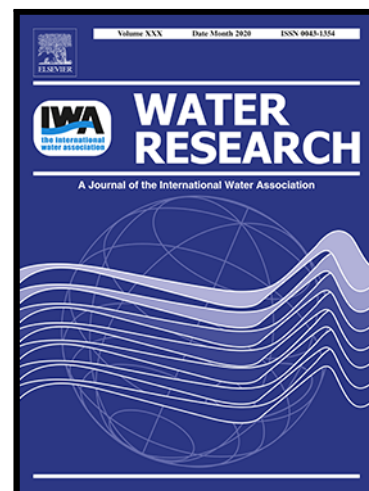# Journal Pre-proof

Influence of Natural Organic Matter and pH on Phosphate Removal by and Filterable Lanthanum Release from Lanthanum-Modified Bentonite

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Influence of Natural Organic Matter and pH on Phosphate Removal by and Filterable Lanthanum Release from Lanthanum-Modified Bentonite

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Graphical abstract
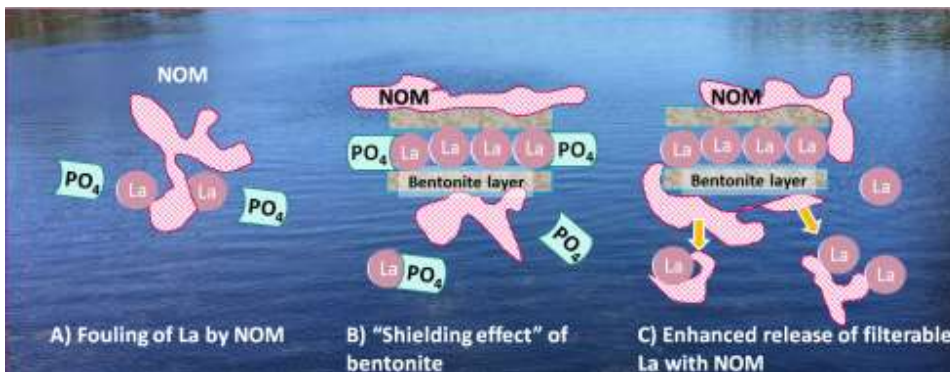
Highlights:

- Natural organic matter (NOM) adversely impacted phosphate removal

- Impact of NOM on phosphate removal was pH-dependent

- PO_4 removal by lanthanum-modified bentonite decreased by 11-25% under the highest NOM loading

- NOM increased release of filterable lanthanum from lanthanum-modified bentonite

Keywords:

Eutrophication

Lake restoration

Lanthanum release

Humic and fulvic acid

Phosphate management

Abstract

Lanthanum modified bentonite (LMB) has been applied to eutrophic lakes to reduce phosphorus (P) concentrations in the water column and mitigate P release from sediments. Previous experiments suggest that natural organic matter (NOM) can interfere with phosphate (PO_4)-binding to LMB and exacerbate lanthanum (La)-release from bentonite. This evidence served as motivation for this study to systematically determine the effects of NOM, solution pH, and bentonite as a La carrier on P removal. We conducted both geochemical modeling and controlled-laboratory batch kinetic experiments to understand the pH-dependent impacts of humic and fulvic acids on PO_4-binding to LMB and La release from LMB. The role of bentonite was studied by comparing PO_4 removal obtained by LMB and La^{3+} (added as $LaCl_3$ salt to represent the La-containing component of LMB). Our results from both geochemical modeling and batch experiments indicate that the PO_4-binding ability of LMB is decreased in the presence of NOM, and the decrease is more pronounced at pH 8.5 than at 6. At the highest evaluated NOM concentration (28 mg C L^{-1}), PO_4-removal by La^{3+} was substantially lower than that by LMB, implying that bentonite clay in LMB shielded La from interactions with NOM, while still allowing PO_4 capture by La. Finally, the presence of NOM promoted La-release from LMB, and the amount of La released depended on solution pH and both the type (i.e., fulvic/humic acid ratio) and concentration of NOM. Overall, these results provide an important basis for management of P in lakes and eutrophication control that relies on LMB applications.

1. Introduction

Phosphorus (P) is typically the primary limiting nutrient for algae in standing freshwater bodies such as lakes, ponds, and reservoirs (Conley et al., 2009; Cooke et al., 2005; Douglas et al., 2016; Schindler, 1974; Schindler et al., 2016). Management of P is therefore important to control excessive growth of phototrophic organisms. To help lower P concentrations in eutrophic lakes, in-lake treatment techniques have been employed to remove orthophosphate (PO_4, which is the sum of PO_4^{3-} and its protonated forms) from the water column and inhibit release of mobile PO_4 from lake sediments (Cooke et al., 2005). Lanthanum (La)-modified bentonite (LMB, commercially known as Phoslock®) is an PO_4-binding product that has been applied to more than 200 water bodies (Copetti et al., 2015). Currently available data highlight its high specificity and efficacy for PO_4 binding in complex waters (Haghseresht et al., 2009; He et al., 2017; Huang et al., 2014; Kurzbaum and Bar Shalom, 2016; Li et al., 2019; Min et al., 2019; Ross et al., 2008; Wasay et al., 1996). Mineralogical characterization of the reaction products from LMB contact with PO_4 in solution indicates the formation of insoluble $LaPO_4$ minerals (Dithmer et al., 2015). If all La in LMB was available for PO_4 binding, one mole of P would be removed by each mole of La added to the water column. However, recent studies have indicated that not all of the added La in LMB is available for PO_4 binding, suggesting possible interferences from solutes or particulates in natural waters (Dithmer et al., 2016; Li et al., 2020; Lürling et al., 2014; Reitzel et al., 2013).

Laboratory-scale studies of LMB applied to real waters indicate that natural organic matter (NOM) may constrain PO_4-binding by LMB (Dithmer et al., 2016; Douglas et al., 2000; Lai et al., 2016; Lürling et al., 2014; Song et al., 2020; Wu et al., 2019). Moreover, NOM can considerably alter the speciation, distribution, and mobility of La in aquatic environments

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(Chakraborty et al., 2011; Li et al., 2020; Moermond et al., 2001; Sholkovitz, 1992) and, accordingly, affect the bioaccumulation and ecotoxicity of La and LMB (Das et al., 1988; Herrmann et al., 2016; Sun et al., 1997). For example, free La^{3+}, which is the most toxic form, will likely bind to NOM at circumneutral pH (e.g., humic acid) (Moermond et al., 2001; Tang and Johannesson, 2010, 2003). Thus, in aquatic environments with high levels of natural ligands such as NOM, little to no uncomplexed La^{3+} should be present (Lürling and Tolman, 2010). In this context, it is critical to understand how NOM interacts with LMB; however, past studies that evaluated NOM effects relied on lake water samples, in which other water quality parameters (e.g., dissolved inorganic carbon) may have confounded results and obscured the impact of NOM on PO_4 removal and La release (Dithmer et al., 2016, 2015; Lürling et al., 2014).

