye contact may cause mild transient physical irritation due to the presence of clay particles. Phoslock™ is not expected to be a skin irritant.

Inhalation exposure to dusts from dried bentonite clay or dried Phoslock™ may cause chronic lung disease such as bronchial asthma and there is information to suggest that the rare earths may contribute to the risk of pneumoconiosis and chronic pulmonary reactions in workers. In addition, as Phoslock™ may be manufactured from bentonite containing crystalline silica, silicosis may result after chronic inhalation. Therefore, inhalation of lanthanum modified bentonite dust may lead to respiratory illness.

Due to the proportions of lanthanum and bentonite in the notified chemical, the toxicity profile is likely to resemble that of bentonite. Based on the available information and the low toxicity of bentonite, Phoslock™ is unlikely to be classified as a hazardous substance according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b).

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Ecotoxicological data were supplied in the form of an extensive array of tests, using predominantly USEPA TCLP (Toxicity Characteristic Leach Protocol) evaluation scheme.

Due to its intended use as a treatment for both natural (eg. rivers and lakes) and artificial (eg. farm and water supply authority dams) water bodies entailing deliberate and relatively large

release of the modified clay to the water compartment, the notifier has supplied a large amount of data on ecotoxicity studies.

The initial sets of data were laboratory studies on fish, daphnia and algae conducted with leachate solutions prepared from the clay (Section 10.1).

After application of the clay to an 800 metre stretch of the Canning river (WA) in two large scale field trials conducted in January and April 2000, a large number of toxicity tests (fish, *Ceriodaphnia* and algae) were conducted with the river water collected before and after application (Section 10.2). In addition to these toxicity data, in situ observations of resident biota were also conducted before and after clay application (Section 10.5).

It is important to note that the trial conducted in April 2000 utilised lanthanum exchanged clay from which most of the readily leachable free lanthanum had been removed through a prior chemical conditioning process during manufacture. It was reasoned that reduced lanthanum concentration in the water column after clay application would reduce the potential for toxic effects arising from this element, and the results of post application monitoring appeared to confirm this.

In conjunction with these tests, a series of lanthanum calibration bio-assays for fish, *Ceriodaphnia* and algae were also conducted in order to establish realistic toxicities of lanthanum against these species (Section 10.3).

These studies are discussed in detail below.

### 10.1 Initial Laboratory Tests with Leachate Prepared from Modified Clay

The initial laboratory data were generated using leachate solutions prepared in synthetic soft water and/or deionised water (Milli-Q, reverse osmosis) derived from the modified clay and are summarised in the following table. The test procedures and results obtained are described and the implications of the observed toxicity to some species are discussed. The tests were performed in compliance with OECD/EEC Test Methods and according to OECD Principles of Good Laboratory Practices.

The leachate solutions were prepared using the TCLP (Toxic Characteristic Leachate Procedure) method developed by the US EPA. In this method the solid test material (50 grams of a laboratory preparation of the modified clay) was tumbled in a teflon bottle for 18 hours with 1 L of either the synthetic soft water (48 mg/L NaHCO<sub>3</sub>, 30 mg/L CaSO<sub>4</sub>.2H<sub>2</sub>O, 30 mg/L MgSO<sub>4</sub> and 2 mg/L KCl; hardness equivalent to 40-48 mg/L CaCO<sub>3</sub>; alkalinity equivalent to 30-35 mg/L CaCO<sub>3</sub>) or deionised (reverse osmosis) water. Following the tumbling procedure the liquor was filtered through a 45 µm filter and used in the toxicity tests.

#### Laboratory Ecotoxicity Test Results

<i>Test</i>	<i>Species</i>	<i>Water type</i>	<i>Results</i>
Sub-acute Toxicity (Imbalance Static Test) (OECD TG 203)	Eastern rainbow fish <i>Melanotaenia duboulayi</i>	Synthetic soft water	96 h EC <sub>50</sub> >100% leachate (127 µg/L La – see notes below).

Acute Toxicity - Immobilisation (Static Test) (OECD TG 202)	Water Flea ( <i>Ceriodaphnia dubia</i> )	Synthetic soft water	48 h EC <sub>50</sub> = 49% leachate (80 µg/L of La.) NOEL = 25% leachate.
Acute Toxicity - Immobilisation (Static Test) (OECD TG 202)	Water Flea ( <i>Ceriodaphnia dubia</i> )	Milli-Q water	48 h EC <sub>50</sub> = 10% leachate (approximately 40 µg/L of La.)
Chronic Toxicity – (Static Test) (OECD TG 202)	Water Flea ( <i>Ceriodaphnia dubia</i> )	Synthetic soft water	7 day EC <sub>50</sub> = 41% leachate (12 µg/L of La.) NOEC < 6.25% leachate
Growth Inhibition (OECD TG 201)	Green Algae ( <i>Selenastrum capricornutum</i> )	Milli-Q water	Promoted algal growth at all leachate concentrations ≥ 6.25% – see notes below.

