



# Lanthanum modified bentonite behaviour and efficiency in adsorbing phosphate in saline waters

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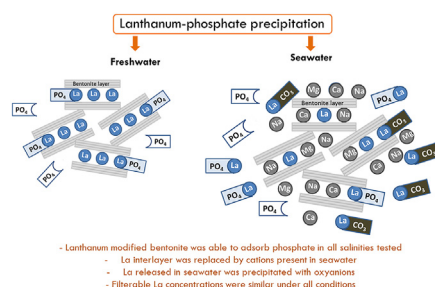
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## HIGHLIGHTS

- La-modified bentonite (LMB) is able to adsorb FRP at all salinities tested.
- Filterable La concentrations are similarly low in seawater and freshwater.
- La dissociated from clay matrix and was replaced by cations in saline waters.
- Free  $\text{La}^{3+}$  released in seawaters was removed by complexation with carbonate.
- The use of LMB in saline environments must be further evaluated.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Lanthanum-modified bentonite (LMB, commercially called Phoslock®) has been widely applied in freshwater systems to manage eutrophication. Little is known, however, about its behaviour and efficiency in binding filterable reactive phosphorus (FRP) in saline environments. We assessed if LMB would adsorb phosphate over a range of salinities (0–32 ppt) comparing the behaviour in seawater salts and equivalent concentrations of NaCl. Lanthanum release from the bentonite matrix was measured and the La species prevailing in saline environments were evaluated through chemical equilibrium modelling. We demonstrated that LMB was able to adsorb FRP in all the salinities tested. Filterable lanthanum (FLa) concentrations were similarly low ( $<5 \mu\text{g L}^{-1}$ ) at all seawater salinities but considerably elevated, on occasion >2000 times greater in equivalent NaCl salinities. Mineralogical analysis indicates that La present in the clay interlayer was (partially) replaced by Na/Ca/Mg present in the seawater and a possible secondary P-reactive phase was formed, such as kozoite ( $\text{LaCO}_3\text{OH}$ ) or lanthanite ( $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ) that may be physically dissociated from the LMB. Geochemical modelling also indicates that most FLA dissociated from LMB would be precipitated as a carbonate complex. In light of the identification of reactive intermediate phases, further studies including ecotoxicological assays are required to assess any deleterious effects from the application of LMB to saline waters.

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## 1. Introduction

Over the past century in particular, human activities have resulted in the export of increasing quantities of nutrients to

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waterbodies resulting in the rise of eutrophication and cyanobacterial blooms on a global scale (Downing, 2014; Smith and Schindler, 2009). These blooms may cause several negative effects in aquatic systems impairing the use of such for fishing, aquaculture, irrigation, recreation and as a source of drinking water all of which may result in substantial negative socio-economic outcomes (Dodds et al., 2009; Hamilton et al., 2013). In coastal environments in Europe, the marine algal toxins impact tourism and recreation, and the shellfish industry with estimated losses of 720 M€ and 166 M€ respectively (Gerssen et al., 2010). From 1987 to 1992 the economic cost from red tides in US coastal waters were estimated to be US\$500 M (Smith and Schindler, 2009).

Eutrophication of coastal environments is considered the second most important stressor on estuaries worldwide after habitat loss and alteration (Kennish, 2002) and an important factor in the creation of so-called “Dead Zones” (Diaz and Rosenberg, 2008). In addition to fluvial inputs from municipal, industrial and agricultural sources, coastal eutrophication may also be contributed to by commercial aquaculture which can create nutrient-rich effluents from excrement and unutilised food with serious impacts on aquatic systems (Burford et al., 2003; Herbeck et al., 2013; Nóbrega et al., 2014; Soares et al., 2007).

With eutrophication is ultimately being an imbalance between nutrient inputs and outputs, the first step in curtailment is the reduction of external nutrient inputs (Cooke, 2005; Hilt et al., 2006; Paerl et al., 2014). Such actions generally require stringent catchment mitigation measures including reducing atmospheric nutrient fluxes (Mackey et al., 2017), state-of-the-art wastewater treatment, and where present, reductions in nutrient inputs to, and net nutrient exports from, aquaculture. In many cases, concurrent actions of such breadth and cumulative cost are often not feasible, or at least will not be fully implemented in the short term. Thus, cases of eutrophication have continued to increase (Bricker et al., 2008). Crucially, responses in aquatic systems to external load reductions may be delayed or have a seemingly small effect because recycling of in-situ nutrients as internal loading may continue to sustain eutrophication and nuisance phytoplankton blooms (Lürling et al., 2016; Søndergaard et al., 2001). In these cases, in-situ remedial actions are important and needed to expedite system recovery (Huser et al., 2016; Lürling et al., 2016). Particularly in cases where the only source of drinking water is suffering a bloom a fast and safe solution is needed, even if it is not long-lasting and needs repeating. Thus, primarily in freshwater systems, restoration projects have been done using geo-engineering approaches (Lürling et al., 2016; Lürling and Van Oosterhout, 2013; Spears et al., 2014; Waajen et al., 2016). Geo-engineering practices typically use materials and techniques that seek to intervene in aquatic system biogeochemical cycles, particularly the interception and binding of P released from internal sediment inventories. One of the most widely applied and studied geo-engineering materials to adsorb P (usually determined as filterable reactive P, FRP) and mitigate P release from sediment (internal loading) is lanthanum modified bentonite (LMB) (Douglas, 2002; Douglas et al., 2016). Lanthanum-modified bentonite, commercially called Phoslock®, was developed by the CSIRO in Australia (Douglas, 2002; Douglas et al., 2000, 1999), has been applied in around 200 freshwater environments worldwide as well as being studied extensively in laboratory and field experiments (Behets et al., 2020; Copetti et al., 2016; D’Haese et al., 2019).

The efficiency of LMB for FRP uptake has been tested in a broad range of environmental conditions, such as different pH, humic substance concentrations and redox conditions, (Gibbs et al., 2011; Lürling et al., 2014; Mucci et al., 2018; Noyma et al., 2016; Reitzel et al., 2013; Ross et al., 2008; Spears et al., 2013b). Information on

the performance of LMB in more saline conditions is, however, limited. Reitzel et al. (2013) found that FRP sequestration by LMB was equally efficient in freshwater and brackish waters of different salinities. Recent experiments in water and sediment from a brackish lagoon showed excellent FRP uptake by LMB and interception of sediment P fluxes (Magalhães et al., 2018).