In addition, the roles of pH and the clay carrier material of LMB (i.e., bentonite) are not well understood in the context of NOM impacts on PO_4 removal by, and La release from, LMB. We hypothesize that pH is an important parameter controlling LMB performance, as pH affects: (1) speciation of La binding sites of NOM; (2) speciation of aqueous La as well as solubility of La; and (3) speciation of PO_4 (Sonke, 2006; Sonke and Salters, 2006; Tang and Johannesson, 2003; Tipping and Tipping, 2002). Further, in addition to the La present in LMB, bentonite may interact with NOM in addition to the La present in LMB, but these interactions remain unexplored.

Our overall objective was to obtain a better understanding of the effects of NOM and pH on PO_4 binding by LMB. More specifically, our research objectives were to: (1) investigate the roles of solution pH and NOM type (fulvic/humic acid) and concentration on PO_4 removal by La; (2) assess the role of bentonite on PO_4 binding to LMB; and (3) investigate roles of solution

pH and NOM on concentration of filterable La (FLa, which refers to La in water after filtration) release from LMB during PO_4 sequestration. We conducted geochemical modeling as well as laboratory batch kinetic experiments. In the models, speciation profiles of P and La were assessed as a function of pH, NOM concentration, and NOM type (i.e., ratio of fulvic acid/humic acid, FA/HA). Laboratory batch experiments were performed with La^{3+}, LMB, and four NOM standards to validate model predictions. Given that effects from a changing climate are expected to lead to a "brownification" effect (i.e., an increased release of terrestrial humic substance into surface waters (Ekvall et al., 2013; Monteith et al., 2007)), the results of this work will provide an important basis for lake management and eutrophication control that relies on LMB applications in the coming years.

2. Materials and Methods

2.1. Chemicals

LMB was supplied by SePRO Research and Technology Campus (Whitakers, NC, USA). Prior to use, the as-received LMB sample was ground to pass through a 50-mesh sieve. $LaCl_3 \cdot 7H_2O$ (64.5–70.0%, $LaCl_3$ basis) was purchased from Sigma-Aldrich. $NaH_2PO_4 \cdot H_2O$, NaOH (1 M and 10 M) and HCl (1 M and 10 M) were supplied by Fisher Scientific (NH, USA). Four NOM standards [Leonardite coal humic acid (LHA), Elliot soil humic acid (ESHA), Suwannee River fulvic acid (SRFA), and Suwannee River natural organic matter (SNOM)] used in batch experiments were purchased from the International Humic Substances Society. LHA, ESHA, and SRFA are standard humic substances that were used to derive La-NOM complexation stability constants (Sonke, 2006; Sonke and Salters, 2006). These constants were

used in Model VII (see Section 2.2) to simulate La-NOM interactions (Tipping et al., 2011). The elemental composition of the NOM standards is listed in **Table S1**.

2.2. Geochemical Model

The impact of NOM on PO_4-removal by LMB was first evaluated by chemical equilibrium modelling using the program CHEAQS Pro (Verweij, 2005). In this program, formation of La complexes with HA or FA were modeled by Model VII (Tipping, 1998; Tipping et al., 2011; Tipping and Hurley, 1992). Model VII is a discrete site model for HA and FA ligands and uses carboxylic acid and phenolic groups as the two main binding sites. Detailed descriptions of the parameters of the model can be found in Sonke (2006) and Tipping et al. (2011). The model calculations matched conditions in our batch experiments (details in Section 2.3) as follows: 8.8 mg L^{-1} of La (based on 200 mg L^{-1} of LMB containing 4.4% La, and assuming all La in the bentonite is available to bind PO_4) and 2 mg L^{-1} of P at pH values of 6, 7, and 8.5. The La:P ratio corresponded to a molar ratio of 1:1, and possible solids were allowed to precipitate. In Model VII, concentrations of NOM were varied from 0 to 30 mg C L^{-1}; in the organic complexation tab, the FA fraction was set to 0 for LHA and ESHA, to 1 for SRFA, and to 0.73 for SNOM (Green et al., 2015). Additional details regarding model inputs for CHEAQS Pro are provided in **Table S2**.

2.3. Batch Experiments

Batch kinetic experiments were conducted to study PO_4-sequestration by LMB as a function of solution pH and initial NOM concentration. Filterable La release over time was also monitored in these experiments. Four NOM standards were dissolved in ultra-pure water (UPW) separately to give a stock concentration of 100 mg L^{-1}. The pH of the NOM stock solution was adjusted to 10 using 10 M NaOH and mixed for 3 days by magnetic stirring. The stock solutions

were then filtered through glass fiber membranes (0.45 μm) to remove suspended particles. Phosphate stock solutions (500 mg P L^{-1}) were prepared by dissolving $NaH_2PO_4 \cdot H_2O$ in CO_2-free UPW.

Batch kinetic experiments were conducted in duplicate according to the following steps. First, four NOM standards were prepared by diluting their respective NOM stock solutions with UPW using 249 mL of each NOM standard, each with three working concentrations (0, ~5, and ~25 mg C L^{-1}, total = 24 bottles). NOM concentrations were determined to cover typical values for oligo- and mesotrophic lakes (2–3 mg C L^{-1}) and eutrophic and dystrophic lakes (10–30 mg C L^{-1}) (Thurman, 2012). The exact starting concentrations of NOM in the solutions were determined as dissolved organic carbon (DOC, mg C L^{-1}) using a total organic carbon (TOC) analyzer (Shimadzu TOC-V CSN, Japan). Second, 1 mL of PO_4 stock solution was spiked into each NOM solution to achieve an initial P concentration of 2 mg L^{-1}. Third, initial solution pH was adjusted to 8.5 with 1 M solutions of NaOH or HCl. The volume of acid/base added was <0.5% (v/v) of each experiment. Finally, 50 mg of LMB solid was added to each HDPE bottle (200 mg L^{-1}) and the pH of the solution was re-adjusted to 8.5. Bottles were capped immediately and shaken horizontally on a reciprocating shaker at 21 relative centrifugal force and 25°C. The experiments were carried out in batches, and the duration time of each test varied from 400 to 552 hours; 5–8 samples were collected in the first 48 hours as the PO_4 concentration decreased rapidly. The sampling time interval became longer (~50–100 hours) when changes in PO_4 concentrations became smaller. At each sampling time, an aliquot was collected from each bottle and filtered through a 0.45 μm PVDF membrane before analysis. Also, the pH of the remaining suspension was measured and adjusted back to the target pH (ΔpH of 0.05–0.5 was the deviation that required adjustment) after each sampling. When

apparent equilibrium was reached, an aliquot was collected and sequentially filtered through 0.45-μm and 0.1-μm PVDF membranes. Filtrates were analyzed for P and La as described in Section 2.4.