### 10.1.1 Fish (Lim, 1999; Stauber, 2000)

The sub-acute toxicity test on fish was performed over a 96 hour period in leachate solutions prepared from synthetic soft water (hardness 40-45 mg/L as CaCO<sub>3</sub>) using a static methodology without replacement of the test media. The test was conducted at 22.4±1.3°C using test concentrations containing 0 (control), 12.5, 25, 50, 75 and 100% of the leachate made up by mixing the appropriate volume of the 100% leachate with synthetic soft water. Four juvenile eastern rainbow fish were used in each test, and their general behaviour and appearance was monitored over the 96 hour test period. Throughout the test the dissolved oxygen was always between 79 and 108% saturation, while pH was always between 7.15 and 7.7.

In the 75% leachate and lower concentrations, no imbalance in swimming was observed over the 96 hour test period, but one fish (out of the four) in the 100% leachate exhibited some imbalance after 96 hours.

The conclusion from these results is that the soft water leachate from the modified clay has a Lowest Observed Effect Level (LOEL) of 100% leachate for this fish species although the EC<sub>50</sub> > 100%. The leachate was analysed for Zn, Cu and La and found to contain 127 µg/L, <1 µg/L and 127 µg/L of each of these elements, respectively.

### 10.1.2 Aquatic Invertebrates – Cladoceran (Stauber, 2000)

Acute toxicity tests were conducted over 48 hour periods against *Ceriodaphnia dubia* at 25±1°C using leachate solutions prepared with synthetic soft water, ultrafiltered synthetic soft water and Milli-Q water. The test concentrations were performed at 0 (control), 6.25, 12.5, 25, 50, 75 and 100% of leachate concentrations, with four replicate tests carried out at each concentration using five test animals in each test vessel (ie. 20 daphnia exposed to each test concentration).

The leachate in synthetic soft water exhibited significant toxicity to this species, with the 48 hour EC<sub>50</sub> calculated from the observed immobilisation data as 49% leachate, with the corresponding No Observed Effect Concentration (NOEC) being 25% leachate. The soft

water leachate used in this test was analysed and found to contain 163 µg/L lanthanum, and 49% leachate would correspond to approximately 80 µg/L of lanthanum.

Toxicity tests on *Ceriodaphnia dubia* using a leachate prepared using Milli-Q (reverse osmosis) water and the solutions were found to be more toxic than for the soft water leachates, with a 48 hour LC<sub>50</sub> of 10% leachate (compared with the Milli-Q water control). The lanthanum concentration was 396 µg/L, so 10% leachate would correspond to around 40 µg/L of lanthanum. However, interpretation of the results was not straight forward because there was significant mortality in the control water (ie. Milli-Q water) which suggested that threshold concentrations of some ions (possibly Ca<sup>2+</sup>) in the water are required for normal survival of this species. The report suggested that this species of cladoceran (*Ceriodaphnia dubia*) will not survive in water with conductivity lower than 100 µS/cm.

A chronic (reproduction) test against *Ceriodaphnia dubia* was also conducted over a seven day period using diluted leachate from a separate batch of synthetic soft water leachate prepared from a different laboratory preparation of the clay. Seven day survival of the daphnids (10 animals for each concentration) was significantly reduced for all tested leachate concentrations above 25%, and the 7 day EC<sub>50</sub> was calculated as 41% leachate. There was also a significant reduction in the number of young daphnids produced at all tested leachate concentrations, giving a NOEC < 6.25% leachate. This particular soft water leachate was analysed for lanthanum and found to contain 2.01 mg/L after filtration, so the 41% EC<sub>50</sub> corresponds to approximately 820 µg/L of lanthanum. When compared with the acute 48 h EC<sub>50</sub> of approximately 80 µg/L, this result is surprising, and is discussed below.

### 10.1.3 Algae (Stauber, 2000)

A test on the toxicity of Milli-Q water leachates on the growth of green algal (*Selenastrum capricornutum*) biomass at 24±2°C was conducted over a three day period. Surprisingly rather than showing toxic effects, the algae grew significantly faster in the leachate than in the Milli-Q water controls. The test was conducted using 0 (control), 6.25, 12.5, 25, 50, 75 and 100% leachate, and the test at each concentration was conducted in triplicate. For all the leachate test solutions, the growth rate of the algae was approximately twice that of the control suggesting that some component of the leachate acts as a growth promoter for this species. Although the lanthanum concentration was not reported for this leachate, it is assumed to be the same as for the *Ceriodaphnia dubia* test in Milli-Q water, so 6.25% leachate would correspond to a lanthanum concentration of around 25 µg/L.