Information on behaviour of LMB in saline conditions is limited to FRP removal in NaCl solutions, which does not reflect saline waters (Zamparas et al., 2015), or to removal of the fish-killing haptophyte *Prymnesium parvum* (Seeger et al., 2015). Little information exists on brackish waters (Reitzel et al., 2013). Magalhães et al. (2018) observed an effective decrease in FRP efflux from the sediment in cores treated with LMB from a brackish tropical lagoon (~5 ppth) over 3 months. In the slightly brackish Sulphur Creek Reservoir (USA), LMB treatment reduced water column P and created a shift in sediment P towards more strongly bound forms (Bishop et al., 2014). Hence, LMB seems to possess a FRP removal capacity in brackish waters. In a cautionary note, however, Copetti et al. (2016) stated a caution that based on earlier experimentation (Douglas et al., 2000) that substantial amounts of La would be released in more saline waters and that therefore “the application of the LMB in even moderately saline environments of > 0.5 ppth is to be avoided”.

In the absence of definitive studies of the performance of LMB in brackish to saline waters detailed information is required both on performance in terms of FRP uptake as well as the potential for the release of La, and hence potential ecotoxicity. In this study we evaluated LMB performance over a range of salinities prepared using either NaCl or sea salt, determined La speciation over a range of salinities using chemical equilibrium modelling, and characterized LMB using X-Ray Diffraction (XRD).

## 2. Methods

### 2.1. P-adsorption and La release experiments in different salinities

The effect of salinity on FRP adsorption by LMB was assessed over 14 days. Six base solutions of a synthetic seawater at salinities of 0, 2, 4, 8, 16 and 32 (parts per thousand – ppth) were prepared by dissolving commercially available sea salt (La Baleine, Sel de Mer, France) in ultra-pure water with 1 mg FRP L<sup>-1</sup> prepared using K<sub>2</sub>HPO<sub>4</sub> (Sigma-Aldrich, Darmstadt, Germany). Four graduated 1 L cylinders were filled with each of the six base solutions created, totaling twenty-four cylinders. To each cylinder 5 mL of 10 g LMB L<sup>-1</sup> slurry was added by spraying it equally on the water surface, equivalent to a dose of 50 mg LMB L<sup>-1</sup> that was sufficient to remove 50% of the FRP. The LMB was obtained from Phoslock Europe GmbH (Zug, Switzerland). The experiment was run with four replicates per salinity. The cylinders were placed in a dark room at 21 °C, and pH was measured after 1, 7 and 14 days of LMB addition using a WTW pH-320 pH meter (Burladingen, Germany). Samples were taken before the LMB application, and 1 h, 1 day, 4 days, 7 days and 14 days after LMB addition. Twenty mL subsamples were filtered through unit filters (Aqua 30/0.45CA, Whatman, Dassel, Germany), of which 10 mL was used to analyse FRP on a Skalar SAN + segmented flow analyser (Breda, The Netherlands) following the Dutch standard (NEN-EN-ISO 15681-1, 2005). The remaining 10 mL was acidified with 100 µL 7 M HNO<sub>3</sub> (Sigma-Aldrich, Darmstadt, Germany) and the lanthanum (La) concentration determined by ICP-MS (Thermo Fisher Scientific, Waltham, USA) in the Chemical Biological Soil Laboratory of the Department of Soil Sciences (Wageningen University). Ten mL unfiltered subsamples were taken for analysis of total La concentration. An extra control was performed to test if the synthetic seawater would affect the

FRP concentration. To this end, 15 glass tubes of 125 mL were filled with 100 mL FRP solution ( $1 \text{ mg L}^{-1}$ ) at 2, 4, 8, 16 and 32 ppth salinity. Subsamples for FRP analysis were taken before the salt addition and after 1 week; samples were filtered and analysed for FRP as described above. Solution pH, FRP and La concentrations were statistically evaluated via repeated measures ANOVAs ( $\alpha = 0.05$ ) followed by Tukey post hoc tests. The extent of FRP removal was evaluated via a paired T-test of initial and final concentrations. Normality and homoscedasticity were tested with Shapiro-Wilk and Levene tests, respectively, using SPSS 22.0.

## 2.2. Lanthanum release experiments in NaCl and synthetic seawater solutions

Lanthanum release from the bentonite clay matrix was analysed in water with high salinity and lower FRP concentration to simulate a typical application scenario. Excess La (as LMB) was added over that required to bind the available FRP in the water column. This method was chosen as an LMB application is normally directed towards potential sediment P release, which constitutes a much higher dose than that required to bind P immediately present in the water column. Twenty-four Falcon bottles (Thermo Fisher Scientific, Waltham, USA) were filled with 50 mL stock solution of  $0.1 \text{ mg FRP L}^{-1}$  prepared using  $\text{K}_2\text{HPO}_4$  (Sigma-Aldrich, Darmstadt, Germany) and with a salinity of 32 ppth. For half of the Falcon bottles 32 ppth salinity was prepared by dissolving commercially available sea salt (La Baleine, Sel de Mer) as a synthetic seawater and the other half by dissolving NaCl (Sigma-Aldrich, Darmstadt, Germany). The LMB was then added in different concentrations (0, 50 and  $500 \text{ mg LMB L}^{-1}$ ). The experiment was undertaken using four replicates. The Falcon bottles were continuously mixed on a shaker at 180 rpm for 7 day at  $22^\circ\text{C}$  in darkness. After one and seven days, samples were taken and filtered through unit filters (Aqua 30/0.45CA, Whatman, Dassel, Germany). Filtrates were analysed for their La concentration as described above. The La concentrations between different LMB dose (0, 50 and  $500 \text{ mg L}^{-1}$ ), salts (NaCl or sea salt) and time (1 and 7 days) were statistically tested using three-way ANOVA.

## 2.3. Kinetic experiment

Batch experiments were carried out to evaluate the kinetics of FRP adsorption on LMB at the lowest (0 ppth) and highest salinity (32 ppth). The methodology details can be found at the supplementary information-Appendix A.

