



Review article

Emerging lanthanum (III)-containing materials for phosphate removal from water: A review towards future developments

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ABSTRACT

The last two decades have seen a rise in the development of lanthanum (III)-containing materials (LM) for controlling phosphate in the aquatic environment. >70 papers have been published on this topic in the peer-reviewed literature, but mechanisms of phosphate removal by LM as well as potential environmental impacts of LM remain unclear. In this review, we summarize peer-reviewed scientific articles on the development and use of 80 different types of LM in terms of prospective benefits, potential ecological impacts, and research needs. We find that the main benefits of LM for phosphate removal are their ability to strongly bind phosphate under diverse environmental conditions (e.g., over a wide pH range, in the presence of diverse aqueous constituents). The maximum phosphate uptake capacity of LM correlates primarily with the La content of LM, whereas reaction kinetics are influenced by LM formulation and ambient environmental conditions (e.g., pH, presence of co-existing ions, ligands, organic matter). Increased La solubilization can occur under some environmental conditions, including at moderately acidic pH values (i.e., < 4.5–5.6), highly saline conditions, and in the presence of organic matter. At the same time, dissolved La will likely undergo hydrolysis, bind to organic matter, and combine with phosphate to precipitate rhabdophane (LaPO₄·H₂O), all of which reduce the bioavailability of La in aquatic environments. Overall, LM use presents a low risk of adverse effects in water with pH > 7 and moderate-to-high bicarbonate alkalinity, although caution should be applied when considering LM use in aquatic systems with acidic pH values and low bicarbonate alkalinity. Moving forward, we recommend additional research dedicated to understanding La release from LM under diverse environmental conditions as well as long-term exposures on ecological organisms, particularly primary producers and benthic organisms. Further, site-specific monitoring could be useful for evaluating potential impacts of LM on both biotic and abiotic systems post-application.

1. Introduction

Eutrophication from nutrient-rich agricultural, industrial, and untreated domestic waste discharges threatens freshwater bodies worldwide (Downing, 2014; Smith and Schindler, 2009). Although nitrogen (N) and phosphorus (P) are both contributors to eutrophication, P is

typically the limiting nutrient in freshwater bodies (Schindler et al., 2008). Management plans to mitigate eutrophication often involve control, diversion, and treatment of excessive P loading from external sources, such as wastewater or industrial discharge and surface runoff from urban and suburban areas (Carpenter et al., 1998). Because elimination or reduction of external loading may not be sufficient to produce

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long-lasting (or even immediate) improvements due to internal P recycling (i.e., release of legacy P from sediments) (Cooke et al., 2005; Welch and Cooke, 1995), additional in-lake treatments are often necessary to prevent prolonged eutrophic states following nutrient diversion (Cooke et al., 2005; Jeppensen et al., 1991; Søndergaard et al., 1999).

Although P can exist in a variety of forms in natural waters and wastewater sources, orthophosphate (PO_4^{3-} and its protonated forms) is most readily assimilated by plants (Correll, 1998; Ekholm and Krogerus, 1998), and therefore frequently the target of removal in eutrophic water bodies (Weiner, 2008). Conventional approaches to remove phosphate from the water column, such as aluminum (Al) and iron (Fe) amendments, bind P (Cooke et al., 2005) via precipitation or adsorption (De Vicente et al., 2008; Eddy et al., 2003; Immers et al., 2013; Reitzel et al., 2006; Wilfert et al., 2015). However, the effectiveness, as well as potential impacts on ecological systems, of using these chemical agents for phosphate sequestration are highly dependent on alkalinity, pH, and other solutes, such as ions, ligands, and dissolved organic carbon (DOC) (Cooke et al., 2005; Kelly Vargas and Qi, 2019). Despite the popularity of using Al-containing materials for freshwater P remediation, acidification and adverse impacts on ecological organisms can be consequences of concern (Egemose et al., 2010; Reitzel et al., 2013b). While the use of Fe-containing materials is not expected to cause ecotoxicological effects, acidification can be a concern along with phosphate release from Fe-containing amendments when Fe(III)-reducing or sulfate-reducing bacteria reduce Fe(III) to soluble Fe(II) under anoxic conditions (Cooke et al., 2005; Wilfert et al., 2015).

Lanthanum (La)-containing materials (LM) are alternatives to conventional Al or Fe-containing materials and can effectively and selectively bind phosphate in diverse environmental matrices (Douglas et al., 2016; Johansson Westholm, 2006; Loganathan et al., 2014). LM (defined herein to include both La salts, such as $\text{La}_2(\text{CO}_3)_3$, and La-modified carrier) have gained considerable attention in recent years because La predominantly exists in a trivalent oxidation state that strongly binds phosphate to precipitate sparingly soluble, redox-stable minerals (e.g., $\text{LaPO}_4(\text{s})$ and its hydrated forms) (Cotton, 2013; Dithmer et al., 2015; Douglas et al., 2000; Huang, 2011). Since LM have high selectivity towards phosphate, La salts have been used in human and veterinary medicine to sequester excess phosphate in the body (i.e., La carbonate-based pharmaceutical Fosrenol®) (Autissier et al., 2007; Schmidt et al., 2012). LM are also especially effective for removing phosphate from wastewater and natural water (Haghseresht et al., 2009; He et al., 2017; Huang et al., 2014a,b; Kurzbaum and Bar Shalom, 2016; Li et al., 2019; Min et al., 2019; Ross et al., 2008; Wasay et al., 1996). For example, commercially-available La(III)-modified bentonite clay products (LMB, trademark name Phoslock®) have been developed for phosphate sequestration and applied in >200 water bodies worldwide (Copetti et al., 2016). Since some LM such as LMB are designed for *in situ* use, a growing number of studies have investigated potential impacts of LM on ecosystems (Álvarez-Manzaneda et al., 2019; Behets et al., 2020; Lüring and Tolman, 2010; Spears et al., 2013); however, additional work is needed to comprehensively understand potential impacts of LM on ecological systems, including long-term ecotoxicological effects on aquatic communities, particularly benthic organisms (Álvarez-Manzaneda et al., 2019; Behets et al., 2020; Copetti et al., 2016; Herrmann et al., 2016; Spears et al., 2013).

In this review, we evaluate the state of knowledge on the development and use of 80 LM for phosphate removal. Specifically, we aim to: 1) summarize the scientific literature on what is known and not known about LM applied for phosphate removal; 2) identify and critically evaluate the current state-of-practice for determining the performance of LM in laboratory studies and field scale applications; and 3) highlight key environmental factors important for understanding potential impacts of LM on ecological systems and highlight areas for future research. The contents of our review may be helpful for material developers and other stakeholders interested in using LM for phosphate removal in natural water and wastewater systems.