### 10.1.4 Discussion

It is reasonable to assume that any toxic properties of the leachate solutions are most likely associated with leached lanthanum. The toxic properties of the leachate solutions derived from the new lanthanum modified clay are unusual in that –

- a) fish are apparently not affected, or only slightly affected (lanthanum concentration around 127 µg/L),

b) *Ceriodaphnia dubia* are extremely sensitive to acute exposure, and the 48 hour EC<sub>50</sub> in synthetic soft water was determined as 49% of the leachate concentration which corresponded to a lanthanum concentration of around 80 µg/L. However, in a chronic (seven day) survival and reproduction test, the EC<sub>50</sub> was determined as 41% of leachate concentration which in this case corresponded to a lanthanum concentration of around 820 µg/L. These results appear contradictory since it is usual for chronic end points to be lower than acute ones. In the present case it must be assumed that differences in the composition (eg hardness, HCO<sub>3</sub><sup>-</sup> concentration) of the water used in preparing the leachates in the two test types was responsible for the seven day reproduction EC<sub>50</sub> being significantly higher than the acute 48 hour EC<sub>50</sub>. Unfortunately no comprehensive analyses of water chemistry were provided to substantiate this possibility.

c) Green algal growth is apparently promoted in the leachate, and the test results suggest that lanthanum concentrations as low as 6.25% of the leachate concentration (lanthanum approximately 7 µg/L) stimulate growth of *Selenastrum capricornutum*.

The *Ceriodaphnia dubia* results are in general accord with those of an independent Australian study on the acute and chronic toxicity of lanthanum chloride to *Daphnia carinata* (Barry and Meehan, 2000), with these workers finding an acute 48 hour LC<sub>50</sub> of 43 µg/L in soft water (hardness equivalent to 22 mg/L as CaCO<sub>3</sub>). However, the toxicity was reduced in harder water and the LC<sub>50</sub> in ASTM water (hardness = 160 mg/L as CaCO<sub>3</sub>) was 1180 µg/L. However, Barry and Meehan (2000) reported chronic effects (7 day) at concentrations > 40 µg/L in both the soft water and ASTM water. It is important to note that the tests of Barry and Meehan (2000) did not occur in the presence of humic substances which are likely to ameliorate the effects of free lanthanum in solution.

In respect of promotion of algal growth, it is of interest that agricultural applications of rare earth salts in China have been reported to significantly increase crop production (eg. Tribe et al., 1990).

It should also be pointed out that the amount of free lanthanum released from the clay in these leachate tests is only a very small fraction of the total lanthanum contained in the clay. For example, the Milli-Q water leachate contained a concentration of lanthanum which is estimated to correspond to a loss of less than 0.02% of the total lanthanum contained in the clay.

The notifiers provided a hazard quotient (Q = estimated environmental concentration/effect concentration of most sensitive species) of < 0.004. However, assuming that the clay is applied at a typical application rate to one hectare of water of depth 1 metre and assuming the highest leaching rates encountered in the laboratory tests, then the derived PEC in the water is estimated as around 20 µg/L. Using the *Ceriodaphnia dubia* EC<sub>50</sub> of 80 µg/L, this provides a hazard quotient of 0.25. This scenario is considered to be a very much worst case one, and as indicated previously improved production techniques are expected to eliminate or significantly reduce the amount of free lanthanum leached from the clay and this will lead to a concomitant increase in the safety factor. In addition it is likely that the free ion concentration of La in a waterbody will be further reduced due to precipitation with dissolved phosphate, adsorption to particles and/or complexation with humic substances, thus further decreasing the hazard quotient.

## 10.2 Tests in “treated” Canning River Water

### 10.2.1 Fish (Stauber and Binet, 2000)

The sub-acute toxicity test on fish was performed over a 96 hour period in 76 samples (40 from Phoslock<sup>TM</sup> treated sites, and 36 from control sites) of the Canning River water taken from a number of sites after the second field application of the clay in April 2000. Samples were collected prior to clay application, on the day of application and on days 1, 3 and 7 after application. Four replicate tests were conducted for each sample, using 5 juvenile eastern rainbow fish for each test (ie. 20 fish used in each test). No renewal of test media was performed, although gentle air sparging ensured that the dissolved oxygen levels were always > 60% of O<sub>2</sub> saturation.

No significant imbalance of the fish was observed in most of the test samples over the 96 hour test period, although up to 15% of the fish (ie. 3 of 20) showed some effects after 96 hours. These data indicate that the clay treatment of the river did not contaminate the water with residues at levels sufficient to produce acute toxic effects in this species. Unfortunately, although pH, dissolved oxygen and temperature were monitored throughout the tests, the level of dissolved lanthanum in the samples was not reported.

In a supplementary lanthanum bio-assay test conducted with solutions of lanthanum chloride made up in water at lanthanum concentrations between (nominally) 750 µg/L and 48 mg/L, 100% mortality of eastern rainbow fish was found for all nominal lanthanum concentrations, indicating a 96 hour LC<sub>50</sub> significantly less than the nominal 750 µg/L (measured as 600 µg/L) (see Section 10.3.1).

Consequently, all that can be concluded from these results is that the samples collected from the Canning River sites treated with the new clay contained available lanthanum at significantly less than the nominal 750 µg/L (600 µg/L measured). The report mentioned that it was not possible to perform tests at lower concentrations due to the shortage of rainbow fish.