## 2.4. Chemical equilibrium modelling

To evaluate the lanthanum species prevailing at each salinity made with sea salt, chemical equilibrium modelling was performed using CHEAQS Next – version P2017.1 (Verweij, 2017). As input for the model we used the pH measured in the two weeks adsorption experiment, the amount of La and FRP added and the composition of standard seawater (Supplementary Information Table S1). In addition, extra model runs were performed at 32 ppth (pH 8 and in  $1 \text{ mg FRP L}^{-1}$ ) to predict the amount of free  $\text{La}^{3+}$  released as function of La concentrations. To assess the difference in La species between NaCl and synthetic seawater solution, we used the amount of La and FRP used in the specific experiment ( $2.5 \text{ mg La L}^{-1}$  and  $0.1 \text{ mg FRP L}^{-1}$ , respectively) and pH 8 as inputs in the model. In addition, model runs were performed at 32 ppth to predict La species as function of pH, using  $2.5 \text{ mg La L}^{-1}$  and  $0.1 \text{ mg FRP L}^{-1}$  as input.

## 2.5. LMB mineralogical analysis

Slurries of LMB ( $500 \text{ g L}^{-1}$ ) were prepared at 0, 4 and 32 ppth salinity and placed in 500 mL Schott bottles containing either 0 or  $0.1 \text{ mg FRP L}^{-1}$ . The bottles were continuously mixed on a shaker at 180 rpm for 24 h at  $22^\circ\text{C}$ . After which they were centrifuged at 2500 rpm for 10 min and standing water removed. The pellet, which was mostly LMB, was washed with ultra pure water once and centrifuged again. The supernatant was discarded and the LMB dried in an oven for 24 h at  $60^\circ\text{C}$ . X-ray diffraction (XRD; Bruker Fitchburg, USA) analysis was undertaken using Cu radiation ( $1.548 \text{ \AA}$ ) with a step size of  $0.02^\circ$  and step time of 1 s between 5 and  $65^\circ 2\theta$ .

## 3. Results

### 3.1. P-adsorption and La release experiment in synthetic seawater

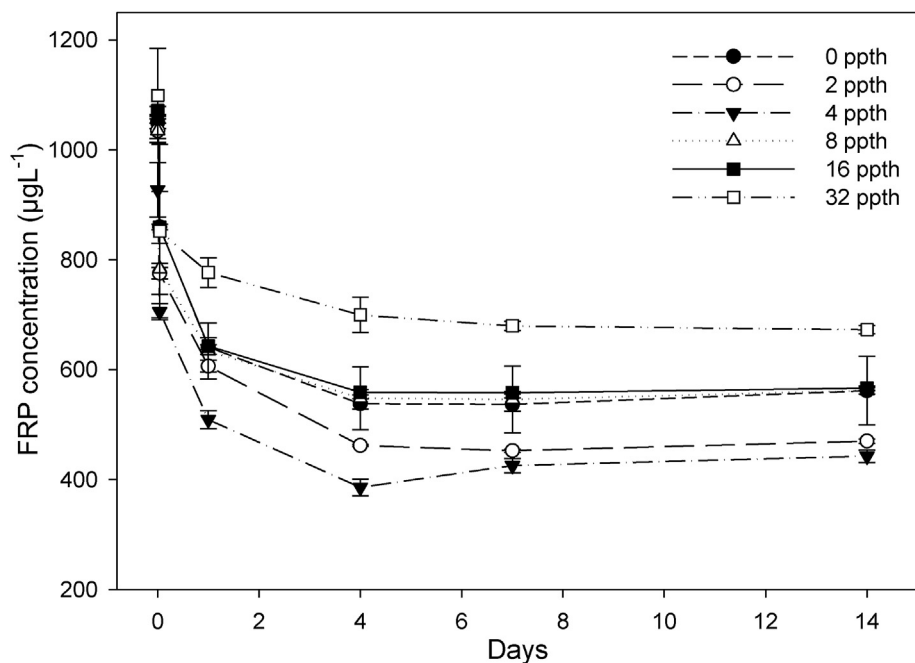
The final FRP concentrations, after incubation with LMB, varied with synthetic seawater salinity (Fig. 1, rmANOVA  $F_{5,18} = 29.669$ ,  $p < 0.001$ ). The post hoc comparison between salinities showed no difference in FRP concentration 2, 8 and 16 ppth with that in 0 ppth ( $p = 0.050$ ,  $p = 0.976$ ,  $p = 0.998$ , respectively). The FRP concentration in 4 ppth was significantly lower than at 0 ppth ( $p < 0.001$ ). At 32 ppth the FRP concentration was significantly higher than at 0 ppth ( $p = 0.003$ ) reflecting a 8% lower FRP removal by LMB (Fig. 1). Statistical (Tukey's) testing revealed four homogeneous groups: 1) adsorption was highest at 4 ppth, 2) similar at 0, 2 and 8 ppth, 3) 0, 8 and 16 ppth were also similar and 4) lowest adsorption occurred at 32 ppth (Fig. 1). A paired T-test indicated that without LMB addition initial FRP concentrations were similar to those measured after one week ( $p > 0.335$ ) (Supplementary Information Fig. S1).

Filterable lanthanum (FLa) concentrations were similar at all synthetic seawater salinities ( $F_{5,18} = 2.619$ ;  $p = 0.620$ ), although marginally higher at the lowest salinities (Fig. 2). One hour after application FLa was highest at 2 ppth ( $12.4 \mu\text{g FLa L}^{-1}$ ) and lowest at 32 ppth ( $2.1 \mu\text{g FLa L}^{-1}$ ). After 1 day the FLa concentration declined to  $5.1 \mu\text{g FLa L}^{-1}$  at 2 ppth and  $0.5 \mu\text{g FLa L}^{-1}$  at 32 ppth. After 14 days, the FLa concentration was the highest at 0 ppth ( $2.5 \mu\text{g FLa L}^{-1}$ ), while it was  $< 1 \mu\text{g FLa L}^{-1}$  at all other salinities (2–32 ppth). After two weeks FLa concentrations were 0.11%, 0.04%, 0.02%, 0.008%, 0.009% and 0.007% of the initial concentration at 0, 2, 4, 8, 16 and 32 ppth salinities, respectively.