2. La(III)-containing materials for phosphate removal

2.1. Overview of La(III)-containing materials

There are currently around 80 different types of LM in use or under study for phosphate removal. Table S3 in the Supplementary Information (SI) provides a list of these different LM types along with their main characteristics based on a review of 73 peer-reviewed scientific articles. Excluding La oxides or hydroxides (Fang et al., 2018b; Xie et al., 2014a; Xie et al., 2014c), most LM have a carrier material into which La species are incorporated. These LM carriers include: 1) carbonaceous materials (e.g., graphene, activated carbon fiber, biochar) (Chen et al., 2016; Cheng et al., 2018; Kumar et al., 2019; Liao et al., 2018; Liu et al., 2013, 2011; Qiu et al., 2017; Rashidi Nodeh et al., 2017; Shin et al., 2005; Tang et al., 2019; Wang et al., 2016; Wei et al., 2019; Zhang et al., 2012b; 2018); 2) (alumino)silicates (Chen et al., 2019; Copetti et al., 2016; Goscińska et al., 2018; Haghseresht et al., 2009; He et al., 2017; Huang et al., 2014a,b; Huang et al., 2014a,b; Huang et al., 2015; Kong et al., 2018; Lai et al., 2016; Ou et al., 2007; Pham et al., 2019; Reitzel et al., 2013a; Shi et al., 2019; Waajen et al., 2016; Wasay et al., 1996; Wu et al., 2017; Wu et al., 2019; Xie et al., 2014b; Yang et al., 2012; 2011; Yuan et al., 2018; Zhang et al., 2011; 2010); 3) polymers (Chen et al., 2018; Dong et al., 2017; Du et al., 2018; He et al., 2015; Liu et al., 2013; Wu et al., 2007; Zhang et al., 2012a; Zhang et al., 2016); 4) iron and iron oxides (Ding et al., 2018; Fang et al., 2018a; Fu et al., 2018; Lai et al., 2016; Lin et al., 2019; Liu et al., 2013; Wu et al., 2017); 5) aluminum hydroxide (Xu et al., 2017); and 6) combinations of these materials (Lai et al., 2016; Min et al., 2019).

La^{3+} , $\text{La}_2\text{O}_3(\text{s})$, and $\text{La}(\text{OH})_3(\text{s})$ are common sources of La ions when non-La-carriers are transformed into LM (Table S3). During synthesis, La^{3+} is incorporated into the structure of a carrier by exchange with Ca^{2+} or Na^{+} (Douglas et al., 2000; Du et al., 2018; Goscińska et al., 2018; Shin et al., 2005; Wu et al., 2007), whereas $\text{La}_2\text{O}_3(\text{s})$ and $\text{La}(\text{OH})_3(\text{s})$ are incorporated into the carriers via co-calcination (Wei et al., 2019), co-precipitation (Shi et al., 2019), calcination (Emmanuelawati et al., 2013; Huang et al., 2015; Huang et al., 2014a,b; Yang et al., 2012; 2011), or precipitation of material preloaded with La^{3+} under alkaline conditions (Chen et al., 2019; 2018; Fang et al., 2018a; He et al., 2015; Liao et al., 2019; 2018; Qiu et al., 2017; Rashidi Nodeh et al., 2017; Tang et al., 2019; Wu et al., 2017; Zhang et al., 2016; 2012b).

Carrier materials with internal and surface structures (e.g., porous structures with relatively high specific surface areas) are often selected to facilitate La access to phosphate (He et al., 2015; Rashidi Nodeh et al., 2017; Zhang et al., 2016) and enhance La dispersion to promote the crystallization of $\text{LaPO}_4(\text{s})$ (Zhang et al., 2016). Other material design factors include enhancing the affinity of phosphate for surface adsorption, such as an overall positive charge of the carrier as characterized by the point of zero charge (pH_{PZC}) (Tang et al., 2019). Depending on the intended use, it may also be important to consider properties beyond phosphate binding. For example, it may be important to minimize La^{3+} release from the carrier matrix during LM application given the inherent toxicity of dissolved La to aquatic organisms (He et al., 2015). For applications that require LM recovery from the aqueous phase, facile separation by gravity settling and/or filtration is desirable (Min et al., 2019); some nano-sized materials may therefore require a supporting matrix (He et al., 2015) or modification with Fe_3O_4 for magnetic separation (Fang et al., 2018a; Lai et al., 2016; Wu et al., 2017).

2.2. La(III)-containing materials functionality and performance for phosphate removal

When designing and selecting the type of LM for phosphate removal, it is important to consider its phosphate uptake performance, such as equilibrium capacity and uptake kinetics, as well as influence of co-existing environmental constituents [e.g., natural organic matter (NOM), competing ions], regenerability and reuse, and feasibility of

phosphate recovery or direct use of the resulting P-containing mineral in agricultural applications. To provide more details on these aspects, we summarize the scientific literature in the section below and identify key parameters involved in LM performance based on laboratory studies.

2.2.1. Phosphate uptake capacity

Most published studies have used adsorption isotherms, such as the Langmuir model (Eq. S1), to estimate the maximum phosphate uptake capacity, q_m (mg P g⁻¹ of LM), of LM (q_m values from our literature review are listed in Table S5, please refer to SI for the Langmuir isotherm model and q_m calculation method). The q_m value is commonly used for comparison of the total phosphate removal capacity of different LM. Our review of results for 80 LM in 73 peer-reviewed articles found that the majority of studies deemed phosphate removal as an adsorption phenomenon because the Langmuir isotherm model described the experimental data well (Dong et al., 2017; Fang et al., 2017; Huang, 2011; Wu et al., 2017; Xie et al., 2014b; Xu et al., 2017; Zhang et al., 2012b). It has been speculated that mechanisms of phosphate adsorption by LM include electrostatic interactions (Dong et al., 2017; Wu et al., 2017), ion exchange (Park et al., 2020; Xie et al., 2014b), ligand exchange (Dong et al., 2017; Fang et al., 2017; Wu et al., 2019, 2017; Xie et al., 2014b; Xu et al., 2017; Zhang et al., 2012b), Lewis acid-base interactions (Huang, 2011; Zhang et al., 2012b), and inner-sphere complexation (Wu et al., 2020). However, the mechanism of removal from solution cannot be reliably inferred from the goodness of fit of an isotherm model (Sposito, 1982; Veith and Sposito, 1977), and the exact mechanism for phosphate uptake by LM is still uncertain. Apart from various adsorption mechanisms (Dong et al., 2017; Fang et al., 2017; Huang, 2011; Wu et al., 2019, 2017; Xie et al., 2014b; Xu et al., 2017; Zhang et al., 2012b), the most commonly-cited mechanism of phosphate removal by LM is precipitation of LaPO_{4(s)} and its hydrated forms (Dithmer et al., 2015; Haghseresht et al., 2009; He et al., 2015; Qiu et al., 2017).