To evaluate pH-dependence, kinetic experiments were carried out with NOM (e.g., LHA) concentrations of 0, 5.5, and 28 mg C L^{-1} at pH 6, 7, and 8.5. The pH values were selected within the environmentally relevant pH range. As described above, the pH of the NOM-LMB solutions was checked and adjusted daily to maintain the target pH. To identify the role of bentonite clay in the LMB matrix, kinetic experiments were repeated in the same manner with La^{3+} (LaCl$_3$ salt as source) in the presence of NOM (three concentration levels: 0, 5.5, and 28 mg C L^{-1}) at pH values of 6, 7, and 8.5. The initial P concentration was 2 mg L^{-1}. The dosage of LaCl$_3$ used was equivalent to that of La in LMB, ensuring an identical amount of La in the system (i.e., 8.8 mg La L^{-1}). The corresponding percentage of PO$_4$ removed was calculated by dividing the final concentration by the measured starting concentration and compared with model predictions. It was expected to be close to 100% as P and La were dosed to the 1:1 molar ratio. PO$_4$ concentrations with LMB or LaCl$_3$ treatment under three pH levels were statistically evaluated via repeated measures ANOVAs followed by Tukey post hoc tests, using SPSS (IBM SPSS Statistics).

2.4. Analysis of Aqueous Species

Concentrations of PO$_4$ in the range of 0.02–2.5 mg P L^{-1} were analyzed with the molybdovanadate method (Hach low range reactive phosphorus Test'N Tube vials with a Hach DR500 spectrometer). Samples with PO$_4$ concentration below 0.02 mg P L^{-1} were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP 7600, Thermo, Bremen, Germany). Selected water samples after filtration (0.45 or 0.1 μm, PVDF) and

acidification (2% v/v, HNO_3) were also analyzed by ICP-OES to quantify FLa release during PO_4 sequestration. To estimate the La content of LMB, 200 mg L^{-1} of LMB was added to HNO_3 (5 M) in 250-mL bottles in triplicate, and the bottles were shaken vigorously on a microplate shaker (Fisherbrand) for 3 days. Filterable La in the solution after filtration (0.45 μm, PVDF) was determined by ICP-OES. The method reporting limit for P by molybdovanadate method was 0.02 mg L^{-1}; and reporting limits for P and La analysis by ICP-OES were 1.87 μg L^{-1} and 0.04 μg L^{-1}, respectively.

Measured concentrations of La using ICP-OES represent FLa (i.e., colloidal and aqueous La) in water samples. To distinguish between La concentrations determined by ICP-OES and aqueous La, the levels determined by ICP-OES in the filtrate after 0.45 μm or 0.1 μm filtration was termed FLa, whereas the total dissolved La obtained from geochemical models (e.g., $La^{3+}_{(aq)}$, $LaOH^{2+}_{(aq)}$, and other inorganic complexes) was termed aqueous La (Aq-La).

3 Results

3.1 Chemical Equilibrium Modeling of PO_4 Removal by La Salt

We first assessed PO_4 removal by LMB as a function of pH and initial NOM concentration through geochemical equilibrium simulations. Since equilibrium models do not include LMB or bentonite clay as possible inputs, we used La^{3+} (i.e., the La-containing component of LMB) to represent LMB. The model thus does not consider interactions between solutes, including PO_4 and NOM, and the bentonite LMB carrier matrix. All simulations were conducted with 8.8 mg La L^{-1} (based on 200 mg L^{-1} of LMB containing 4.4% La, and assuming all La in the bentonite is available to bind PO_4). The starting PO_4 concentration was 2 mg L^{-1} of P, resulting in a molar La:P ratio of 1:1. In the model outputs, we focused on the formed concentrations of $LaPO_{4(s)}$; (i.e., the dominant product of PO_4 removal by La (Copetti et al.,

2015; Dithmer et al., 2015; Zhi et al., 2020)) and aqueous total dissolved P (Aq-P) (i.e. the PO_4 that was not removed). In the absence of NOM, the model indicated that nearly all the Aq-P would be removed as $LaPO_{4(s)}$ at pH 6, 7, and 8.5 (**Fig. 1A-B**).
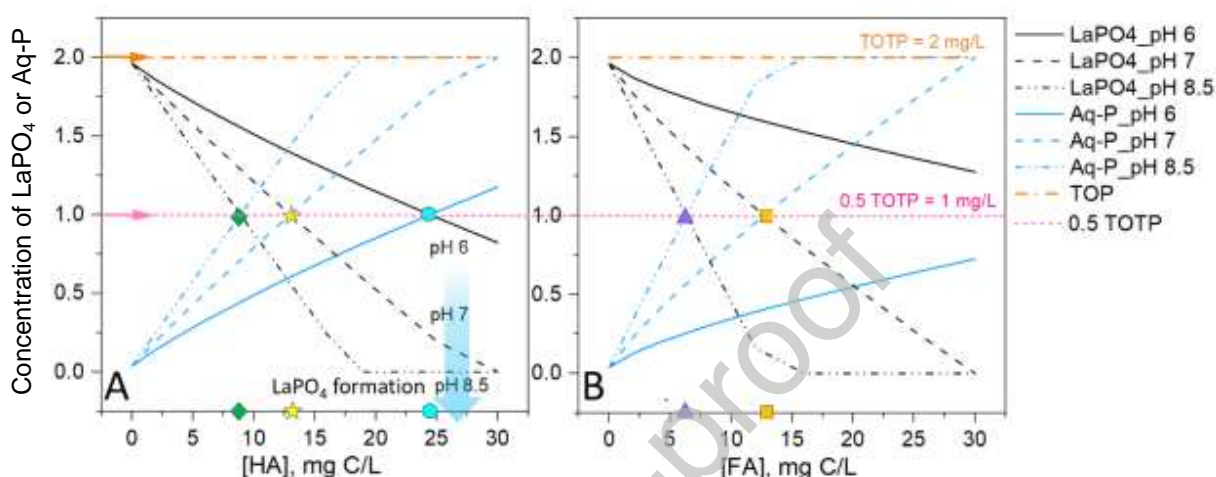

Fig. 1. Effect of NOM type (HA, panel A; FA, panel B), NOM concentration, and solution pH on predicted $LaPO_{4(s)}$ formation and aqueous total dissolved P (Aq-P = PO_4^{3+} + HPO_4^{2+} + $H_2PO_4^+$ + H_3PO_4 + $LaH_2PO_4^{2+}$) at equilibrium. Total P in the system: TOTP (Orange dash-dot line) = Aq-P + $LaPO_{4(s)}$ = 2 mg P L^{-1}. The blue arrow in A) shows the trend of $LaPO_{4(s)}$ formation as a function of increasing solution pH at a fixed HA concentration. The symbols (green diamonds, yellow stars, blue circles, violet triangles, and orange squares) on the figure demonstrate concentrations of HA or FA that cause a 50% reduction (pink dotted line) in P removal.