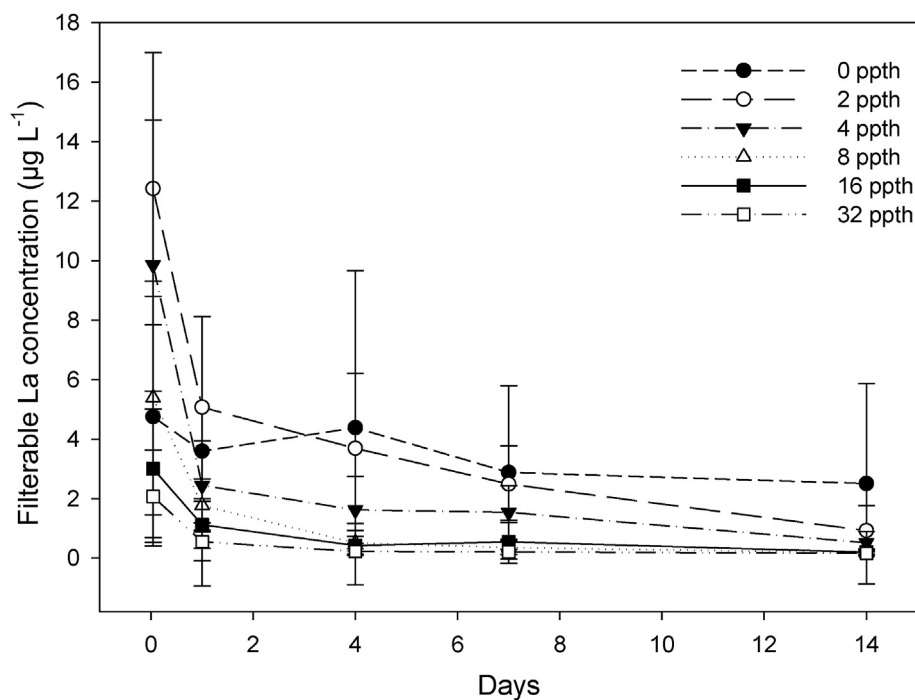
Total lanthanum (TLa) concentrations were similar among all synthetic seawater salinities ( $F_{5,18} = 0.750$ ;  $p = 0.597$ ), significantly different over time ( $p < 0.001$ ) but with a similar salinity versus time profile ( $p = 0.036$ ) indicating that the decline in TLa concentrations over time was similar at all salinities (Fig. S2). After 1 h, TLa, was highest at 32 ppth ( $1073 \mu\text{g TLa L}^{-1}$ ) and lowest at 0 ppth ( $398 \mu\text{g TLa L}^{-1}$ ). Only one day following LMB application the TLa concentration at 32 ppth had declined to  $86 \mu\text{g L}^{-1}$  whilst at 0 ppth it had declined to  $113 \mu\text{g L}^{-1}$ . After 14 days the highest concentrations of 13 and  $8 \mu\text{g TLa L}^{-1}$  were found at 0 ppth and in the 4 ppth treatments, respectively; in all the other salinities TLa was below  $2 \mu\text{g L}^{-1}$  (Fig. S2). The pH at the end of the experiment varied between pH 6.50 and pH 6.80 at all salinities (Table S2).

### 3.2. Lanthanum release experiments in NaCl and synthetic seawater solutions

No filterable La (FLa) was found in the treatment where no LMB was added (data not shown). The three-way ANOVA testing showed that FLa was significantly higher in NaCl solution than in synthetic seawater across a range of salinities ( $F_{1,6} = 974$ ;  $p < 0.001$ ). Lanthanum release was more than 2000 times higher in the 32



**Fig. 1.** Filterable reactive phosphorus (FRP) concentration over time in different synthetic seawater salinities treated with 50 mg L<sup>-1</sup> LMB. Errors bars indicate 1 SD (n = 4).



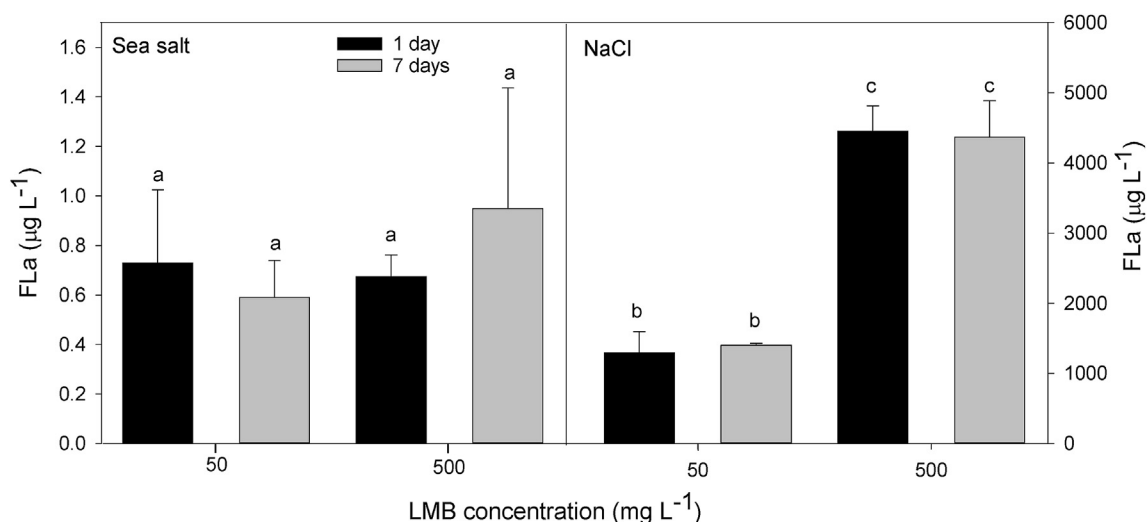
**Fig. 2.** Filterable lanthanum over time in different synthetic seawater salinities in a solution with 1 mg FRP L<sup>-1</sup> and 50 mg LMB L<sup>-1</sup>. Errors bars indicate 1 SD (n = 4).

ppth NaCl solution than in the 32 ppt synthetic seawater solution (Fig. 3). Time was not influential as at day 1 and 7 FLA concentrations were similar ( $F_{1,6} = 0.004$ ;  $p = 0.950$ ) for both type of salts used ( $p = 0.950$ ), and also independent of LMB concentrations ( $p = 0.606$ ). The main effects for LMB concentration were dependent on the type of salt used ( $F_{1,6} = 276.1$ ;  $p < 0.001$ ) with NaCl solutions having a higher FLA concentration when more LMB was added (500 mg L<sup>-1</sup>), but in synthetic seawater the FLA concentration was similarly low and independent of the amount of LMB

(Fig. 3).