Understanding the underlying phosphate-removal mechanism by LM is critical to estimate q_m . For this purpose and to identify the primary physicochemical property(ies) of LM that may control uptake capacity, q_m is plotted as a function of three commonly measured LM characteristics: La content, surface area, and pH at the point of zero charge (pH_{pzc}) (Fig. 1). As shown in Fig. 1A and Table S4, q_m strongly correlates with La content for the 61 LM. This relationship spans more than an order-of-magnitude range in phosphate uptake capacity (Table S5). Furthermore, the trend shown in Fig. 1A is consistent with the 1:1 stoichiometry

of precipitation of 1:1 solids (with a simple solid shown in Eq. (1) to represent this La to P = 1:1 stoichiometry and hydrated forms of the mineral) (Wall, 2013):



A few previous studies have identified LaPO_{4(s)} precipitation as the dominant mechanism of phosphate sequestration (Dithmer et al., 2015; Haghseresht et al., 2009; He et al., 2015; Qiu et al., 2017). Specifically, Dithmer et al. (2015) characterized the reaction products by LMB in contact with phosphate in solution and demonstrated the formation of rhabdophane (LaPO₄·nH₂O_(s)). The aging of rhabdophane may lead to the formation of monazite (LaPO_{4(s)}), which is even more stable than rhabdophane (Cetiner et al., 2005; Dithmer et al., 2015).

The 1:1 relationship between q_m and La content also suggests that La is the only part of LM that provides specific binding to phosphate, regardless of the La form (ionic vs. solid) and specific formulation of LM that covered a wide range of carrier materials. Although some carrier materials, e.g. Fe₃O₄ (Wu et al., 2017), are expected to possess intrinsic phosphate binding capacity, most carrier materials show little or no phosphate removal before being modified by La (Goscianska et al., 2018; Kong et al., 2018; Liao et al., 2018; Min et al., 2019; Qiu et al., 2017; Zhang et al., 2012a, 2016). Regarding La sources, Wu et al. (2019) concluded that the specific composition or form of La (i.e., La₂O_{3(s)}, La(OH)_{3(s)}, La³⁺) may influence the overall phosphate uptake capacity of LM by causing different interactions with phosphate, although few studies have investigated this (Dong et al., 2017; Wu et al., 2019). Evidence can be found in Dong et al. (2017), where the effect of La species on phosphate uptake using three lab-synthesized La-loaded magnetic cationic hydrogels (MCH) was explored: 1) La³⁺-MCH; 2) La(OH)₃-MCH-W [La loading conducted in water (W)]; and 3) La(OH)₃-MCH-EW [La loading conducted in ethanol/water (EW)]. The q_m estimated by Langmuir model fitting decreased in the order of: La(OH)₃-MCH-EW (90.2 mg P g⁻¹) > La³⁺-MCH (70.5 mg P g⁻¹) ≈ La(OH)₃-MCH-W (69.2 mg P g⁻¹). The differences in q_m across the three LM were attributed to the higher amount of loaded La and higher surface area of La(OH)_{3(s)} compared to La³⁺ modified MCH (Dong et al., 2017). However, if the q_m was normalized by its La content, the three LM all had the same stoichiometry of La:P 1:1; that is, 1.0, 0.84, and 0.93 mmol P mmol⁻¹ La for La(OH)₃-MCH-EW (42.9 mg La g⁻¹), La³⁺-MCH (26.4 mg La g⁻¹), and La(OH)₃-MCH-W (29.0 mg La g⁻¹), respectively.

