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Effects of lanthanum and lanthanum-modified clay on growth, survival and reproduction of *Daphnia magna*

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ABSTRACT

The novel lanthanum-modified clay water treatment technology (Phoslock®) seems very promising in remediation of eutrophied waters. Phoslock® is highly efficient in stripping dissolved phosphorous from the water column and in intercepting phosphorous released from the sediments. The active phosphorous-sorbent in Phoslock® is the Rare Earth Element lanthanum. A leachate experiment revealed that lanthanum could be released from the clay, but only in minute quantities of 0.13–2.13 $\mu g\,l^{-1}$ for a worst-case Phoslock® dosage of 250 $mg\,l^{-1}$. A life-history experiment with the zooplankton grazer *Daphnia magna* revealed that lanthanum, up to the 1000 $\mu g\,l^{-1}$ tested, had no toxic effect on the animals, but only in medium without phosphorous. In the presence of phosphorous, rhabdophane ($LaPO_4 \cdot nH_2O$) formation resulted in significant precipitation of the food algae and consequently affected life-history traits. With increasing amounts of lanthanum, in the presence of phosphate, animals remained smaller, matured later, and reproduced less, resulting in lower population growth rates. Growth rates were not affected at 33 $\mu g\,La\,l^{-1}$, but were 6% and 7% lower at 100 and 330 $\mu g\,l^{-1}$, respectively, and 20% lower at 1000 $\mu g\,l^{-1}$. A juvenile growth assay with Phoslock® tested in the range 0–5000 $mg\,l^{-1}$, yielded EC_{50} (NOEC) values of 871 (100) and 1557 (500) mg Phoslock® l^{-1} for weight and length based growth rates, respectively. The results of this study show that no major detrimental effects on *Daphnia* are to be expected from Phoslock® or its active ingredient lanthanum when applied in eutrophication control.

1. Introduction

Cyanobacterial proliferation and accumulation of biomass in nuisance scums are an obvious symptom of anthropogenic nutrient over-enrichment of surface waters (Fogg, 1969; Reynolds, 1987; Reynolds and Walsby, 1975; Paerl, 1988, 2008). Such cyanobacterial blooms may cause high turbidity, anoxia, fish kills, bad smells and pose potentially serious environmental and human health problems, because several cyanobacteria can produce a variety of very potent toxins (Codd et al., 2005; Dittmann and Wiegand, 2006; Paerl, 2008; Paerl and Huisman, 2008). Climate change is expected even to aggravate hazardous blooms (Paerl and Huisman, 2008), while safe and aesthetically acceptable water is a growing need in a modern society (Steffensen, 2008). Hence, water management is faced world-wide with a call for reducing this vulnerability to the threats of harmful cyanobacterial blooms. This means that eutrophication control remains one of the key challenges to global environmental sustainability for the 21st Century (Sharpley and Tunney, 2000; Schindler, 2006).

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Inasmuch as the most important cause of lake eutrophication is phosphorous pollution (Schindler, 1974, 1975, 1977; Correll, 1998), phosphorous (P) control is critical to mitigating eutrophication (Carpenter, 2008; Schindler et al., 2008). This requires both input control from point and nonpoint sources as well as the P-removal from the water column and P-retention in the bottom sediments (Welch and Cooke, 1995; Carpenter et al., 1998; Søndergaard et al., 2003; Mehner et al., 2008).

In the Netherlands, from the early 1980s a variety of restoration techniques have been employed. However, more long-term failures than successes have been recorded that are largely related to inadequate treatment of or neglect of in-lake P control (Gulati and Van Donk, 2002).

As the European Union Water Framework Directive (2000/60/EC) aims to restore all waters to a good ecological status or potential by 2015, it is obvious that additional remedial measures are needed to reduce in-lake P concentrations to low levels and to overcome P-release from the P-rich bottom sediments (Gulati and Van Donk, 2002). Here, the novel lanthanum-modified clay water treatment technology (Phoslock®) developed by CSIRO (Australia) seems very promising in remediation of degraded water. Phoslock® is highly efficient in stripping dissolved P from the water column and in intercepting P released from the sediments (Douglas et al., 1999; Robb et al., 2003; Akhurst et al., 2004; Ross et al., 2008).