### 3.3. Filterable reactive phosphorus uptake capacity

The maximum FRP adsorption capacity of LMB in synthetic seawater (32 ppt) and freshwater (0 ppt) were similar (Fig. S3). Based on the *Langmuir* isotherm a maximum FRP adsorption capacity of 11.3 ( $\pm 3.2$ ;  $p = 0.016$ ) mg FRP per gram of LMB was found in synthetic seawater (32 ppt) and 11.4 ( $\pm 1.5$ ;  $p < 0.001$ ) mg P g<sup>-1</sup>



**Fig. 3.** Filterable lanthanum concentrations (FLa) after one day (dark bars) and seven days (gray bars) in a FRP solution ( $0.1 \text{ mg L}^{-1}$ ) with 50 or 500  $\text{mg LMB L}^{-1}$  in a water with 32 ppth of salinity made by dissolving commercially sea salt (left panel) or NaCl (right panel). Letters indicates significant differences.

in freshwater (Fig. S3), data previously published (Mucci et al., 2018).

### 3.4. Chemical equilibrium modelling

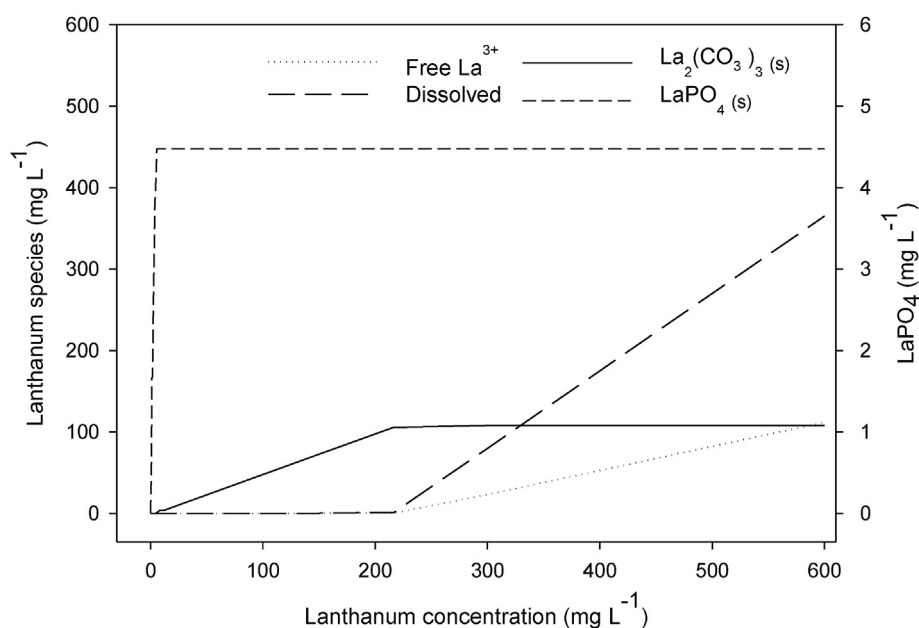
Chemical equilibrium modelling indicated that for all seawater salinities, La would precipitate with phosphate as  $\text{LaPO}_4$  (Table 1),

with a very low concentration ( $\leq 1.57 \times 10^{-6} \text{ mg L}^{-1}$ ) of free La species occurring in any of the salinities. In seawater (32 ppth) free  $\text{La}^{3+}$  ions would only start to appear when high concentrations of La were added ( $>200 \text{ mg La L}^{-1}$ ; equating to 4 g of added LMB  $\text{L}^{-1}$ ) (Fig. 4). At La concentrations below 200  $\text{mg La L}^{-1}$ , all the La is precipitated with phosphate and carbonate. When the oxyanions have mostly been depleted, dissolved La starts to increase, of which

**Table 1**

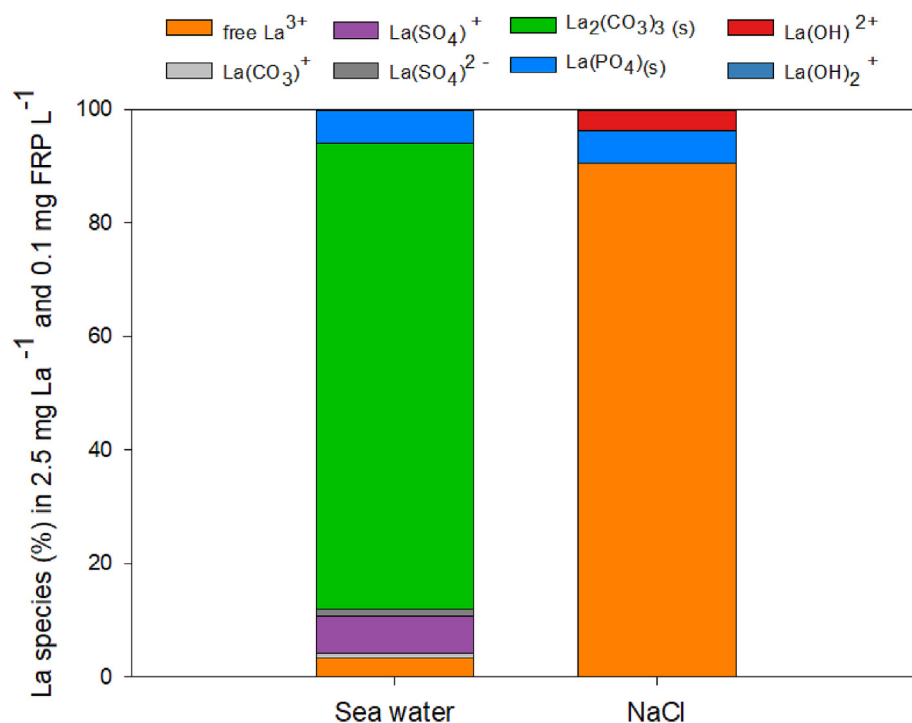
Chemical equilibrium modelling showing Free  $\text{La}^{3+}$  concentration ( $\text{mg L}^{-1}$ ) and amount of La bound to  $\text{PO}_4$  (solids) in each salinity in a solution with 3.06 mg FRP treated with 2.5 mg of lanthanum  $\text{L}^{-1}$  equating to 50 mg of LMB  $\text{L}^{-1}$ .