### 10.2.2 Aquatic Invertebrates – Cladoceran (Stauber and Binet, 2000)

#### *Acute tests*

Samples of the river water were taken from four sites before and after (on the first day, and then 1, 2, 3 and 4 weeks after application) the first application of the modified clay (January 2000), and these samples were used in laboratory toxicity (immobilisation) tests conducted against *Ceriodaphnia*. Some acute toxicity was observed in all samples collected on the first day after application (up to 29% compared with controls), although the water samples taken one week and later after clay application did not exhibit toxicity. Although a detailed breakdown of lanthanum concentrations in the samples was not provided in the report, for the first day samples which exhibited some toxicity, a rough correlation was apparently established between the lanthanum concentration and degree of immobilisation. It was remarked that – with two exceptions – only those water samples with total lanthanum concentrations in excess of the 2.6 mg/L NOEC established in the bio-assay calibration tests (see further below) were toxic.

The tests were repeated after the second application of clay in April 2000 with water samples taken on the day of application and 1, 3 and/or 7 days after application. This trial was conducted with lanthanum exchanged clay which had been treated to remove most of the available “free” metal. No toxic effects were observed in any of these samples, but it was remarked that the lanthanum concentrations in the water never exceeded 1.7 mg/L which was less than the above NOEC of 2.6 mg/L.

### ***Chronic tests***

In the first field trial (January 2000), chronic toxicity tests of the river water (post clay application) to *Ceriodaphnia* were apparently conducted only with the samples collected the first day after application. The tests were conducted over 7 days and all water samples were toxic, giving reduced survival and reproduction rates compared with the controls. In some cases the number of young produced was < 1 per female.

In the second trial (April, 2000) river water was collected on the day of application and 1, 3 and/or 7 days after application. No chronic toxicity to *Ceriodaphnia* was observed. The mean number of young produced per female was between 81 and 149% of the controls, despite the lanthanum concentration in some of the water samples exceeding the 0.09 mg/L LOEC established in the bio-assay calibration tests (Section 10.3).

### **10.2.3 Algae (Stauber and Binet, 2000)**

Samples of the river water were taken from a number of sites on the first day, and 1, 2, 3 and 4 weeks after the first clay application in January 2000, and used in laboratory algal growth tests. Although the lanthanum concentrations in the samples were not provided in the report these were apparently measured and on the first day after application lanthanum concentrations as high as 3 mg/L were recorded in water from some of the sampling sites. However, mostly the water showed no inhibitory effect on algal growth even when lanthanum concentrations exceeded the LOEC of 0.13 mg/L (Section 10.3). In only one case (water taken from site designated P3) was significant toxicity observed in bottom and surface water samples taken on the first day after application and measured lanthanum concentrations were very high at 11-15 mg/L. However, it was mentioned in the report that the growth inhibition may have been caused by the removal of bio-available phosphorus rather than reflecting the true toxicity of the lanthanum. This possibility is discussed in Section 10.3.3.

A similar series of tests was conducted after the second application of clay in April 2000, with water samples being taken on the day of application then 1, 3 and/or 7 days after application. Again, no toxic effects were observed, but stimulation of algal growth was between 65 and 450% of controls.

### **10.2.4 Discussion**

Most tests showed that toxic effects to *Ceriodaphnia* were observed in water samples taken on the first day after the first application of the modified clay to the river. Lesser toxic effects were observed for green algae, but in all cases the toxicity was attributed to free lanthanum liberated from the modified clay. In water samples taken one week and more after clay application, toxic effects were absent.



In the second application the clay had been treated to mitigate release of residual free lanthanum, and the available information indicates that this treatment did reduce release of lanthanum, although concentrations as high as 1.7 mg/L were measured in some samples.

Nevertheless, no toxic effects were observed in fish, *Ceriodaphnia* or algae, despite the measured total lanthanum concentrations sometimes exceeding the NOEC for the test species. This is attributed to mitigation of lanthanum toxicity through the prior removal of residual free (leachable) lanthanum during the manufacturing process.

### 10.3 Bio-Assay Calibration Tests

These tests were conducted in the laboratory in order to establish toxic levels of lanthanum in synthetic soft water (prepared as indicated in the previously described leachate tests) to representative fresh water species of fish, invertebrates and green algae.

#### Laboratory Bio-assay Results

<i>Test/test media</i>	<i>Species</i>	<i>End Point</i>	<i>EC<sub>50</sub>**</i> (mg/L)	<i>LOEC</i> (mg/L)	<i>NOEC</i> (mg/L)
Fish/not specified	<i>Melanotaenia duboulayi</i>	96 h ( Immobilisation*)	< 0.6	< 0.6	< 0.6
Invertebrates/ artificial soft water	<i>Ceriodaphnia dubia</i>	48 h (Immobilisation)	5		2.6
		7 day (Immobilisation)	0.51		
		7 day (Reproduction)	0.43	0.09	0.05
Algae/ algal test media	<i>Selenastrum capricornutum</i>	72 h (Growth inhibition)	0.45	0.13	< 0.13

\*It was not clear from the report whether this end point was immobilisation (imbalance) or true fish mortality.

\*\* In all tests apart from those on fish these end point lanthanum concentrations refer to total La, which includes both truly dissolved lanthanum and particulate lanthanum. Analytical data tabulated in the report strongly suggested that much of the lanthanum was present in the test media as fine particles.