As HA or FA concentrations increased from 0-30 mg C L^{-1}, the predicted formation of $LaPO_{4(s)}$ decreased, resulting in higher Aq-P concentrations (**Fig. 1A-B**). Furthermore, the NOM impact was more pronounced at higher solution pH (**Fig. 1A-B** and highlighted by blue arrow in **Fig. 1A**). At pH 8.5, no PO_4 removal was predicted for HA > 19 mg C L^{-1} (**Fig. 1A**) or FA > 16 mg C L^{-1} (**Fig. 1B**). The impacts of HA and FA on PO_4 removal differed across the evaluated pH range (6–8.5). A 50% reduction in PO_4 removal at pH 8.5 was predicted to occur with 8.75 mg C L^{-1} of HA (green diamond, **Fig. 1A**) or 6.25 mg C L^{-1} of FA (violet triangle, **Fig. 1B**). At

pH 6, 24.8 mg C L^{-1} of HA (blue circle, **Fig. 1A**) or > 30 mg C L^{-1} of FA would lead to this same level of reduction in PO$_4$ removal. At pH 7, the effect of FA and HA was comparable, requiring 13 mg C L^{-1} of HA or FA for a 50% reduction (indicated by the yellow star and orange square in **Fig. 1A-B**). It is worth noting that the model does not allow for the formation of ternary NOM-La-PO$_4$, as the possible occurrence and stability of the complexes is unknown. However, the existence of analogous NOM-Fe-PO$_4$ ternary complexes is well known (Hesterberg, 2010).

3.2 Batch Experiments of PO$_4$ Removal by LMB and Influence of NOM

To evaluate PO$_4$ removal by LMB, we conducted batch kinetic experiments with varying initial NOM concentrations and a fixed concentration of LMB and PO$_4$ at pH values of 6, 7, and 8.5. We first established baseline PO$_4$ removal data in the absence of NOM by conducting batch tests in UPW. There were no significant differences (p =0.908) in PO$_4$ removal kinetics and concentrations at apparent equilibrium at pH 6, 7, and 8.5 when NOM was absent (**Fig. S1**). These results were consistent with the modeling results (**Fig. 1**).

In the presence of NOM, PO$_4$ removal decreased, and the magnitude of the decrease was dependent on the concentration of NOM and the solution pH. At each sampling point, the concentration of PO$_4$ in the reactors with 28 mg C L^{-1} of LHA was always higher than that in reactors with 5.5 mg C L^{-1} and 0 mg C L^{-1} of LHA (**Fig. 2**). This trend held true even after 420-444 hours. At a LHA concentration of 5.5 mg C L^{-1}, P removal decreased as solution pH was increased from 6 to 8.5, a trend that was consistent with that predicted by the model (**Fig. 1**). However, at a LHA concentration of 28 mg C L^{-1}, P removal was not affected as solution pH was increased from 6 to 8.5. At pH 8.5, model predictions suggested that P removal would be

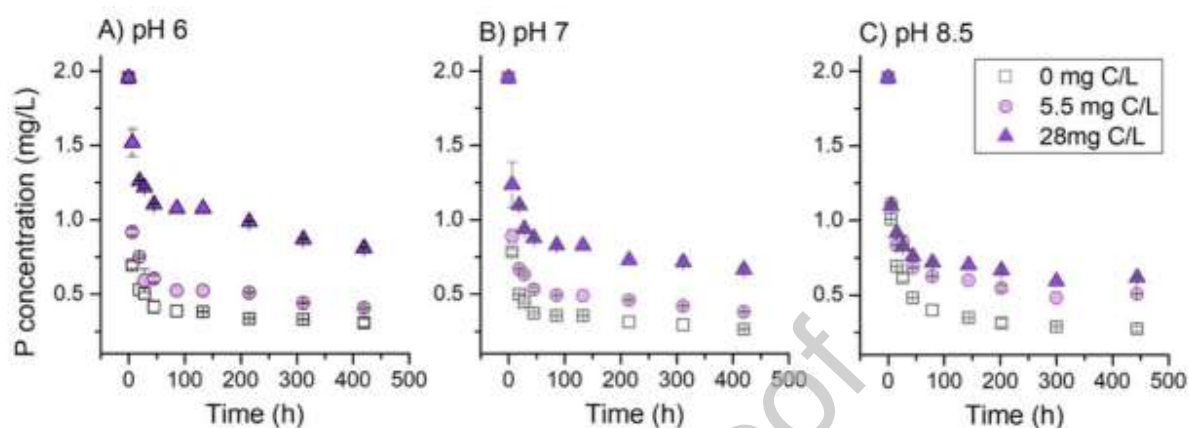negligible, but P removal in the experiment was >60%. This discrepancy will be discussed further below.

Fig. 2. PO$_4$-removal kinetics in batch reactors as a function of NOM (Leonardite coal humic acid, LHA) concentrations (0, 5.5, and 28 mg C L^{-1}) and solution pH (6, 7, and 8.5) at 25°C. The starting concentration of PO$_4$ was 2 mg L^{-1} as P, and the LMB dose was 200 mg L^{-1}.

Additional tests were completed with the NOM standards ESHA, SRFA, and SNOM to determine if their effects were consistent with LHA (**Fig. S2**). These kinetic experiments were carried out at pH 8.5, as the effect of NOM was predicted to be most pronounced at pH 8.5 (**Fig. 1**). Results show that the PO$_4$ removal profiles in the presence of ESHA, SRFA and SNOM (**Fig. S2**) closely matched those obtained with LHA (**Fig. 2c**); one exception was ESHA at 22 mg C L^{-1}, which adversely impacted P removal more strongly that the other NOM types, but still less than what was predicted by the model. At pH 8.5, average P concentration after 400 hours ranged from 0.13 to 0.27 mg P L^{-1} in UPW, from 0.41 to 0.51 mg P L^{-1} at ~5 mg C L^{-1} and from 0.52 to 0.94 at ~26 mg C L^{-1} (**Figs. 2c and S2**).

3.3 Comparison between Model Predictions and Experimental Results of PO$_4$-Removal

We compared the aforementioned experimental results with the model predictions (section 3.1). In the absence of NOM, our experimentally measured PO$_4$ removal after filtration through