La species	0 ppth	2 ppth	4 ppth	8 ppth	16 ppth	32 ppth
free $\text{La}^{3+}$ ( $\text{mg L}^{-1}$ )	$2.39 \times 10^{-10}$	$1.71 \times 10^{-8}$	$2.70 \times 10^{-8}$	$1.25 \times 10^{-7}$	$5.10 \times 10^{-7}$	$1.57 \times 10^{-6}$
$\text{La}(\text{PO}_4)_s$	2.50000	2.50000	2.50000	2.50000	2.499999	2.499994



**Fig. 4.** Different lanthanum species concentration in function of lanthanum added predicted from chemical equilibrium modelling in a standard sea water (32 ppth) solution with 3.06 mg FRP  $\text{L}^{-1}$  at pH 8. Subscript s in the legend signifies solid minerals.





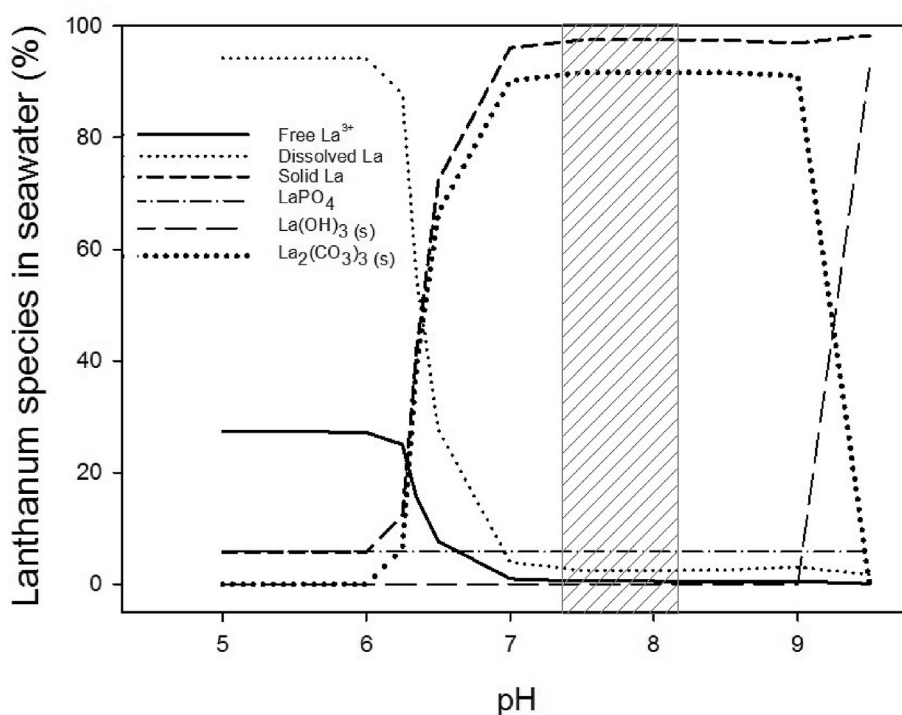
**Fig. 5.** Different lanthanum species in % predict from chemical equilibrium modelling in seawater of 32 ppt (left bar) or NaCl solution of equivalent salinity right bar in 0.1 mg FRP L<sup>-1</sup> solution at pH 8.

a small fraction is predicted to consist of free La<sup>3+</sup> ions (Fig. 4).

In a scenario with 2.5 mg La L<sup>-1</sup> and 0.1 mg P L<sup>-1</sup> in seawater at pH 8, the majority of La is predicted to precipitate as LaPO<sub>4</sub> and as La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. In contrast, in a solution of 32 ppt NaCl with 0.1 mg P L<sup>-1</sup> at a pH 8 chemical equilibrium modelling predicted that the

majority of La would be present as free La<sup>3+</sup> (Fig. 5).

At pH below 6.25, 26% of the La was present as free La<sup>3+</sup> as limited carbonate was available for complexation (Fig. 6). However, when pH increased above pH 6.25 free La<sup>3+</sup> decreased via formation of La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. At pH 6.5 free La<sup>3+</sup> constituted only 7% of all La



**Fig. 6.** Different lanthanum species in % in function of pH predicted from chemical equilibrium modelling in a seawater (32 ppt) solution with 0.1 mg FRP L<sup>-1</sup>. Subscript s in the legend means solids. Striped square is the range of oceanic pH (Chester and Jickells, 2012).

species and at  $\text{pH} \geq 7$  it decreased to less than 1% (Fig. 6). At  $\text{pH}$  greater than 9, La precipitated as a hydroxide -  $\text{La}(\text{OH})_3$ . In contrast, when in the presence of carbonate, La preferentially precipitated stoichiometrically with available  $\text{PO}_4$  independently of the  $\text{pH}$  (Fig. 6).