Results from the literature suggest that phosphate removal capacity

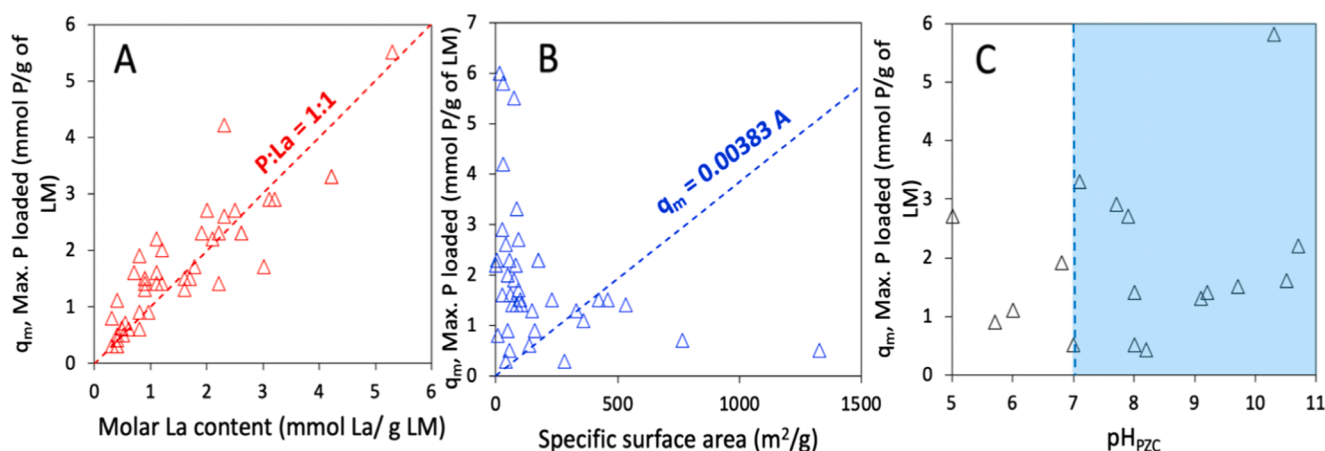


Fig. 1. Maximum phosphate uptake capacity (q_m , estimated from Langmuir isotherm model) of 61 La-containing materials (LM) as a function of (A) molar La content, (B) specific surface area of the LM, and (C) point of zero charge (pH_{pzc}). The dashed line in panel A represents a La:P molar ratio of 1:1. The dashed line in panel B represents a $q_m = 0.00383 \text{ mmol/m}^2 \times \text{specific surface area of LM}$. The slope of 0.00383 mmol/m^2 was inverted and converted from typical surface site densities of minerals (2.3 sites nm⁻²) (Davis, 1990; Dzombak and Morel, 1990; Field et al., 2019). The dashed line in panel C represents pH = 7. In pure water, LM with pH_{pzc} greater than ambient pH (assuming pH = 7 in freshwater) carries a positive charge indicated by the blue shaded region, which can attract phosphate anions via electrostatic interactions and vice versa. See Table S1 for all details based on the synthesis of 73 peer-reviewed articles that contained 73 LM. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is independent of both the specific surface (Fig. 1B) and pH_{pzc} of LM (Fig. 1C). Because adsorption (e.g., surface complexation or electrostatic interaction) is a surface phenomenon with phosphate ions adheres to the surface (Fig. 2A), the lack of correlation (Table S2) may suggest that adsorption is not the dominant mechanism of phosphate removal. It is worth noting that typical surface site densities of minerals were found to be $\sim 2.3 \text{ sites nm}^{-2}$ (Davis, 1990; Dzombak and Morel, 1990; Field et al., 2019), suggesting the maximum number of phosphate ions that can fit in a square meter is 0.00383 mmol. If we assume this steric condition also dictates the maximum sorption density on LM, the P sorption density can be used to tentatively assign the removal mechanism. If surface P loading of a LM is much larger than the maximum site density (i.e., falling on the left side of the dashed line in Fig. 1B), P is likely to be removed by precipitation instead of adsorption. As illustrated in Fig. 1B, 78% of data points are located on the left side of the dashed line, suggesting a precipitation mechanism for phosphate removal by these LM. In contrast, in the case of precipitation, phosphate draws into the bulk of the phase of LM and can reach a La:P of 1:1 M ratio at equilibrium (Fig. 2B).

2.2.2. Uptake kinetics

In addition to phosphate uptake capacity, the rate of phosphate uptake is critical to describe the effectiveness of LM. The rate-limiting step for phosphate removal is dependent on the specific LM formulation, given that a range of carrier materials and forms of La (ionic vs. solid) are used. In these cases, the rate of phosphate removal depends on either the dissolution of La solids or precipitation/adsorption of phosphate. For LM that use carrier materials, reaction scenarios may occur as shown in Fig. 3. First, phosphate may transfer from the bulk aqueous solution to LM surfaces (possibly via intraparticle transport, such as pore diffusion) before binding to La sites or forming $\text{LaPO}_4(\text{s})$ (or its hydrated forms) on the LM (pore) surface (Fig. 3A). Carrier materials may also affect the reaction kinetics of LM by altering the diffusion path (Fig. 3). For instance, some fibrous matrix carrier materials may enhance La dispersion (He et al., 2015), improve the accessibility of La to phosphate, facilitate the crystallization of $\text{LaPO}_4(\text{s})$, and improve reaction kinetics (Zhang et al., 2016).

Alternatively, La release via dissolution and/or desorption and

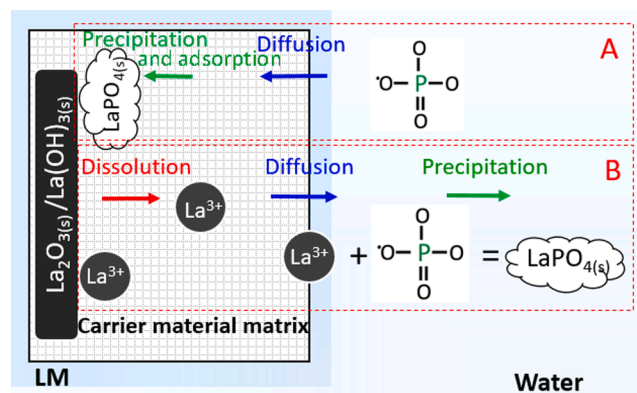


Fig. 3. Two mass transfer pathways that may occur related to phosphate uptake by LM. A) phosphate can diffuse from the bulk aqueous solution to LM (pore) surfaces, forming $\text{LaPO}_4(\text{s})$ on the surface of LM. B) La may dissolve or desorb from LM and react with phosphate in the bulk solution.

diffusion may lead to $\text{LaPO}_4(\text{s})$ formation by reaction of phosphate with La^{3+} in bulk solution (Fig. 3B). In this case, PO_4 removal kinetics are expected to vary with changes in solution pH. As pH increases, concentrations of both OH^- and CO_3^{2-} increased, decreasing the rate of La dissolution and thus the reactant concentration for $\text{LaPO}_4(\text{s})$ formation (Haghseresht et al., 2009; Reitzel et al., 2013). Other than pH, the presence of La ligands (e.g., SO_4^{2-} , NO_3^- , CO_3^{2-} , NOM, biogenic exudates) that can bind free La decrease the activity of La^{3+} , interfere with $\text{LaPO}_4(\text{s})$ precipitation kinetics (Dithmer et al., 2016a; Zhang et al., 2016), and thereby reduce the overall rate constant for phosphate removal by LM (Zhang et al., 2012a; Zhang et al., 2016).

2.2.3. Influence of coexisting inorganic ions

As discussed above, diverse constituents in environmental matrices, such as co-existing ions and ligands, may impact the performance of LM. In general, such influences were observed to be minor for the phosphate uptake capacity of LM but could have more pronounced impacts on uptake kinetics. Across a range of complex aqueous matrices, such as