a 0.45-µm filter ranged from 84–87% (**Fig. 3A-C**), which was lower than the essentially complete removal we had anticipated based on model predictions shown in **Fig 1**. We explored whether the discrepancy might be attributable to fine LMB or $LaPO_{4(s)}$ particles that may have passed through the 0.45-µm filters, leading to an underestimation of aqueous PO_4 removal. To test this hypothesis, we filtered our samples a second time through 0.1-µm filters. PO_4 removal increased slightly to 87–89% (pH 8.5) after this additional filtration step (**Fig. 3A**) but remained below the essentially complete removal we had expected based on model predictions shown in **Fig. 1**. We then measured the La content of LMB in triplicate and found that the La content was 3.74 ± 0.08 wt%, which is lower than the value of 4.4 wt% that had been reported in prior publications (Dithmer et al., 2016; Lürling et al., 2014; Reitzel et al., 2017). The experimentally determined La content of LMB results in 7.5 mg La L^{-1} rather than the originally expected 8.8 mg L^{-1} (at 200 mg LMB L^{-1}). When the model was corrected to this La concentration, it predicted 85% PO_4 removal in the absence of NOM at equilibrium, which agreed well with our experimental data (**Fig. 3A-C**).
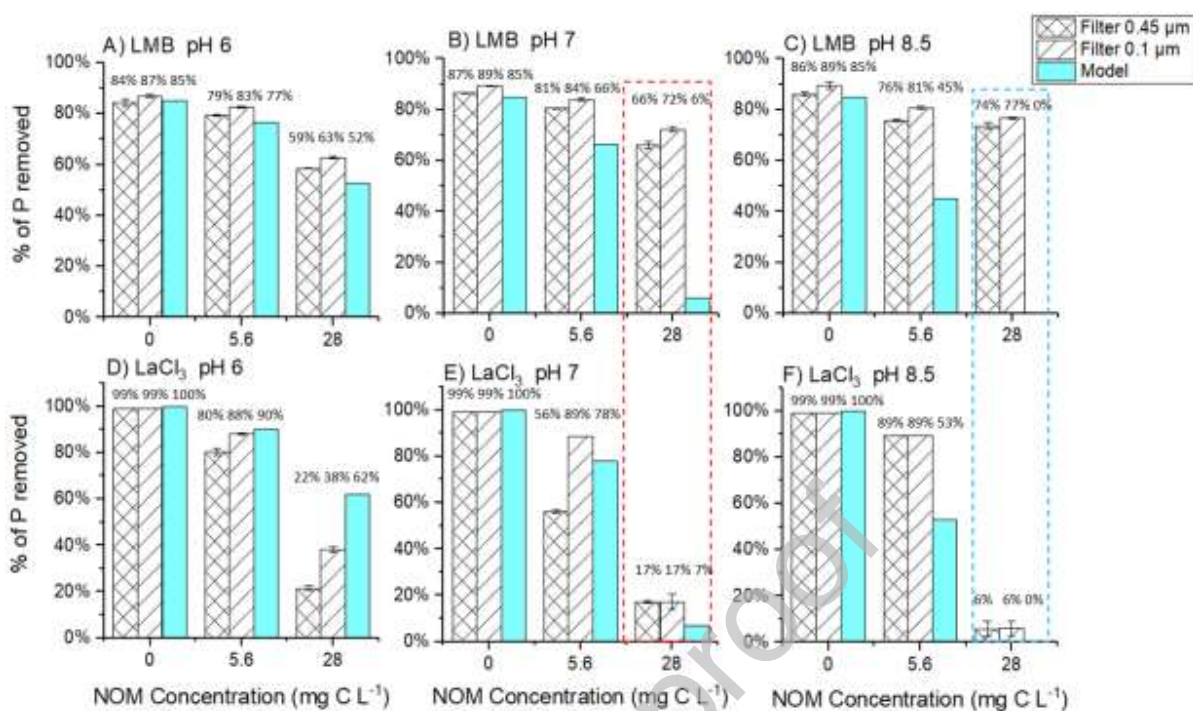
Figure 3. Comparison of experimentally determined PO$_4$-removal and chemical equilibrium model results with corrected La content for LMB. Panels A-C: PO$_4$ removal by LMB (7.5 mg La L^{-1}) as a function of solution pH (pH 6, 7, 8.5) and concentration of Leonardite coal humic acid (LHA) at 25°C. Panels D-F: PO$_4$ removal by LaCl$_3$ (8.8 mg La L^{-1}). Dotted boxes show that at pH 7 and 8.5, differences between experimentally determined values and model predictions were most pronounced in the presence of LMB and 28 mg C L^{-1} LHA.

For experiments conducted with LMB, the difference between experimental results and model predictions increased as solution pH and NOM concentration increased (**Fig. 3A-C**). Model predictions and empirical observations showed the best agreement at pH 6 (**Fig. 3A**). However, with 5.6 mg C L^{-1} of LHA, the model predicted PO$_4$-removals of 66% at pH 7 and 45% at pH 8.5, which were systematically lower than experimentally determined removals: 81–84% at pH 7 and 76–81% at pH 8.5 (**Fig. 3B-C**). When the LHA concentration was increased to 28 mg C L^{-1}, the discrepancy between model predictions and experimentally determined values became more pronounced (red and blue boxes, **Fig. 3B-C**). Predicted PO$_4$ removal was 6% at

pH 7 and 0% at pH 8.5, while experimentally determined removals were 66–72% at pH 7 and 74–77% at pH 8.5 (highlighted by red and blue arrows, **Fig. 3B-C**).

Experimental results for the other three NOM standards (ESHA, SRFA, SNOM) (**Fig. S3A-C**) were also compared with model predictions under the same corresponding conditions (i.e., solution pH, HA/FA ratio, and concentration of NOM). The results were similar to those obtained with LHA, in that in the absence of NOM, the empirical PO_4 removal was 89–96%, which was greater than the model prediction of 85% (**Fig. S3**). In the presence of NOM, the empirical PO_4 removal was also greater than the model prediction. At the highest concentration of all three NOM types, predicted PO_4 removal was essentially zero at pH 8.5, and all La was predicted to be complexed by NOM (either HA or FA, **Fig.1**). However, significant PO_4 removal by LMB (52–83%) was observed during the experiments (**Figs. S2, S3**).

3.4 PO_4-Removal by Dissolved La^{3+} in the Presence of NOM

To understand the role of bentonite in PO_4 removal by LMB, additional batch experiments were performed, in which La^{3+} was added as a soluble $LaCl_3$ salt instead of LMB to eliminate the bentonite phase. Model results were again compared with experimental results (**Fig. 3D-F**). In the absence of LHA, PO_4-removal by $LaCl_3$ was 99%, close to the predicted value (100%). This result was expected because La and PO_4 were dosed at a molar ratio of La: P = 1:1. In the presence of LHA (5.6 mg C L^{-1}) at pH 6, the empirical PO_4 removal was similar to the model prediction (**Fig. 3D**). At pH 7, sequential filtration resulted in a difference in percentage of PO_4 removed. The empirical PO_4-removal after 0.45-µm filtration (56%) was lower than that predicted by the model (78%), whereas the removal after 0.1-µm filtration (89%) was higher than that predicted by the model (**Fig. 3E**). At pH 8.5, the empirical PO_4-removal was 89%, which was greater than the model prediction (53%). At the highest LHA

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concentration (28 mg C L^{-1}), empirically determined PO$_4$-removals by La^{3+} decreased from 38% at pH 6 to 6% at pH 8.5, and results at pH 7 and 8.5 were more consistent with model predictions compared to those obtained with LMB. Comparing Fig. 3A-C with D-F with 28 mg C L^{-1} of LHA, PO$_4$-removal by La^{3+} was significantly lower than by LMB (especially at pH 7 and 8.5, as highlighted by red and blue boxes, respectively, in **Fig. 3)**. More specifically, LMB removed 59%-77% of PO$_4$ whereas PO$_4$ removal by La^{3+} was 6%-17%. This discrepancy will be discussed further below.