#### 10.3.1 Fish

In the tests on rainbow fish (Lim, 2000), it appears that solutions of lanthanum chloride were prepared containing lanthanum at nominal concentrations between 0.75 and 48 mg/L. Five juvenile Eastern rainbow fish were placed in vessels containing 500 mL of each solution and the behaviour noted over a 96 hour period. Test media were not renewed, and over the 96 hour test period the temperature, pH and dissolved oxygen levels were 23.4-24.5°C, 6.5-8.1 and 85-106% saturation, respectively while water conductivity was reported between 997 and 1064 S/cm.

No detailed description of test results was provided, but it appears that all fish were immobilised (or dead) at all test concentrations after the 96 hour test period, indicating that the 96 hour LC<sub>50</sub> of lanthanum for this species was less than the (nominal) 0.75 mg/L. The report did not specify whether the water used to prepare the solutions was deionised (reverse osmosis) or a synthetic water made up for the test. No detailed analysis of the water was provided, except the measured lanthanum concentration in the nominally 0.75 mg/L solution was given as 0.6 mg/L.

It is not possible to reach any definite conclusions from these data except that, with an  $LC_{50} < 0.6$  mg/L, lanthanum is at least highly toxic to this fish species in this water (Mensink *et al*, 1995).

### 10.3.2 *Ceriodaphnia dubia*

The tests on *Ceriodaphnia dubia* (Stauber and Binet, 2000) were conducted over a 48 hour period in artificial soft water (48 mg/L  $NaHCO_3$ , 30 mg/L  $CaSO_4 \cdot 2H_2O$ , 30 mg/L  $MgSO_4$  and 2 mg/L  $KCl$ ; hardness equivalent to 40-48 mg/L  $CaCO_3$ ; alkalinity equivalent to 30-35 mg/L  $CaCO_3$ ) using six nominal lanthanum concentrations between 0 (control) and 23 mg/L. Four replicates vessels at each test concentration were employed, with each vessel initially containing 5 daphnia. After 48 hours exposure to a (nominally) 2.6 mg/L solution of lanthanum, 28% of the daphnia were immobile, increasing to 44% at (nominally) 7.6 mg/L and 94% at 23 mg/L. Probit analysis provided a nominal  $EC_{50}$  of 5 mg/L lanthanum and a corresponding NOEC of 2.6 mg/L. However, precipitation of the lanthanum was apparent and after 48 hours, the measured values of total lanthanum in the solutions were always close to the nominal concentrations, however those in filtered samples (filter pore size not specified) were usually  $< 10$   $\mu g/L$ . This indicates that although most of the lanthanum in the test media was present associated with fine particles, the lanthanum appears to be assimilable to the animals in this form and produces toxic effects. Alternatively, the observed toxicity may be due to physical effects, eg irritation of sensitive animal organs by fine particles of insoluble lanthanum salts.

A chronic reproduction test on this species was conducted over a 7 day period using solutions of lanthanum (measured on day one of the test) between 0 (control) and 0.62 mg/L. The lanthanum solutions were found to significantly inhibit reproduction relative to the controls, with 16.5 young produced from each original female daphnid after 7 days for the control, compared to 11.6 young per individual at 0.34 mg/L and 2.4 young at 0.62 mg/L. The 7 day  $EC_{50}$  for reproduction was determined as 0.43 mg/L with the corresponding 7 day NOEC was 0.05 mg/L. These concentrations are based on the measured lanthanum concentrations (total lanthanum) determined on day 1 of the test, and as with the acute data above, it is likely that much of the lanthanum was present in association with fine particles.

### 10.3.3 Algae

A test for lanthanum inhibition of green algal growth (Stauber and Binet, 2000) was conducted over a 72 hour period, using *Selenastrum capricornutum* and seven nominal lanthanum concentrations between 0 (control) and 8.1 mg/L in algal test medium. The tests will not be described in detail, but the solutions inhibited algal growth with an apparent 72 hour  $EC_{50}$  for lanthanum calculated from the growth data as 0.45 mg/L. However, this result must be treated with caution because, as with the *Ceriodaphnia dubia* tests, precipitation of lanthanum took place over the test period. The algal test medium contained 0.57 mg/L  $PO_4$  (which is required as a nutrient for algal growth), and there is a strong possibility that the observed toxicity may be an indirect effect associated with removal of available  $PO_4$  from the growth medium through precipitation as  $LaPO_4$ .

#### 10.3.4 Discussion

It is clear from the above that interpretation of toxicity data for lanthanum to aquatic species is difficult, and the results appear to be strongly dependent on the chemical composition of the water or test media used. In particular, under the pH regimes used in toxicity tests (typically 7-8), lanthanum phosphate and other salts are highly insoluble so interpretation of toxicity data can be confounded through at least two effects –

- a) Uncertainty in true lanthanum toxicity due to its removal through association with particulate material, and
- b) The possibility of “growth inhibition” caused through removal of nutrients such as  $\text{PO}_4$  from the water through interaction with lanthanum.

In the present series of tests it is not possible to make any definite statement in regard to fish toxicity since the quality of the water was not specified. The 96 hour  $\text{LC}_{50}$  of  $< 0.6$  mg/L found in the present tests indicates that lanthanum may be at least highly toxic to fish in some water.