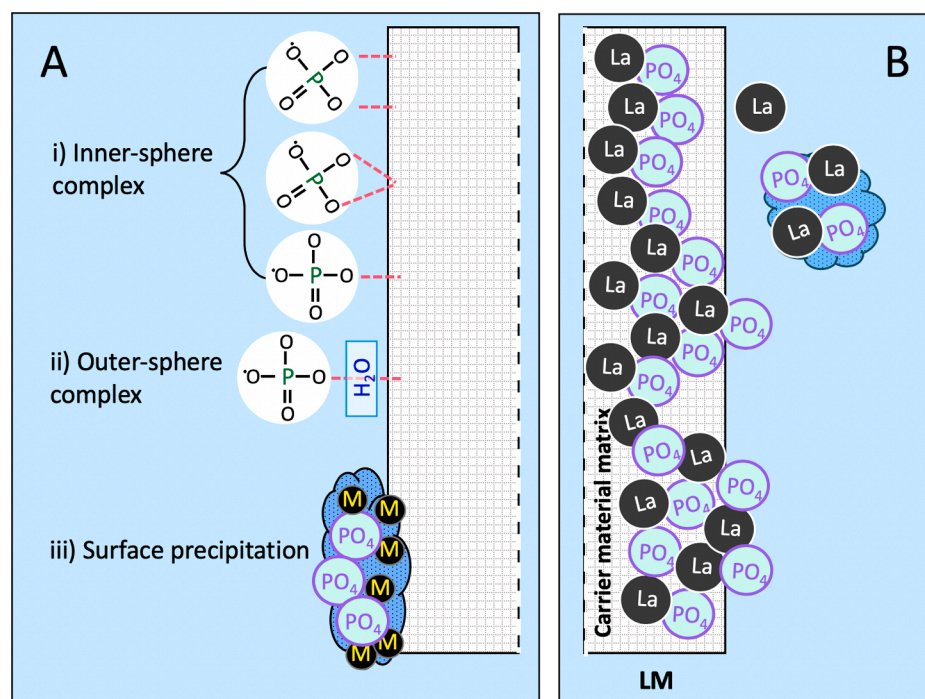


Fig. 2. Illustration of A) adsorption and B) precipitation mechanisms of phosphate removal. As shown in panel A, a phosphate anion can bind to a sorbent via i) inner-sphere complexation (i.e., mononuclear monodentate, mononuclear bidentate, and binuclear bidentate), ii) outer-sphere complexation, in which water molecules are present between the sorbent surface and the phosphate ion; and iii) precipitation in which dissolved metal from the sorbent contributes to the formation of multiple layers of metal-P precipitate on the surface (Cooke et al., 2005; Loganathan et al., 2014; Wilfert et al., 2015). Panel B shows phosphate removal by LM via precipitation of $\text{LaPO}_4(\text{s})$ either on LM surface or in the bulk solution (Dithmer et al., 2015; Haghseresht et al., 2009; He et al., 2015; Qiu et al., 2017).

surface water (Dithmer et al., 2016b; Reitzel et al., 2013a; Waajen et al., 2016), brackish water (Reitzel et al., 2013a), seawater (Mucci et al., 2020; Wu et al., 2007), and wastewater (Haghsereht et al., 2009; Wu et al., 2007), LM exhibit high phosphate capture efficiencies. LM possess high selectivity for phosphate anions in the presence of competing anions and ligands (e.g., Cl^- , NO_3^- , F^- , SO_4^{2-} , SO_3^{2-} , HCO_3^- , SiO_4^{4-} , and Br^-), even when the molar concentration of competing ions exceeds that of phosphate by up to 50 times (Chen et al., 2016; Dong et al., 2017; Huang et al., 2014a,b; Rashidi Nodeh et al., 2017; Wu et al., 2017; 2007; Zhang et al., 2011; Zhang et al., 2016) (Table S3).

We modeled phosphate removal by LM in the presence of major anions in natural water. Visual MINTEQ results showed that major anions (i.e., SO_4^{2-} , Cl^- , NO_3^- , CO_3^{2-}) have a negligible impact on $\text{LaPO}_4(\text{s})$ formation at equilibrium (Figs. S1 and S2) over the entire pH range. This observation is true even for anions, such as SO_4^{2-} and CO_3^{2-} , that can form complexes with La (forming $\text{La}(\text{SO}_4)_2^-$ and LaSO_4^+ (Fig. S1b) or $\text{La}(\text{CO}_3)_2^-$ and LaCO_3^+ (Fig. S2a and b), and is consistent with prior studies of LMs (Chen et al., 2016; Dong et al., 2017; Huang et al., 2014a,b; Wu et al., 2017; 2007). Overall, model results illustrate that La^{3+} preferentially reacts with PO_4 at environmentally relevant pH values. The selectivity of La for P is attributed to the strength of the La- PO_4 bond, which is reflected in a relatively low Gibbs free energy of formation of $\text{LaPO}_4(\text{s})$ ($\Delta G_f^\circ = -439.10 \text{ kcal mol}^{-1}$) compared to other phosphate minerals (Tardy and Vieillard, 1977).

2.2.4. Influence of natural organic matter

The adverse effect of NOM on PO_4 removal has been observed in a series of laboratory-scale studies. NOM carries strong acid (pK_a of 3.3–4.0) and weak acid groups ($pK_a > 6$), as well as a few bidentate sites (pK_a of 4–16) that may act as major competitor ligands for La (Sonke, 2006; Tipping and Hurley, 1992) and thus interfere with $\text{LaPO}_4(\text{s})$ formation. Experiments of phosphate removal by LM indicate that NOM may constrain phosphate binding by LM (Dithmer et al., 2016a; Douglas et al., 2000; Lai et al., 2016; Lüring et al., 2014; Song et al., 2020; Wu et al., 2019). Specifically, Lüring et al. (2014) found the efficiency of LMB was reduced in the presence of humic substances in both short- (1 day) and long-term (42 day) experiments. Moreover, Dithmer et al. (2016a) tested LMB in 16 lake and pore waters from 16 Danish lakes with a variety of properties. The data showed a significant negative correlation between lake water dissolved organic carbon (DOC) concentrations and phosphate binding capacity of the LMB. However, a few other studies concluded that NOM or humic acid had insignificant effects on phosphate removal capacity by LM (Fang et al., 2017; Wei et al., 2019; Yuan et al., 2018; Zhang et al., 2018; 2016). The apparent contradiction is likely related to the impact of NOM on PO_4 removal kinetics. Dithmer et al. (2016a) demonstrated that the negative effect of NOM is principally kinetic, and given enough time, phosphate will eventually be bound to La, thereby overcoming the interference by DOC (Dithmer et al., 2016a). Because NOM can considerably alter the speciation, distribution, and mobility of La in the aquatic environment (Chakraborty et al., 2011; Moermond et al., 2001; Sholkovitz, 1992) and subsequently affect the bioaccumulation and ecotoxicity of La and LMB (Das et al., 1988; Herrmann et al., 2016; Sun et al., 1997), it is critical to evaluate NOM effects on LM; however, most 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., 2016a; 2015; Lüring et al., 2014).