3.5 Filterable La Release from LMB

To assess the effects of pH and NOM on La-release from LMB, we conducted batch experiments with LMB (200 mg L^{-1}) in (1) UPW amended with LHA (0, 5.5, 28 mg C L^{-1}) at pH 8.5 and (2) UPW amended with PO$_4$ (2 mg P L^{-1}) and LHA (0, 5.5, 28 mg C L^{-1}) at pH 6, 7, and 8.5. In UPW at pH 8.5 (no NOM, no PO$_4$), the concentration of FLa (i.e., total La passing through a 0.45-μm filter) was 1.2 ± 1.1 μg L^{-1}; in the presence of 5.5 and 28 mg C L^{-1} LHA, the concentrations of FLa were 986 ± 125 μg L^{-1} and 3430 ± 44 μg L^{-1}, respectively [1] (**Fig. 4A**). The addition of PO$_4$ decreased the concentration of FLa in solutions amended with LHA, especially at the highest LHA dose, at which the FLa concentration decreased to about one-third (1180 μg L^{-1}) of that observed in the absence of PO$_4$ (**Figs. 4B and S4**). To understand the effect of solution pH, experiments were conducted at the same LHA concentrations with pH controlled at 6, 7, and 8.5 (**Fig. 4B-D**). Similar to **Fig. 4A**, the amount of La that was released from the LMB matrix at the three pH values increased with increasing LHA concentration. At 5.5 mg C L^{-1} of LHA, the concentration of FLa increased with increasing pH, while at 28 mg C L^{-1} of LHA, the concentration of FLa increased with decreasing pH (**Fig. S4**).
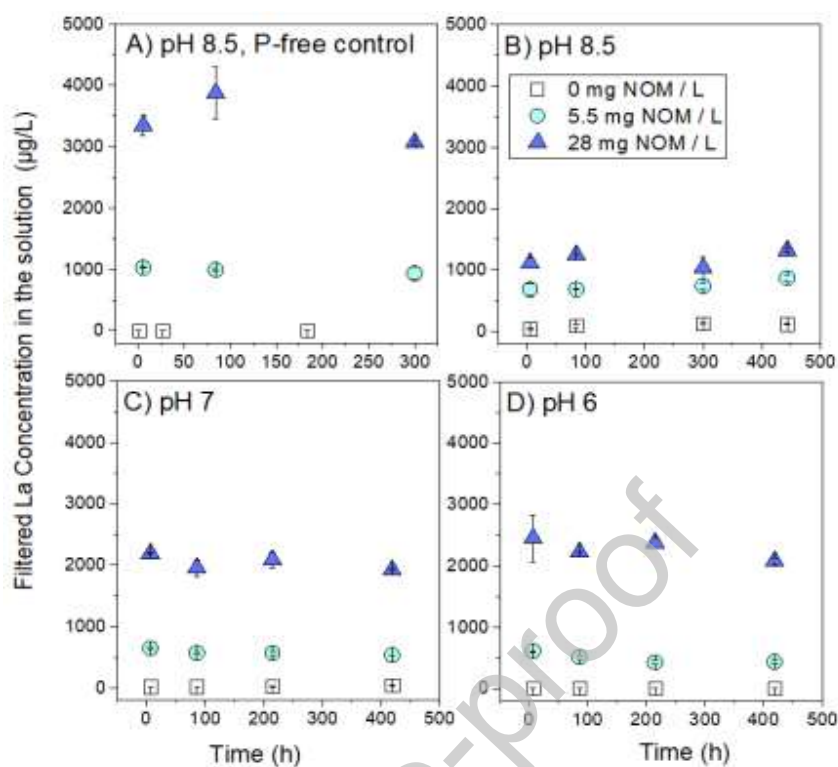
Figure 4. Release of filterable La (FLa) from LMB over time in the absence of PO_4 at pH 8.5 (panel A) and in the presence of PO_4 as a function of pH [pH 8.5 (panel B), 7 (panel C), 6 (panel D)] and Leonardite coal humic acid (LHA) concentration (0 – 28 mg C L^{-1}). The initial concentration of PO_4 was 2 mg P L^{-1}, and the dose of LMB was 200 mg L^{-1}. Note that concentration of FLa in this figure was determined by ICP-OES after being filtered through 0.45 μm PVDF membranes.

La-release experiments were also carried out with ESHA, SRFA, and SNOM at a pH of 8.5 (**Fig. S5**). Similar to LHA, the other three NOM standards caused enhanced La-release, as determined by FLa, from LMB, and La-release increased as the concentration of NOM increased (**Fig. S5**). In contrast to LHA, FLa gradually increased over time in the presence of ESHA and SNOM (**Fig. S5**), suggesting the release of La or the complexation reaction with NOM is a dynamic process. Further inspection of **Figs. 4** and **S5** revealed that concentrations of FLa in the presence of different NOM standards (i.e., LHA, ESHA, SRFA, and SNOM) at apparent equilibrium were different ($p < 0.001$). As shown in **Figs. 4** and **S5,** the amount of FLa

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released from the LMB matrix depended on the type (i.e., FA/HA ratio) and concentration of NOM. Sequential filtration through filters with 0.45- and 0.1-µm pore sizes confirmed that the concentration of FLa decreased as the pore size of the filter membrane decreased (**Fig. S4**), which was consistent with the PO_4 removal experiments (**Fig. 3**). The presence of FLa that passes through a 0.45-µm but not a 0.1-µm filter suggests the presence of colloidal particles containing La in the form of $LaPO_4$, La-NOM, and/or LMB; additionally, there may also be particulate forms containing La that are larger than 0.45 µm (including La-NOM particles), and thus the discrepancy between modeled La and FLa shown in **Fig. S4** is not unexpected.

Experimental results obtained with LMB are consistent with geochemical model results, in that the model predicted enhanced formation of La-NOM complexes with increasing NOM concentrations (**Figs. S4** and **S6**). Moreover, model predictions show that the concentrations of Aq-La (defined here as the sum concentration of La^{3+}, $LaOH^{2+}_{(aq)}$, and other inorganic complexes) were 10^{-15}-10^{-7} mg L^{-1}, and concentrations decreased with increasing concentration of NOM. Such decreases in Aq-La were accompanied by decreases in $LaPO_4$ and increases in La-NOM concentration until all La bonded with NOM (**Fig. S6**).

4. Discussion

4.1 pH-Dependent Effect of NOM on PO_4 Sequestration

Both modeling and experimental results indicate that PO_4 removal decreased in the presence of NOM. These findings are consistent with previous studies in which humic substances or dissolved organic carbon adversely affected PO_4-removal after 400 days (Dithmer et al., 2016) and 42 days (Lürling et al., 2014). Moreover, the magnitude of the decrease was dependent on the concentration and type of NOM and the solution pH (**Figs. 1-3**, **S2** and **S3**). NOM contains both relatively strong acidic (*pKa* of 3.3–4.0) and weak acidic