In *Ceriodaphnia dubia*, the acute 48 hour  $\text{LC}_{50}$  of 5 mg/L and chronic 7 day  $\text{EC}_{50}$  of 0.43 mg/L indicate toxicity. However, removal of dissolved lanthanum through precipitation was noted and quantified and it is unclear whether the observed toxicity was due to assimilation of dissolved lanthanum or particulate lanthanum. In respect of this, the results of Barry and Meehan (1997) show that the 48 hour  $\text{LC}_{50}$  of dissolved lanthanum to some daphnia species may be as low as 43  $\mu\text{g/L}$  in soft water.

The green algal test results were confounded by probable removal of  $\text{PO}_4$  from the test media by  $\text{La}^{3+}$ . Although toxic effects were observed, with an apparent 72 hour  $\text{EbC}_{50}$  for lanthanum of 0.45 mg/L, it is possible that this was an indirect effect caused through the un-availability of phosphorus to the algae.

#### 10.4 CONCLUSIONS FROM ACUTE AND CHRONIC ECOTOXICITY RESULTS

There seems little doubt that dissolved lanthanum has at least high acute and chronic toxicity to fresh water fish and to various species of daphnia in soft water, although water quality parameters appear to have a very large effect on the toxicity. In sufficiently hard water free lanthanum may be precipitated reducing lanthanum availability to aquatic species and mitigating toxicity.

Similarly, the lanthanum ion is expected to have high affinity for the negatively charged humic material present in most natural waters. This mechanism will also remove lanthanum from the water column.

In the toxicity data available from Canning River water treated with the modified clay, no toxic effects were observed, although total lanthanum concentrations were occasionally higher than the NOEC values determined in soft water. The data presently available indicates that the amount of free lanthanum likely to be released from the clay after it has been applied to water bodies is very dependent on the chemical procedures used during clay preparation, and improved preparation procedures can give the clay little tendency for lanthanum release.

## 10.5 FIELD MONITORING DATA

The notifiers provided a number of reports concerned with the effects of the clay application on water chemistry, sediment and water microbial activity and the populations of aquatic biota.

### 10.5.1 Water chemistry

After the first field trial (January, 2000) a number of important water chemistry parameters were monitored over 140 days in the Phoslock<sup>TM</sup> treated portion of the river and compared with the control section (Douglas and Adeney, 2000). Parameters measured included total phosphorus, filterable reactive phosphorus, ammonia, NO<sub>x</sub>, silica and dissolved organic carbon (DOC). Unfortunately a period of un-seasonal rainfall 15 days after commencement of the trial caused a flood event which disturbed the system and caused dramatic changes in the water chemistry which were not associated with the Phoslock<sup>TM</sup> treatment. Nevertheless, it was possible to extract useful information from the data, and the only significant differences in the water chemistry resulting from application of the Phoslock<sup>TM</sup> were in total phosphorus and filterable reactive phosphorus. This is as expected, with the Phoslock<sup>TM</sup> treated water having statistically less total and filterable reactive phosphorus than the control. In particular, the phosphorus in the sediment pore water was significantly reduced in the Phoslock<sup>TM</sup> treated region.

### 10.5.2 Microbial Status of Sediments

The effect of lanthanum modified clay on the microbial biomass of Swan River sediments was investigated using in-situ mesocosms (Franzmann et al., 2000). Six mesocosms were placed in the Swan River. Three were treated with the modified clay and three were used as controls. After seven days, core samples were taken from each mesocosm and 2 cm sections were analysed for bacterial biomass using total phospholipid composition and conventional techniques based on culturing and counting. It is not appropriate to describe the methodology and techniques in detail, but analysis of the data indicated that the application of the modified clay to the sediments had little effect on the community composition of the sediment microbiota, and no apparent effect on the numbers of nitrate reducing and denitrifying bacteria.

In a second study, the effect of Phoslock<sup>TM</sup> application on the function of nitrifying and denitrifying bacteria in the sediments and water column after clay application was investigated (Hancock et al., 2000). No effects on the total heterotrophic count of bacteria in either the water column or the underlying sediment were observed as a consequence of Phoslock<sup>TM</sup> application (January 2000) to one area of the Canning River<sup>1</sup>. While analytical difficulties prevented determination of the rate of nitrification (of ammonia) in the water, results from the one test site examined indicated that the clay application had no effect on denitrification (conversion of NO<sub>x</sub> to N<sub>2</sub>).

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<sup>1</sup> This region of the river was also artificially enriched in oxygen by blowing air through perforated pipes laid in the river.

### 10.5.3 Aquatic Biota Populations

During the first field trial (January, 2000), the aquatic biota in the Canning River was monitored both before and after clay application to ascertain whether application of the material had any deleterious effects on the populations of periphyton, zooplankton, macrobenthos, fish, crayfish, turtles and birds (Storey and Rippingale, 2000). Biota were sampled from the deep areas of the river three times prior to and three times after clay application, and both treated and control sections of the river were monitored. Unfortunately, as indicated earlier, the trial was punctuated by an unseasonal flood event which disturbed the system and caused changes in the populations studied. Although both the treated and control sections of the river were equally disturbed, this event introduced some uncertainty in interpretation of the data.