2.2.5. Influence of solution pH

In addition, the binding capacity of phosphate by LM (rather than kinetics) has been shown to be independent of pH across a wide pH range (i.e., 2.7–10.9) (Chen et al., 2019; Cheng et al., 2018; Dong et al., 2017; Fang et al., 2018a; Fu et al., 2018; Huang et al., 2014a,b; Kong et al., 2018; Lai et al., 2016; Qiu et al., 2017; Shi et al., 2019; Shin et al., 2005; Tang et al., 2019; Wu et al., 2017; Zhang et al., 2011). Using the

geochemical model Visual MINTEQ (version 3.1), it was found that the low solubility of $\text{LaPO}_4(\text{s})$ resulted in precipitation of $\text{LaPO}_4(\text{s})$ within the pH range 3–13 (Fig. 4A). This is in contrast to Al(III) salts that are much more sensitive to pH changes (Cooke et al., 2005). As for minerals containing Fe and P, their solubility and hence phosphate sorption capacity are highly sensitive to both pH and redox changes (Wilfert et al., 2015).

2.2.6. Phosphate-recovery and regeneration

As shown in Fig. 4A, dissolution of phosphate from $\text{LaPO}_4(\text{s})$ can theoretically occur but only under very acidic or basic pH conditions (i.e., $\text{pH} < 2$ or $\text{pH} > 13$), and thus release of phosphate from LM requires the use of strong acids or bases (see Table S6) (Chen et al., 2018; Fu et al., 2018; Liao et al., 2018; Ou et al., 2007; Qiu et al., 2017; Rashidi Nodeh et al., 2017; Thagira Banu et al., 2018; Wu et al., 2017, 2007; Wu et al., 2019; Xie et al., 2014a; 2014b; Yuan et al., 2018; Zhang et al., 2012a). Further, the dissolution of $\text{La}(\text{OH})_3(\text{s})$ in ultra-pure water (UPW) has been shown to occur at $\text{pH} < 8.0$ based on results from our modeling work shown in Fig. 4B. Therefore, due to the quasi-insoluble nature of $\text{LaPO}_4(\text{s})$, recovery and reuse of P from solid materials is a challenge. The reversibility of phosphate sequestration by LM should be considered in material selection. Nevertheless, due to the insoluble nature of $\text{LaPO}_4(\text{s})$, recovery and reuse of phosphate from $\text{LaPO}_4(\text{s})$ will pose significant challenges. Instead, LM may be more suitable for preventing P recycling in natural waters. In contrast, other materials, such as Fe-containing materials that rely on an adsorption mechanism may be more suitable for P recovery and reuse from P-rich waste streams.

2.3. Applications and use

LMB, commercially known as Phoslock® and the only form of LM that has been applied *in situ* (Copetti et al., 2016), was developed by the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) (Reitzel et al., 2013a; Robb et al., 2003; van Oosterhout and Lüring, 2013). Phoslock® is one of the main commercial remediation products for P-polluted waters in Europe (Copetti et al., 2016). For field scale site applications, LMB is typically sprayed onto the surface of a water body from a boat or pontoon. The LMB moves down the water column and scavenges up to 95% of P as it drifts to the bottom (Bishop et al., 2014; Robb et al., 2003). As LMB settles on the sediment–water interface, it forms a layer that can intercept P between the sediment and the overlying water (Meis et al., 2013). Post application, LMB buried on the surface sediment is reported to function as a P sink that can capture P from pore water (Douglas et al., 2016). LMB forms strong bonds with phosphate to give rise to rhabdophane, which over time transforms into monazite (Cetiner et al., 2005; Dithmer et al., 2015). Due to the stability of $\text{LaPO}_4(\text{s})$ minerals, the sediment P eventually becomes inactivated by LMB, contributing to the control of internal P release from the sediment (Douglas et al., 2016).

Field managers interested in applying LM to remove phosphate from the aquatic environment need to consider additional dimensions in their choice of remediation technique, such as potential environmental, health, and social implications. To this end, Section 3 highlights and discusses key parameters pertaining to broader implications of using LM with a focus on potential impacts on ecological systems. Further, the discussion section provides guidance on areas of future research that may be helpful to material developers as well as those interested in using LM for phosphate removal from natural water or in waste treatment systems.

3. Potential impacts of La(III)-containing materials on ecological systems

Although LM seem promising in terms of their ability to effectively remove phosphate from water, potential unwanted and/or unintended consequences also need to be considered when developing and using

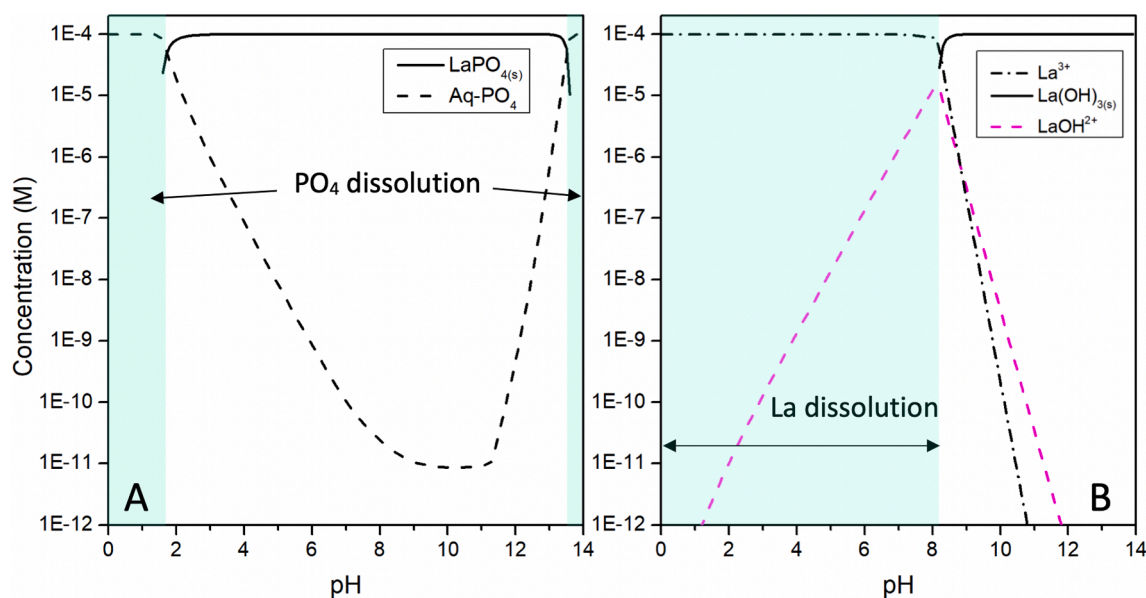


Fig. 4. A) Dissolution of solid $\text{LaPO}_{4(s)}$ in pure water as a function of solution pH at 25 °C. Total La and total P in the system are 100 μM , respectively. B) Dissolution of solid $\text{La}(\text{OH})_{3(s)}$ in pure water as a function of solution pH at 25 °C. Total La in the system is 100 μM . The pH range in which dissolution (i.e., release of La^{3+} or phosphate) occurs is shown by the light green areas. Lines represent modeled values estimated using geochemical equilibrium simulations (Visual MINTEQ, version 3.1), whereby pH was varied from 0 to 14 using increments of 0.2 log units. Solubility product constants ($\log K_{sp}$) of solid phases are -25.75 for $\text{LaPO}_{4(s)}$, and -21.709 for $\text{La}(\text{OH})_{3(s)}$. Details on calculations can be found in the SI. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

