



The influence of lake water alkalinity and humic substances on particle dispersion and lanthanum desorption from a lanthanum modified bentonite



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ABSTRACT

A 12 days laboratory study on potential desorption of Lanthanum (La) from a commercial La modified clay (Phoslock) was conducted using lake water from 17 Danish lakes with alkalinities between 0.02 and 3.7 meq L⁻¹ and varying concentrations of DOC and humic acids (HA's). A similar study was conducted in artificial lake water with alkalinities from 0 to 2.5 meq L⁻¹ in order to exclude interference from dissolved HA's. To test if La in solution (FLa) was associated with fine particles, the water samples were filtered sequentially through three filter sizes (1.2 μm, 0.45 μm and 0.2 μm), and finally, ultracentrifugation was used in an attempt to separate colloidal La from dissolved La. The study showed that higher FLa (up to 2.5 mg L⁻¹ or 14% of the total La in the Phoslock) concentrations were found in soft water lakes compared to hard water lakes, probably due to dispersion of the clay at low alkalinities. In addition, this study showed that HA's seem to increase the FLa concentrations in soft water lakes, most likely through complexation of La retained in the Phoslock matrix. In summary, we conclude that elevated La concentrations in lake water after a Phoslock treatment should only be expected in soft water lakes rich in DOC and HA's.

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1. Introduction

The lanthanum (La) modified clay product Phoslock, developed by CSIRO (Douglas et al., 1999) has been used for controlling excess phosphorus (P) in eutrophic lakes for app. 15 years (Copetti et al., 2016). Phoslock is a bentonite clay where the rare earth metal La has been incorporated in the layered structure by cation exchange. Lanthanum has a very high affinity for P, and is the main constituent responsible for the P adsorption of Phoslock (Dithmer et al., 2015a). Lanthanum constitutes about 4.4% (w/w) of the Phoslock (Reitzel et al., 2013). When P reacts with La, a highly insoluble La–P–H₂O mineral (Rhabdophane) is formed. Over time Rhabdophane may transform into monazite, a La–P mineral, with an even lower solubility product compared to Rhabdophane (Dithmer et al., 2015a). Phoslock has been used in more than 200 lakes worldwide, with the majority of the treatments conducted in Europe (Copetti et al., 2016). Nevertheless, only relatively few peer reviewed publications addressing Phoslocks performance in different lake types

exist, and the majority of these publications focus on its ability to bind P (e.g. Reitzel et al., 2013; Spears et al., 2013). However, free La³⁺ ions may be toxic to the fauna of the receiving lakes (e.g. Spears et al., 2013; Copetti et al., 2016), which is why La is incorporated in the bentonite matrix. A few studies (laboratory as well as full scale) have shown the presence of La in the filtered lake water (referred to as FLa) following Phoslock application (Reitzel et al., 2013; Spears et al., 2013; Lürling et al., 2014) and as a consequence, more knowledge on the factors affecting potential La release from the bentonite matrix is of great importance for a proper and safe usage of Phoslock. As mentioned above, only very few studies have addressed the potential desorption of La from the bentonite matrix of Phoslock. Reitzel et al. (2013) conducted a laboratory P adsorption experiment for 12 days, and followed the La content in the filtered and unfiltered supernatant, as well as the La concentration in the Phoslock residue after adsorption. This was done in water from both a soft water lake and a hard water lake and showed the highest fraction of unfiltered La as well as La in the filtrate in the soft water supernatant after the adsorption experiment. This was ascribed to dispersion of the bentonite clay due to a more negative zeta potential at low alkalinities.

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Spears et al. (2013) reviewed the post-application La concentrations in filtered lake water in a meta-analysis of 16 European Phoslock treated lakes. The authors found a strong negative relationship between FLa and alkalinity of the lake water which was also suggested in the study by Reitzel et al. (2013). Neither of the studies by Reitzel et al. (2013) or Spears et al. (2013), examined any potential effects of DOC on the La desorption, which might very well have affected the La concentrations reported. Hence, Lürling et al. (2014), found that Phoslock incubated in purified water containing humic acids (HA's) resulted in an increased amount of FLa, compared to controls without HA's. The proposed mechanism was complex formation between La and HA's, extracting and dissolving La from the bentonite matrix. These results were further supported by Dithmer et al. (2015b), who found that the short-term P adsorption decreased in the presence of both a commercial DOC product as well as commercial HA's. In addition, Dithmer et al. (2015b) showed that the negative effect of DOC and HA's could be overcome by time, and that the DOC and HA's did not interfere with the La–P bond, indicating that DOC and HA's primarily interfere with the cations associated with the negatively charged clay, supporting the mechanism proposed by Lürling et al. (2014).