This report was comprehensive and contains background information on the various species surveyed, and it is not appropriate to fully summarise the report here. However, with the exception of statistically reduced abundance of Swan River blue spot gobies (bottom dwelling fish – *Pseudogobius alorum*) in the Phoslock™ treated area and some abandonment of nests by water birds which had been over-sprayed with the clay slurry, the overall conclusion was that no significant treatment-related effects on biota populations were observed. The authors indicated that further study on the reaction of gobies to the clay may be warranted, and also suggested that prior construction of refuges for these benthic fish may mitigate the effects of the clay on this species. Also, the effects of the clay application on water bird nesting habits could be avoided through more careful application of the slurry.

In their conclusion, the authors were careful to point out that “the absence of significant changes (to most of the biota surveyed) cannot be taken as conclusive evidence of no effect on the biota that were monitored.” The survey was of short duration (time not reported) and the possibility of longer term effects on the river biota cannot be eliminated. However, it should also be noted that the Phoslock™ clay used in the first field trial (after which the biota monitoring study was conducted) was prepared in the simplest manner without the benefit of more recently developed processing designed to reduce leaching of lanthanum. Consequently, this study is perhaps a “worst case scenario” in respect of clay quality, and the minimal effects observed on aquatic biota, with the exception of gobies, is encouraging.

## 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The new clay is intended to treat water bodies susceptible to algal blooms. Available data indicates that it is effective when properly applied to susceptible water bodies. However, there is a possible hazard connected with release of free lanthanum to the water, although the propensity with which this occurs is apparently dependent on the method of manufacture of the modified clay.

Dissolved lanthanum is very toxic to species of daphnia in both acute and chronic tests. It may also be toxic to other species, although no definitive tests results with these organisms were available for this assessment. However, the field monitoring data available from one short trial in the Canning River has shown no adverse effects on aquatic biota except for an apparent avoidance of areas covered by the clay by gobies (bottom dwelling fish), although it

is not certain this effect is directly attributable to application of the clay. Some water birds living and nesting in the riparian verges of the river were disturbed through activities associated with clay application. This will need to be prevented by more careful application techniques. Nevertheless, more extensive field monitoring of the indigenous biota at clay application locations would have been preferred. It is understood additional data will be acquired during future field trials.

The available data on microbial populations and metabolism indicates that application of the clay to river sediments has no effect on the bacterial population or function.

Release of the new clay could be as high as 5,000 tonnes per annum, which would be associated with a significant quantity of lanthanum. However, the majority of this is incorporated and strongly bound into the matrix of the clay particles, and is unlikely to be released to the water column. Significant release of free lanthanum from the clay and associated toxicity appears to occur for one or two days after application and may have resulted from excess lanthanum in the preparation. The notifier indicated that a modified production process may reduce the amount of free lanthanum released and hence any consequent toxicity. Test data to date support this, but further confirmation is needed.

As a worst case scenario, assuming that the clay is applied at a typical application rate to one hectare of water of depth 1 metre and assuming the highest leaching rates encountered in the laboratory tests, then the derived PEC in the water is estimated as around 20 µg/L. The *Ceriodaphnia dubia* EC<sub>50</sub> of 80 µg/L derived from the leachate toxicity tests in soft water provides a hazard quotient of 0.25. This is not a large safety margin, but it is important to note that the leaching rate from the clay of 0.02% was based on data derived from preliminary clay production runs, and since production techniques have reportedly been improved, the above PEC may overestimate environmental lanthanum concentrations encountered during representative field trials. Also, the new clay has been designed as a treatment for polluted water likely to contain significant quantities of humic material. The presence of humic material is very likely have a significant mitigating effect on toxicity by forming complexes with lanthanum and lowering the effective PEC of free lanthanum in the water column. There is also mitigation of lanthanum toxicity in hard water.

Once the lanthanum in the clay has become associated with phosphate in the clay matrix it is unlikely to be mobile. The clay is not subject to biodegradation and will persist and become incorporated into aquatic sediments. Some redistribution of the clay in rivers and streams is likely following flood events which disturb and mobilise benthic sediments.

## **12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS**

No toxicological data were provided for the notified chemical. Based on data for the two ingredients, lanthanum modified clay is expected to have very low acute oral toxicity in humans. The MSDS states that Phoslock™ is not expected to be a skin irritant but it may cause mild transient physical eye irritation. Inhalation exposure to dusts of dried bentonite clay or dried Phoslock™ may cause chronic lung disease such as bronchial asthma. Rare earths may also contribute to the risk of pneumoconiosis and chronic pulmonary reactions. In addition, respiratory illness such as silicosis may result after chronic inhalation since bentonite contains crystalline silica. Based on the available information, Phoslock™ is

unlikely to be classified as a hazardous substance according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b).

### ***Occupational health and safety***

At the manufacture site, workers may experience inhalation and dermal exposure when handling dried bentonite clay and lanthanum chloride powder. Since Phoslock™ is formulated as a water slurry, skin would be the main route of occupational exposure. The mixing tank is filled with water and fitted with an agitation paddle to enhance mixing and reduce dust. Other engineering controls include adequate ventilation and local exhaust at the manufacturing site. Workers at the manufacturing site wear facemasks, eye protection, gloves and long sleeved and long trousered work clothing. These engineering control measures and personal protective equipment will minimise the occupational health risk.