these novel materials, particularly for *in situ* applications (e.g., Bates et al., 2016; Grieger et al., 2012, 2010). In response, a growing body of literature has started to investigate the potential impacts of La^{3+} and LM (such as LMB) on ecological systems across various test species (Álvarez-Manzaneda et al., 2019; Lürding and Tolman, 2010; van Oosterhout and Lürding, 2013), including several review articles published in recent years (Copetti et al., 2016; D'Haese et al., 2019; Herrmann et al., 2016; Spears et al., 2013). While this body of literature continues to grow and a number of research areas still require additional investigations, the key parameters to consider when evaluating potential ecological impacts of La and LM include release of La from LM (e.g., La dissolution), bioavailability, bioaccumulation, and ecotoxicity of La from LM deployment. The following therefore provides an overview of these parameters, which may also be helpful when guiding the responsible research, development, and use of LM for phosphate removal in waters, especially for use *in situ*.

3.1. La solubilization from La(III)-containing materials

The dissolution of La^{3+} from LM is strongly influenced by a number of physical and chemical parameters, including pH, alkalinity, and the presence of different organic and inorganic complexing agents (Gonzalez et al., 2014; Herrmann et al., 2016; Lürding et al., 2014; Moermond et al., 2001; Reitzel et al., 2017) (see Table S6 for full details). Increased solubilization of La^{3+} from LM was found to occur at moderately acidic pH (i.e., $\text{pH} < 4.5$ – 5.6) (Shin et al., 2005; Wu et al., 2017) and high salinity conditions (Douglas et al., 2000) in laboratory-based studies (Table S6). As discussed earlier, the dissolution of $\text{La}(\text{OH})_{3(s)}$ in UPW has been shown to occur at $\text{pH} < 8.0$ based on results from our modeling work (see Fig. 4B). Further, NOM has a strong affinity towards La in LM (Sonke, 2006; Tipping and Hurley, 1992) and increased La dissolution from LM has been shown to occur via complexation (Lürding et al., 2014; Reitzel et al., 2017). For instance, Lürding et al. (2014) observed a strong increase of filterable La (i.e., passing a $0.45\text{-}\mu\text{m}$ pore size filter) in the presence of 10 mg L^{-1} of NOM (humic substances) with $>270\text{ }\mu\text{g La L}^{-1}$ detected after a week (Lürding et al., 2014). Reitzel et al. (2017) also found that NOM (humic acid) increases the concentration of filterable La

in soft water lakes, with La complexations retained in the LMB matrix (Reitzel et al., 2017). Overall, these findings on La solubilization are important to consider since partial or complete loss of La from LM may reduce the efficacy of LM in phosphate sequestration. The introduction of soluble La species into the water column is also undesirable since La may subsequently react with ecological organisms, as discussed below (Copetti et al., 2016; Das et al., 1988; Gonzalez et al., 2014; Reitzel et al., 2017).

3.2. Bioavailability and bioaccumulation

Following potential release of La from LM, the bioaccessibility (i.e., environmental availability) and bioavailability of La depends on the speciation of the released La, similar to other metals. While the primary mode of action that results in toxicological responses is driven by ionic La^{3+} (Das et al., 1988), the released La^{3+} will likely undergo hydrolysis, interact with phosphate and carbonate species (forming poorly soluble complexes), and bind to organic matter (e.g., humic acid) (Moermond et al., 2001; Mucci et al., 2020; Tang and Johannesson, 2010; 2003).

In aquatic environments with high levels of ligands such as NOM (e.g., humic acids), carbonate, and phosphate, the concentration of free La^{3+} is expected to be low due to precipitation and complexation reactions. We therefore modeled the impact of NOM (i.e., 1, 5, 20 mg TOC L^{-1}), phosphate (i.e., 0.01, 0.1, 0.2 $\text{mg PO}_4\text{ L}^{-1}$), and carbonate (i.e., 12 and 60 mg C L^{-1}) on the concentration of free La^{3+} across an environmentally-relevant pH range (4.5–8.5) at 25 °C. As shown in Fig. 5, the concentration of free La^{3+} depends on ligand concentrations (i.e., NOM, PO_4 , CO_3) and solution pH. Generally, the effect of carbonate on La^{3+} concentration becomes more significant when $\text{pH} > 6.5$ (Fig. 5), which can be attributed to the formation of $\text{La}(\text{CO}_3)_2$, LaCO_3^+ , and LaHCO_3^{2+} complexes and $\text{La}_2(\text{CO}_3)_3(s)$ precipitation. Concentrations of La^{3+} decreased further with increasing concentration of NOM (Fig. 5), consistent with the formation of La-NOM complexes that have been shown to 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). Moreover, the concentration of La^{3+} in the water column is predicted to decrease with increasing phosphate