groups ($pKa > 6$), as well as a few bidentate sites as major ligands (Sonke, 2006; Tipping and Hurley, 1992) that can compete with PO_4 for La(**Fig. 5A**). Binding of ions by humic substances, such as complexation between NOM and La, can be described as a metal-proton exchange reaction, $La^{3+} + NOM - H \leftrightarrows La - NOM + H^+$, where pH plays an important role (Tipping et al., 2011; Tipping and Tipping, 2002). Our findings with LaCl$_3$ (**Fig. 3D-F**) support the pH-dependent effect of NOM on PO_4 binding to La, which was least pronounced at pH 6 and most pronounced at pH 8.5. At higher pH, weaker acidic groups of NOM become deprotonated, increasing their ability to bind more La, and therefore resulting in more pronounced interference of NOM on PO_4 removal as solution pH increases (**Fig. 5B**). Per **Figs. 1-3, S2 and S3**, the effects of HA and FA on PO_4-removal by LMB were not identical ($p < 0.001$) and varied with pH ($p < 0.001$), which can be attributed to differences in the abundance of (mono-, and bi-dentate) binding sites, intrinsic proton dissociation constant, and electrostatic parameters (Sonke, 2006; Tipping, 1998). It is worth again noting the possible presence of NOM-La-PO_4. Depending on the size of these complexes (e.g., their ability to pass through a 0.45 or 0.1 μm filter), the presence of colloid may result in an increase or decrease in PO_4 concentration in the filterable fraction, affecting estimates or removal efficiency. Given the underprediction of FLa as compared to modeled La-NOM complexes, it is reasonable to think that any ternary NOM-La-PO_4 complexes may contribute to reduced PO_4 removal efficiency compared to the model. However, the expected impact of ternary complexes does not explain the difference between the PO_4 removal efficiency of LaCl$_3$ and LMB.
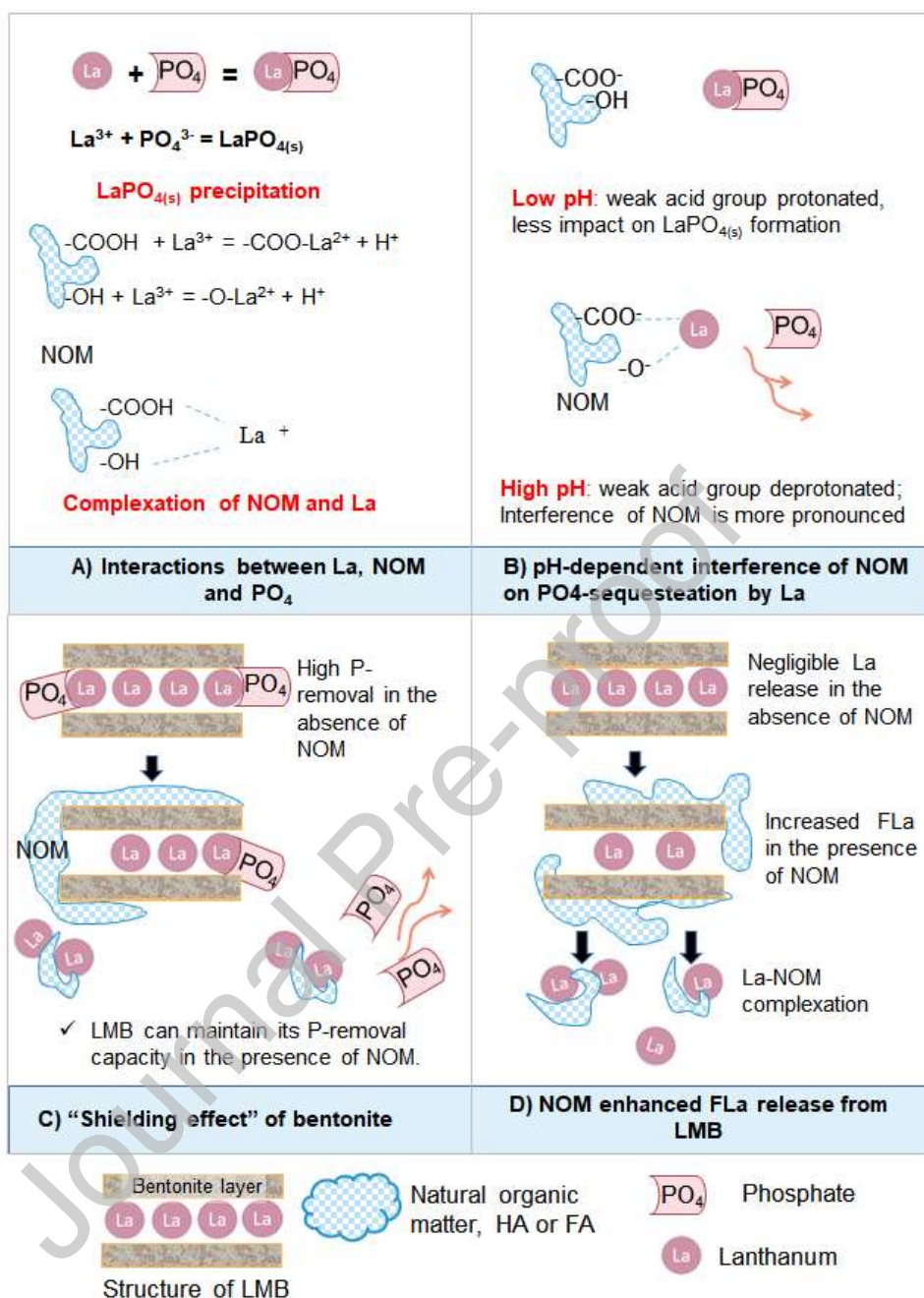
Figure 5. Conceptual diagram showing A) interactions between La, NOM and PO$_4$, B) the pH-dependent interference of NOM on PO$_4$-sequesteation by La, C) the "shielding effect" provided by bentonite, and D) NOM-enhanced filterable La(FLa) release from LMB. (Figure adapted from Lürling et al., 2014)

4.2 Effect of Bentonite Clay

To understand the role of bentonite, PO_4-removal experiments were conducted with La^{3+} and LMB. A comparison of LMB (i.e., La^{3+} incorporated in bentonite matrix) and La^{3+} (i.e., with the soluble salt $LaCl_3$ as a La source) demonstrates that greater PO_4-removal occurred at the highest evaluated NOM concentration when bentonite was present as a carrier material. The higher removal percentages that were obtained with LMB imply that bentonite reduces La-NOM interactions while allowing PO_4 sequestration by La. This enhanced efficiency may be explained in terms of the sorption reactivity of the bentonite clay itself. Although PO_4 may adsorb to clay minerals, bentonite-type clays have a low affinity for PO_4 at pH = 8, suggesting direct adsorption to the surface is not the dominant mechanism for enhanced PO_4 removal by LMB as compared to $LaCl_3$. This low adsorption affinity can be rationalized by noting the overall negative charge (PZC ≈ 3.2; Sperry and Peirce, 1999) of montmorillonite, the dominant mineral in bentonite, and hence repulsive electrostatic interactions with HPO_4^{2-}. However, bentonite may also adsorb NOM, potentially reducing its ability to compete with PO_4 for La. As demonstrated in Li et al. (2020), NOM can be adsorbed by LMB in the presence of PO_4. In addition, Chen et al. (2017) noted significant adsorption (maximum sorbed concentration = 6.7 mg C m^{-2}) of a soil humic acid on montmorillonite even at pH = 8, which was attributed to ligand exchange and hydrophobic interactions. Based on the sorption capacity of montmorillonite and assuming a LMB surface area of 29 m^2 g^{-1} (Baninaam et al., 2020), the maximum mass of NOM that may be sorbed by bentonite in our system can be estimated as 9.7 mg C, which exceed the maximum mass of carbon in even our highest concentrations experiments (7 mg C). The sorption of NOM by bentonite may thus reduce the effective concentration of NOM in solution, reducing its ability to compete with PO_4 for La.