Laboratory workers will handle small samples containing the notified chemical for a short time period. Given the laboratory equipment and personal protective equipment used, the health risk is considered low.

For transport and storage workers, exposure to the notified chemical can only occur in the event of a breach in sealed tankers. The health risk for these workers is low.

Field workers will spray Phoslock™ over water. The main route of exposure for field workers is dermal. Inhalation of aerosols is possible. The MSDS states that protective equipment including eyewear, gloves, work clothing and facemask should be used.

The notifiers indicated that there could be several additional formulations of the notified chemical. No details of these formulations and occupational exposure data have been provided, and the occupational health risk in manufacturing and using these products is not determined.

### ***Public health***

The notified chemical is not available for sale to the public, however its use as a water treatment chemical may lead to widespread public exposure. This exposure will be limited if waterways are closed during treatment processes. Contamination of drinking water with the notified substance would also lead to widespread public exposure. No drinking water guidelines for lanthanum levels have been established at this time.

In treating waterways with this chemical, dissociation of the lanthanum chloride from the bentonite should be avoided as far as possible. Contamination of drinking water with the notified chemical, or with dissociated lanthanum should be avoided, and the public should be excluded from areas under treatment until there has been sufficient opportunity for the chemical to disperse.

## **13. RECOMMENDATIONS**

To minimise occupational exposure to Phoslock™ the following guidelines and precautions should be observed:

- Safety goggles should be selected and fitted in accordance with Australian Standard (AS) 1336 (Standards Australia, 1994) to comply with Australian/New Zealand

Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand, 1992); industrial clothing should conform to the specifications detailed in AS 2919 and AS 3765.1 (Standards Australia, 1990); gloves should conform to AS/NZS 2161.2 (Standards Australia/Standards New Zealand, 1998); all occupational footwear should conform to AS/NZS 2210 (Standards Australia/Standards New Zealand, 1994a); for facemask should conform to AS/NZS 1715 (Standards Australia/Standards New Zealand, 1994b) and AS/NZS 1716 (Standards Australia/Standards New Zealand, 1994c) or other internationally acceptable standards.

- Spillage of the notified chemical should be avoided. Spillages should be cleaned up promptly and put into containers for disposal;
- A copy of the MSDS should be easily accessible to employees.
- Employers should ensure that NOHSC Exposure Standards for all of the components in lanthanum modified clay and inspirable dusts are not exceeded in the workplace. Effective ventilation and enclosed transfer and mixing should be used.

If products containing the notified chemical are hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b), workplace practices and control procedures consistent with State and Territory hazardous substances regulations must be in operation.

To minimise public exposure to Phoslock™ the following guidelines and precautions should be observed:

- The presence of dissociated lanthanum in drinking water should be avoided.
- Public access to areas under treatment should be prevented until the substance has dispersed and the concentration of the notified chemical in surface waters has decreased.

To minimise environmental effects to Phoslock™ the following guidelines and precautions should be observed:

- The manufacturing processes for lanthanum modified clay should be optimised to reduce the amount of free lanthanum released on application to waterways.
- Future commercial development trials of the notified chemical to collect additional ecological test data as identified and to be provided under secondary notification requirements.
- State Environmental Agencies and/or appropriate regulatory authorities responsible for water quality are to be informed prior to each use.
- Adequate measures should be taken to protect sensitive benthic species such as gobies.
- Application of the clay slurry to water bodies using spraying techniques should be performed in a responsible manner. In so far as practically possible precautions



should be taken to prevent over spray onto river and dam banks so as to minimise disturbance to flora and communities of shore dwelling fauna.

- Final outcomes of the commercial development trials should include a set of guidelines relating to appropriate use of the notified chemical and approved methods of clay slurry application to water bodies.

#### **14. MATERIAL SAFETY DATA SHEET**

The MSDS for the notified chemical was provided in a format consistent with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

#### **15. REQUIREMENTS FOR SECONDARY NOTIFICATION**

Under subsection 64(1) of the Act, the Director must be informed when the following data is available.

- Ecotoxicity data on the effect of the notified chemical on (1) burrowing amphipods, (2) physical impact on fish and sediment dwelling biota.
- Chemical and ecological test data from future trial application investigating the efficacy of the notified chemical in mitigating blooms of algae and any observed delayed effects resulting from application of Phoslock™ to these ecosystems.
- The effect of lanthanum modified clay on indigenous species exposed in mesocosms.
- Any other field monitoring of biota and ecotoxicity tests.
- Notifiers commence the production of other formulations containing the notified chemical.
- The conditions of use vary from water treatment to remove oxyanions.

Under subsection 64(2) of the Act, the Director must be informed if any of the circumstances stipulated under the subsection arise. No other specific conditions are prescribed.

The Director must be informed of any circumstances occurring under Section 64, in writing within 28 days. Secondary notification of the notified chemical may be required.

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