The active P-sorbent in Phoslock® is the Rare Earth Element lanthanum which is absorbed to or complexed with the clay. This element may be released from the bentonite clay–La complex when added to water. La^{3+}-ions could be toxic to some aquatic organisms, particularly cladocerans such as *Daphnia* (Barry and Meehan, 2000; NICNAS, 2001). Hence, the potential liberation of La^{3+}-ions from the bentonite could mean a significant environmental risk (Akhurst et al., 2004), but Phoslock® has been classified as not hazardous (Martin and Hickey, 2004). It should be noted, however, that there is no consistency in the results of the few studies on the effects of lanthanum on cladocerans (Barry and Meehan, 2000; Sneller et al., 2000; Stauber, 2000; NICNAS, 2001; Martin and Hickey, 2004). In addition, the effects of Phoslock® have not been tested as such, rather an indirect so-called Toxic Characteristic Leachate Procedure has been employed (Stauber, 2000; NICNAS, 2001; Martin and Hickey, 2004).

The purpose of this study was: 1) to establish a dose response relationship between Phoslock® and the growth of *Daphnia magna*, 2) to determine the amount of lanthanum released from Phoslock®, and 3) to test the effects of lanthanum on life-history characteristics of *D. magna* in artificial P-free and P-containing medium. Based on the very strong binding of lanthanum to oxyanions and especially phosphates (e.g. Haghseresht, 2005a,b; Biswas et al., 2007; Ross et al., 2008), we hypothesize that in the presence of phosphate the formation of the insoluble mineral rhabdophane will dramatically mitigate toxicity of lanthanum.

2. Materials and methods

2.1. Test organisms

Experiments were carried out with the cladoceran *D. magna* Straus that has been isolated from Lake Zwemlust (The Netherlands) and has been maintained for more than 10 years in our laboratory. Here the *Daphnia* are kept at 20 °C in 1 l jars containing 800 ml artificial RT-medium with a pH of 7.6, a conductivity of 270 $\mu S\,cm^{-1}$ and a total hardness of 88 mg $CaCO_3\,l^{-1}$ (Tollrian, 1993). The animals are fed three times a week with the green alga *Scenedesmus obliquus* (Turpin) Kützing (~4 mg $C\,l^{-1}$). *S. obliquus* SAG 276/3a originated from the culture collection of the University of Göttingen (Germany). *S. obliquus* was maintained in 1.0 l chemostat systems in continuous light of 120 μmol quanta $m^{-2}\,s^{-1}$ at 20 °C on a slightly modified WC medium (Lürling and Beekman, 1999) and with a dilution rate of 1.1 d^{-1}.

2.2. Phoslock® leachate experiment

Two batches (25 kg each) of Phoslock were obtained from Phoslock® Water Solutions Ltd. (Australia). About 0.5 g Phoslock® was added to Erlenmeyer flasks that contained 100 ml nanopure water. Each batch was tested in triplicate (0.5033 ± 0.004 g of batch 1 and 0.5022 ± 0.002 g of batch 2). Three additional Erlenmeyers contained only 100 ml nanopure water. The Erlenmeyers were closed with Parafilm and placed for 48 h in an incubator in darkness, at 22 °C with continuous orbital shaking (200 rpm). After this the material was centrifuged for 5 min at 3000 rpm, followed by filtration through a 0.45 μm membrane filter. Filtrates were analyzed for metals (Al, Cd, Cu, Hg, La, Pb, Zn) using AAS (Hg) and ICP-MS (Al, Cd, Cu, La, Pb, Zn) in the Chemical–Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University).

2.3. Effect of lanthanum on life-history traits of D. magna

Juvenile *Daphnia* born on the same day were collected from the stock cultures and placed individually in separate 125 ml test tubes containing 100 ml of *Scenedesmus* food suspension with a concentration of 5 $mm^3\,l^{-1}$ (equivalent to ~2.5 mg $C\,l^{-1}$). These *Daphnia* were transferred daily to new tubes with fresh food and newborns from the third broods were used as experimental animals. The newborns were placed in a 500-ml beaker with RT-medium. For each treatment ten neonates were randomly selected and transferred individually into 125 ml test tubes containing 100 ml of a food suspension (in RT-medium) with different concentrations of lanthanum. Stock solutions of lanthanum were made from $La(NO_3)_3 \cdot 6H_2O$ at 3.3 mg $La\,l^{-1}$, 10 mg $La\,l^{-1}$, 33 mg $La\,l^{-1}$ and 100 mg $La\,l^{-1}$ in nanopure water. Concentrations of La in the water were measured by inductively coupled plasma mass spectrometry (ICP-MS) in the Chemical–Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University). Lanthanum was tested at the following nominal concentrations: 0, 33, 100, 330 and 1000 μg l^{-1} in the absence and presence of phosphate (330 μg l^{-1}), yielding 5 La concentrations × 10 replicates × 2 phosphate levels = 100 experimental units.

Each test tube contained only one experimental animal to avoid density effects (Martínez-Jerónimo et al., 2000). The test tubes were incubated in a temperature-controlled room at 20 °C. The animals were transferred daily to clean tubes with