### 3.5. LMB mineralogical analysis

Mineralogical analysis of LMB prior to, and following the addition of P, in waters of 0, 4 and 32 ppth salinity, prepared from synthetic seawater are shown in Fig. S4 with a differential XRD analysis (LMB minus LMB with P added) shown in Fig. S5. Analysis of the XRD spectra reveal a progressive decrease in the primary LMB interlayer distance from approximately 15.3 Å to 12.5 Å with increasing salinity. Primary peaks are also apparent for kozoite ( $\text{LaCO}_3\text{OH}$ ) for the LMB at all salinities which disappears in the corresponding LMB reacted with P (Fig. S4). In contrast to kozoite, the product following reaction of the LMB/kozoite, rhabdophane is not immediately apparent in the XRD profiles in Fig. S4. Analysis of the differential XRD spectra (LMB minus LMB-0.1P, Fig. S5) reveals both the disappearance of kozoite (positive peaks) and the formation of rhabdophane (negative peaks), particularly at  $\sim 20^\circ$ ,  $29^\circ$  and  $31^\circ$   $2\theta$  where the most prominent peaks for neo-formed rhabdophane (Slade and Gates, 1999) generally occur (Diaz-Guillén et al., 2007; Roncal-Herrero et al., 2011).

## 4. Discussion

Our study has revealed profoundly different behaviour of LMB in the presence of freshwater, synthetic seawater or NaCl of equivalent salinities. These aspects are discussed below in terms of both the composition of the solution, the mineralogy and structure of the LMB, and in the implications of these findings for the potential application of LMB in saline waters.

The LMB reduced FRP in all synthetic seawater salinities with a moderately enhanced removal at 4 ppth and a reduction at 32 ppth. Seawater, however, not only contains divalent cations, but also oxyanions, of which (bi)carbonate can precipitate with La (Firsching and Mohammadzadei, 1986) and potentially impede the rate and extent of FRP removal. This has been demonstrated in other studies where LMB removed less FRP in solutions with higher concentrations of bicarbonate (Liu et al., 2016). Similarly, FRP removal by expanded graphite loaded with lanthanum oxide was reduced most in presence of carbonate (Zhang et al., 2015). Fluoride removal by La was also substantially reduced in presence of bicarbonate/carbonate (Bansawal et al., 2009; Kamble et al., 2009). Hence, the slightly lower FRP removal at higher salinities may be due to the formation of lanthanum carbonate or lanthanum carbonate/hydroxide precipitates such as kozoite ( $\text{LaCO}_3\text{OH}$ ) as observed in this study, or lanthanite ( $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ). While such carbonate compounds might impede phosphate removal in the short term as employed in our experiments, a potential exists for carbonate-bound lanthanum to eventually precipitate with phosphate via ligand exchange. This is supported by the chemical equilibrium modelling in this study in which lanthanum precipitates with phosphate. Humic substances are also known to impede the performance of FRP removal by LMB (Lürling et al., 2014) in a short term, however, over time LMB also eventually binds with FRP (Dithmer et al., 2016).

The maximum FRP adsorption capacities of 11.3  $\text{mg FRP g}^{-1}$  LMB at 32 ppth and 11.4  $\text{mg FRP g}^{-1}$  at 0 ppth are in close agreement with maximum FRP sorption capacities reported in the literature. In freshwater, a maximum sorption capacity of 12.3  $\text{mg FRP g}^{-1}$  was found (Noyma et al., 2016). Douglas (2002) and Douglas et al.

(2000) showed a variation between 9.5 and 10.5  $\text{mg FRP g}^{-1}$ . Reitzel et al. (2013) found only minor variances between the FRP adsorption capacity of LMB in waters with 1.5, 5 or 15 ppth salinity of 8.6, 8.6 and 8.7  $\text{mg FRP g}^{-1}$ , respectively. Hence, there is little apparent difference in maximum sorption capacity of LMB in freshwater or seawater.

Filterable lanthanum concentrations remained low in all seawater salinities tested, indicating either (1) no substantial La release from the clay matrix, or (2) a release of La but rapid precipitation (Fig. 2) likely due the formation of kozoite. After one day of application in all simulated seawater salinities FLA and TLA concentrations were already below the allowed concentration for Dutch water (10.1 and 150  $\mu\text{g La L}^{-1}$ , respectively) (Sneller et al., 2000).

In the experiment, after 14 days between 0.11% (0 ppth) and 0.007% (32 ppth) of the LMB-La was present as FLA. These concentrations are comparable to the 0.02% found in leachate studies (Lürling and Tolman, 2010; NICNAS, 2001). Reitzel et al. (2013) found 0.0%, 0.0% and 0.8% of the La as FLA in water of 1.5 ppth, 5 ppth and 15 ppth, respectively. In addition, in our La release experiment in synthetic seawater at 32 ppth salinity where excess LMB was added relative to FRP, after seven days the FLA concentrations were between 0.59  $\mu\text{g L}^{-1}$  ( $\pm 0.15$ ) and 0.95  $\mu\text{g La L}^{-1}$  ( $\pm 0.49$ ), ten times lower than the Dutch water quality criteria, equating to between 0.029% and 0.002% of the total La present as FLA (Fig. 3). In a previous seawater leaching study of a bentonite containing 4.3% La, only 0.7% or 16% of the total La was released (Spencer et al., 2007). Contrary to Spencer et al. (2011) who found substantially more La desorbed after day ten than day one, we did not observe a temporal effect in FLA concentration. However, Spencer et al. (2011) found the similar leaching behaviour in freshwater suggesting a potentially additional labile La component not present within the bentonite clay interlayers. Yuan et al. (2009) reported a La release from La modified clays of 0.006% at  $\text{pH}$  6.1, and of 0.0007% at  $\text{pH}$  7.85 and referred to it as the trivalent (free) La-ion. However, not all of the La in supernatant (or filtrate) should be viewed as  $\text{La}^{3+}$ , because of the potential for the formation of precipitates or the complexation with humic acids (Reitzel et al., 2017) or filterable colloids. To this end, Reitzel et al. (2017) demonstrated that a large portion of the La that was filtered through a 0.2  $\mu\text{m}$  filter was colloidal and not free  $\text{La}^{3+}$ .

Our chemical equilibrium modelling indicated that in seawater only in excess of 200  $\text{mg La L}^{-1}$  will free  $\text{La}^{3+}$  will be available (Fig. 4). Furthermore, no La free species could be expected in any salinities at an oceanic  $\text{pH}$  of between 7.5 and 8.4 (Chester and Jickells, 2012) since all La is likely to be precipitated as  $\text{LaPO}_4(\text{s})$  or  $\text{La}_2(\text{CO}_3)_3(\text{s})$  (Fig. 6). Spears et al. (2013a) predicated that  $\text{La}^{3+}$  could reach up to 120  $\mu\text{g L}^{-1}$  in low alkalinity waters, but that bicarbonate complexation would substantially diminish free  $\text{La}^{3+}$  concentrations thereafter. These results are in accordance with other studies that indicate the La will form either sparingly soluble rare-earth-metal phosphates (Firsching and Kell, 1993) or carbonates (Byrne and Kim, 1993; Firsching and Mohammadzadei, 1986).