4.3 NOM Influence on La-release

Soluble La released from LMB into aquatic environments is undesirable and may potentially lead to adverse ecological impacts (Copetti et al., 2015; Gonzalez et al., 2014). Published studies have reported that ecotoxicological effects are not expected below a Predicted No Effect Concentration (PNEC) of 4 µg L^{-1} (Herrmann et al., 2016). Further, in The Netherlands, La is subjected to a maximum permissible concentration (MPC) legislation that is applied to the water column and sediments (van Oosterhout et al., 2020). The Netherlands is the only country that has La standards for water and sediment (Sneller et al., 2000), and the maximum permissible FLa concentration is 10.1 µg L^{-1} in surface waters (Crommentuijn et al., 2000). However, this MPC was derived from the No Observed Effect Concentration (NOEC) determined in a 21-day Daphnia reproduction test and divided by 10 (van Oosterhout et al., 2020). The results from our study showed that in UPW, FLa in equilibrium with 200 mg L^{-1} of LMB (1.2±1.1 µg L^{-1}, **Fig. 4A**) was below the safety threshold (i.e., PNEC of 4 µg L^{-1}) as well as regulatory standards (i.e., 10.1 µg L^{-1}). In addition, our results of La release are in agreement with Tang and Johannesson (2010) who studied La release from sediment. In the absence of strong La complexing ligands in solution, the amount of La released from the sediment is small (Tang and Johannesson, 2010). However, La-releasing was much more pronounced in the presence of strong complexing ligands (Tang and Johannesson, 2010), consistent with our findings for NOM here.

Our experimental observations support the hypothesis that NOM can influence the concentration of FLa in the water column (**Fig. 4**). This agrees with previous studies that have shown that 1) NOM (i.e., FA and HA) strongly binds La, and La-NOM complexes dominate La speciation in surface waters (within the pH range of 5.4-7.9, Tang and Johannesson, 2003) and

estuarine waters (Moermond et al., 2001), and 2) HA can "dissolve" La in the LMB by complexation, as illustrated in **Fig. 5D** (Lürling et al., 2014; Reitzel et al., 2017). A previous study that used sequential filtration demonstrated that La could bind to negatively-charged regions of HA, leading to the formation of colloidal La-HA complexes (Reitzel et al., 2017). The authors observed that up to 14% of FLa was released from LMB in soft water lakes with high HA concentration (with 400 mg L^{-1} of LMB and 22 mg C L^{-1}) (Reitzel et al., 2017). Their findings are comparable with ours, wherein 4-10% of La was released at 5.5 mg C L^{-1} of LHA and 13–30% of La was released at 28 mg C L^{-1} of LHA (with 200 mg L^{-1} of LMB) in our study. Further, we found the presence of PO$_4$ limited FLa concentrations, even in the presence of NOM. We therefore conclude that the concentration of FLa is strongly dependent on the concentrations of NOM and PO$_4$.

Consistent with previous investigations, our experiments show that concentrations of FLa are dependent on the size of pores used during sample filtration. FLa concentrations declined as the pore diameters decreased (**Fig. S4**) (Reitzel et al., 2017). Detectable FLa remained in the aqueous phase after filtration through both 0.45- and 0.1-μm membrane filters. Reitzel et al. (2017) demonstrated that FLa concentrations in some samples were as high as 2 mg L^{-1}, and there was detectable FLa even after 30 minutes of ultracentrifuge (62000 × g). Collectively, these results indicate that careful attention to separation methodologies is critical for determining accurate concentrations of FLa.

One interesting point of discussion is the speciation of FLa. It is an important question for lake managers whether the FLa should be considered as truly dissolved La or rather as small non-toxic colloids containing La. Among all possible La-species, ionic La^{3+} has the greatest potential to cause ecotoxicological impacts across various studies (Copetti et al., 2015; Das et

al., 1988; Gonzalez et al., 2014; Herrmann et al., 2016). On the contrary, La-complexation with NOM will reduce the bioavailability of La, and therefore its associated ecotoxicity (Gonzalez et al., 2014; Herrmann et al., 2016). Based on our model results, the concentration of ionic La^{3+} is $<10^{-7}$ mg L^{-1} at all conditions (**Fig. S6**, with 8.8 mg La L^{-1}, 2 mg P L^{-1}, pH 6, 7, 8.5 and NOM concentration 0–30 mg C L^{-1}). In cases where La is limited and strong ligands (NOM and PO_4) are present, ionic La^{3+} will likely be depleted and not contribute substantially to FLa. In addition, as reported by previous studies, FLa concentrations in filtered samples depend on pore size of the filter, suggesting that various colloidal forms of La are present (Lürling et al., 2014; Reitzel et al., 2017; van Oosterhout et al., 2020). Moreover, in hard water lakes and in eutrophic waters with elevated pH, Reitzel et al. (2017) found from sequential filtration and ultracentrifugation that virtually all FLa will be colloidal (Reitzel et al., 2017). This speciation was attributed to La precipitates with (bi)carbonate at higher alkalinity and insoluble La-hydroxide forms at elevated pH. In contrast, in soft water lakes with high NOM content, most of the FLa was on a dissolved form and likely associated with NOM (Reitzel et al., 2017). Generally, how much truly dissolved La^{3+} will be present in FLa depends on water chemistry.

Conclusions

In this study, we evaluated the impacts of natural organic matter (NOM) on PO_4-binding to lanthanum modified bentonite (LMB) and La-release from the LMB matrix as a function of solution pH by using chemical equilibrium modeling and controlled-laboratory batch kinetic experiments. We found that:

- PO_4 removal decreased in the presence of NOM, and the magnitude of the decrease was dependent on the concentration of NOM, type of NOM, and pH;

- The bentonite matrix may adsorb NOM and reduce La-NOM interactions, contributing to LMB efficacy for PO_4 removal in neutral to alkaline waters with high NOM;

- In the presence of 28 mg C L^{-1}, LMB removed 59–74% PO_4 at conditions at which free La^{3+} was not able to achieve meaningful PO_4 removal

- The presence of NOM also enhanced the release of La from the LMB matrix, although PO_4 can limit the amount of FLa in the water.

Overall, these findings provide an important basis for the use of LMB to manage phosphorous and eutrophication problems in lakes and other water bodies. Future research efforts should focus on evaluating the effectiveness of LMB as an effective P-removal strategy in parallel with efforts to evaluate its broader environmental and societal impacts, particularly for in situ applications. Among other research areas, more work is needed to better understand La release from LMB, including underlying mechanisms for release, in a range of environmental contexts, including in waters with high NOM and low phosphate concentrations.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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