A general shortcoming of these studies of FLa in lake waters is the lack of consistency regarding filter size. Hence, Reitzel et al. (2013) used a 0.2 µm filter, to quantify the FLa fraction, Lürling et al. (2014) used a 0.45 µm filter, whereas Spears et al. (2013) reported FLa concentrations characterized by a variety of filter sizes ranging from 1.2 µm to 0.45 µm. As a consequence, these differences in methodology are likely to yield very incomparable FLa concentrations. Therefore, we tested the hypothesis that the amount of FLa in a series of Danish lake waters depends on the alkalinity and the concentration of HA's of the lake water. In addition, we tested the hypothesis that the FLa was not truly dissolved La but rather of colloidal origin. This was done by conducting laboratory study to investigate the effect of using different filter sizes to identify FLa and to evaluate the magnitude of the potential La desorption from Phoslock. By conducting La desorption studies in artificial lake water as well as in lake water from 17 Danish lakes ranging from very soft water lakes to hard water lakes, and containing different concentrations of DOC and HA's identified by analyses of the water colour) we could study the potential release of La and the involved chemical mechanisms. To study the particulate nature of the Phoslock particles the different waters were filtered sequentially through three different filter sizes and La was measured in each of the three filtrates, after 12 days incubation with Phoslock. Finally, as an attempt to isolate the truly dissolved La from colloidal La species, the filtered lake water was ultra-centrifuged prior to La determination. Lanthanum passing through the different filter sizes as well as La in the supernatant after ultra-centrifugation is referred to as FLa throughout this report.

Principal component analyses followed by a multiple linear regression analysis were conducted to detect relationships between the chemical constituents of the lake water and the FLa (in filtrate from 0.20 µm filtration), in order to identify the mechanisms responsible for the potential La desorption or bentonite dispersion.

2. Methods and materials

2.1. Study sites and experimental setup

2.1.1. Desorption of FLa from phoslock in artificial lake water

A sequence of artificial lake water ranging in alkalinity from zero to 2.5 meq L⁻¹ was prepared by adding CaCO₃ to tap water and then diluting with MilliQ water to obtain alkalinities of 0 (pure MilliQ water), 0.2, 0.4, 2.5 meq L⁻¹. pH was adjusted to 7 with NaOH in all of the samples. The SRP concentration in the tap water was below

the detection limit.

Lanthanum desorption experiments were made in triplicates with each type of water. 20 mg (±1 mg) of Phoslock was added to each of three replicate centrifuge tubes followed by addition of 50 ml of artificial lake water. The amount of Phoslock corresponded to 400 mg Phoslock L⁻¹ and represents a high but realistic Phoslock dose compared to previous treated lakes (e.g. Spears et al., 2013). The suspensions were left shaking on a rotating (50 rpm) table for 12 days, after which the supernatant was filtered sequentially through multiple filter sizes. In the first filtration step, the supernatant was filtered through a 1.2 µm GF/C filter and 8 ml of the filtrate was collected for La determination. In the second filtration step the filtrate from the 1.2 µm filtration was filtered through a 0.45 µm membrane filter, and 8 ml of this filtrate was collected for La analysis. In the third filtration step, the remaining 0.45 µm filtrate was filtered through a 0.2 µm membrane filter and again 8 ml of this filtrate was collected for La analysis. In waters where La was detected in the 0.2 µm filtrate, a subsample of the filtrate was ultra-centrifuged at 62 000g for 30 min which should be sufficient to remove any fine colloids in suspension (Gimbert et al., 2005). Following ultracentrifugation the supernatant was collected for La analysis.

2.1.2. Desorption of FLa from phoslock in natural lake water

Surface lake water from 17 Danish lakes was collected in December 2016 (winter season). The lakes were chosen to vary in alkalinity from soft water lakes to hard water lakes. The chemical characteristics of the lakes are presented in Table 1.

As in the study of La desorption in artificial lake water (see 2.1.1.), 20 mg (±1 mg) of Phoslock was added to three replicate centrifuge tubes containing 50 ml of filtered (0.45 µm) lake water from each lake, and left gently shaking at 50 rpm on a rotating table for 12 days. After incubation each sample was centrifuged at 3000 rpm (2000g) for 10 min after which the supernatant was carefully decanted. Then the supernatant was sequentially filtered through multiple filter sizes, in a similar way as for the artificial lake water (see 2.1.1). To test whether the 30 min ultracentrifugation was sufficient to remove all the fine La containing colloids, water from three of the lakes were ultracentrifuged an additional 30 min at 62 000g to obtain a total centrifugation time of 1 h, followed by La analysis of the supernatant. This procedure was repeated 30 days after the La desorption study (for all the lakes), to test if more of the La containing colloids would precipitate during this period.

2.1.3. Chemical analyses of the artificial and natural lake water

Following filtration on a 0.45 µm cellulose acetate membrane filter, soluble reactive phosphate (SRP), conductivity, calcium, lanthanum, dissolved organic carbon (DOC), and colour were analysed in each of the different water types. Soluble reactive P was analysed spectrophotometrically in a 5 cm cuvette according to Hansen and Koroleff (1999). Dissolved organic carbon was analysed by infrared spectrophotometric analysis using a Shimadzu TOC 5000 total organic carbon analyser and colour, reflecting HA's, was measured spectrophotometrically at 410 nm with a platinum standard as reference.

Total alkalinity was determined by Gran plot titration within 24 h after collection of the water. Conductivity was measured on a Jenway 4510 conductivity meter. Dissolved calcium (Ca) and La were measured on an ICP-OES (inductively coupled plasma with optical emission spectroscopy; Perkin Elmer Optima 2100 DV). The detection limit of La was 0.4 µg L⁻¹.

2.2. Statistical analyses

Statistical analyses were performed to examine responses and

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