Contrary to the limited FLA in the presence of seawater, primarily due to carbonate complexation, substantial La release occurred using NaCl at analogous salinities with FLA concentrations after one day of 1291  $\mu\text{g La L}^{-1}$  ( $\pm 249$ ) at 50  $\text{mg LMB L}^{-1}$  and 4450  $\mu\text{g La L}^{-1}$  ( $\pm 297$ ) at 500  $\text{mg LMB L}^{-1}$  added. This equated to a La release of  $68\% \pm 13\%$  and  $23\% \pm 2\%$  respectively or approximately 26 kg or 9 kg of La released from the LMB per tonne of LMB applied. After seven days FLA concentrations were similar to day one concentrations, suggesting rapid release from the clay matrix consistent with a spontaneous cation-exchange process. Moldoveanu and Papangelakis (2013) showed that  $\sim 50\%$  of the La present in natural clay was released after 1 h contact with 0.5 M NaCl solution ( $\sim 29$

ppth) with most of the La liberated in the first 10 min. The much higher FLA present in NaCl solution relative to synthetic seawater at an equivalent salinity (32 ppt) reflects the absence of complexing oxyanions to precipitate the FLA. In analogous clay-REE (rare earth element) systems, other studies have shown that the REE may readily leach in contact with concentrated inorganic salts (e.g. NaCl and  $(\text{NH}_4)_2\text{SO}_4$ ) via cation exchange (Moldoveanu and Papangelakis, 2013; Peelman et al., 2016). Thus, while NaCl solution does not represent a seawater composition, albeit the  $\text{Na}^+$  and  $\text{Cl}^-$  ions are major components of seawater (Table S1), Na, Ca and Mg cations collectively induce considerable cation exchange and La release from LMB, with, as discussed above, oxyanions such as (bi) carbonate, and where present phosphate, crucial in regulating La solubility.

Chemical speciation modelling of La species in seawater demonstrates that most of the La in seawater was precipitated, depending on composition, as  $\text{La}(\text{PO}_4)$  and  $\text{La}_2(\text{CO}_3)_3$  (Fig. 5). In contrast, in NaCl solution La once leached, it was only precipitated when  $\text{PO}_4$  was present, in agreement with the elevated concentrations of FLA found in our experiments (Fig. 3). The circumneutral pH found in most saline waters will also have little influence on the efficiency of La precipitation (Mucci et al., 2018).

Based on the solution analysis of the behaviour of LMB in synthetic seawater and NaCl of equivalent salinity, where it was demonstrated that the solute composition, as opposed to the salinity per se, is the major determinant of lanthanum speciation/precipitation. A complimentary mineralogical study using XRD has provided further insight into the behaviour of LMB during leaching. This study, has revealed profound differences may occur in both the mineralogy and structure of LMB, both as a function of salinity, and also following reaction with dissolved P. Reaction of LMB with synthetic seawater at 4 ppt and 32 ppt has revealed a substantial reduction in the primary LMB d-spacing from approximately 15.3 Å to 12.5 Å consistent with the cation exchange of La out of, and combination of Na, Ca and/or Mg from the seawater entering into the bentonite interlayers. The propensity at which a significant proportion of La may exchange into solution in even moderately NaCl-based salinity as observed in solution-based studies is also evidenced by the change in the LMB primary d-spacing. The release of FLA in the presence of equivalent NaCl-only salinities, but not in synthetic seawater, and the absence of secondary crystalline phases identifiable by XRD, coupled with the uptake of P in parallel experiments, implies the formation of other cryptocrystalline/amorphous reactive phases when LMB reacts with synthetic seawater. Geochemical modelling (Fig. 5) indicates the likelihood that lanthanum carbonate phases such as lanthanite ( $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ) or kozoite ( $\text{LaCO}_3\text{OH}$ ) as observed in this study may form following interaction of the LMB with bicarbonate present in seawater. Thus, the presence of bicarbonate may serendipitously have the effect of ameliorating FLA, and with that a potential to modify La toxicity (as yet to be determined) in saline environments.

The presence of kozoite associated with the LMB at all salinities, and in particular at 0 ppt salinity suggests that this mineral is formed as a by-product of the production of LMB during La cation-exchange into the bentonite and may reflect the presence of residual bicarbonate present following Na-exchange of the Na-bentonite precursor used in LMB production. The loss of kozoite is also important in that this likely constitutes a reactive intermediate phase with respect to dissolved P with lanthanite potentially behaving in an analogous fashion.

Based on geochemical modelling, the association of lanthanite with the reacted LMB, for instance as a surface or edge precipitate is speculative, and more so given the absence of any secondary minerals identified in XRD analysis. Thus, a potential also exists for the formation of secondary P-reactive, possibly lanthanite phase,

physically dissociated from the LMB. Subject to further studies on the association and fate of secondary lanthanite phases, this has major implications for the utility of LMB in saline waters as cryptocrystalline lanthanite will have substantially different hydrodynamic behaviour than the precursor LMB in addition to the potential, with its inherently smaller particle size relative to LMB for enhanced uptake/ingestions by aquatic biota (van Oosterhout et al., 2014; Waajen et al., 2017).

The potential for cation exchange of a combination of Na, Ca and Mg cations into the LMB also has the potential to fundamentally alter the physical behaviour of the bentonite, in particular leading to the formation of cohesive, gel-like clay structures as observed in our laboratory-based studies, with the potential to adversely impact the critical sediment-water interface in saline aquatic systems. On the basis of this study, a combination of laboratory, and in-field mesocosm ecotoxicological studies are recommended before field applications in estuarine and marine environments.

### Author contribution statement

M.M., G.D., and M.L. designed the study. M.M. performed the experiments. M.M., G.D., and M.L. analysed the data and wrote the article.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126131>.

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