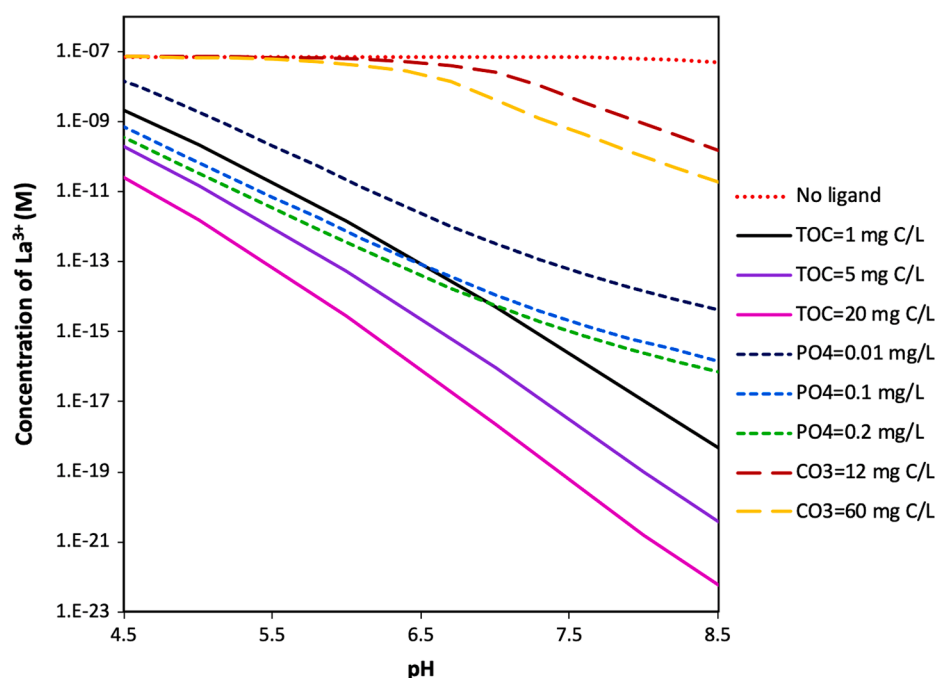


Fig. 5. Dependence of equilibrium concentrations of La^{3+} as a function of solution pH (4.5–8.5) and ligand concentrations. Impact of three ligands (NOM at 1, 5, 20 mg TOC L^{-1} , phosphate at 0.01, 0.1, 0.2 $\text{mg PO}_4 \text{ L}^{-1}$, and carbonate at 12 and 60 mg C L^{-1}) on concentration of free La^{3+} were simulated at 25 °C. Total La in the system is 0.01 mg L^{-1} or 7.2E-8 M. Interactions between La and phosphate or carbonate were modeled by Visual MINTEQ, version 3.1. Interactions between La and NOM were modeled by CHEAQS Pro (Verweij, 2005). In this model, La complex formation with NOM (50% fulvic acid, 50% humic acid) was predicted with Model VII (Tipping, 1998; Tipping et al., 2011; Tipping and Hurley, 1992). Solubility product constants ($\log K_{sp}$) of solid phases are: -25.75 for $\text{LaPO}_4(\text{s})$, -21.709 for $\text{La}(\text{OH})_3(\text{s})$, and -34.4 for $\text{La}_2(\text{CO}_3)_3(\text{s})$.

concentration, where the concentration of dissolved La^{3+} is limited by the solubility of rhabdophane ($\text{LaPO}_4 \cdot \text{H}_2\text{O}$) (Lürling and Tolman, 2010). Overall, these processes reduce the bioavailability of La in aquatic environments (Gonzalez et al., 2014; Herrmann et al., 2016). As stated by Herrmann et al. (2016) a Biotic Ligand Model (BLM) for La would need to be developed to be able to provide more insight in the relation between La speciation, bioavailability and ecotoxicity. Unfortunately, a BLM for La is still not available.

Another key factor to consider in the development and deployment of LM for phosphate removal is the potential for La to bioaccumulate in ecological systems. Several studies have documented that La can accumulate in different aquatic species (Copetti et al., 2016; Figueiredo et al., 2018; Herrmann et al., 2016; Waajen et al., 2017b; Yang et al., 1999), including macrobenthic invertebrates (Pastorino et al., 2020; Pinto et al., 2019), with high bioaccumulation factors observed in aquatic plants, mollusks (D'Haese et al., 2019; Herrmann et al., 2016; Weltje et al., 2002; Yang et al., 1999), as well as in internal fish organs (Figueiredo et al., 2018; Qiang et al., 1994). Bioaccumulation is likely to stem from low aquatic La concentrations ($\mu\text{g-pg L}^{-1}$), as bioaccumulation of La shows an inverse correlation between exposure and accumulation (Herrmann et al., 2016; Weltje et al., 2002), as is the case for most metals (DeForest et al., 2007). Other studies have indicated that most accumulated La in biota may be eliminated in short periods of time (Copetti et al., 2016; Hao et al., 1996; Landman and Ling, 2006), although more research is needed to understand the potential for La elimination from internal organs and skeletons (Copetti et al., 2016). Finally, several authors have noted the need for more long-term investigations into the fate of La following LM applications to more fully understand its bioaccumulation potential, particularly across diverse trophic levels (Copetti et al., 2016; Pastorino et al., 2020; Waajen et al., 2017b).

3.3. Ecotoxicological impacts

There have been various ecotoxicological studies conducted with La and LM, such as LMB. These studies have varied widely in terms of test organism (e.g., aquatic invertebrates, aquatic vertebrates, algae, sediment-dwelling organisms), investigated LM (i.e., La salts such as LaCl_3 , $\text{La}(\text{NO}_3)_3$, $\text{La}_2\text{O}_3(\text{s})$, and $\text{La}_2(\text{CO}_3)_3(\text{s})$, or LMB), experimental

media, environmental conditions (e.g. pH, total organic carbon, presence of oxyanions or humic acids), exposure durations, as well as measured endpoints (e.g., mortality, growth, reproduction) (Douglas, 2002; Haghseresht et al., 2009; Herrmann et al., 2016; Robb et al., 2003). Several review articles have consolidated these ecotoxicology studies, including Spears et al. (2013), Copetti et al. (2016), Herrmann et al. (2016), and D'Haese et al. (2019). The results of these diverse studies have produced divergent conclusions, due to different testing parameters and conditions as well potentially confounding factors that may influence results, as described further below. Nonetheless, based on the current state of knowledge it appears that the use of LM and LMB present a very low risk of adverse effects in natural freshwaters for environmental organisms and humans at the intended doses and under proper environmental conditions (i.e., in water with $\text{pH} > 7$ and moderate-to-high bicarbonate alkalinity). Caution should be taken, however, when considering LM use in aquatic systems with acidic pH values and low bicarbonate alkalinity.

Among other notable findings, Spears et al. (2013) concluded that maximum LMB exposure estimates in waters did not exceed EC50 values or NOEC values (lowest EC50 of 871 mg L^{-1} for *D. magna*; NOEC of 100 mg L^{-1} and EC50 of 150 mg L^{-1} for *B. calyciflorus*) (Lürling and Tolman, 2010; van Oosterhout and Lürling, 2013) for LMB based on laboratory experiments. The authors showed that in lakes with LMB application, the Dutch filterable La (FLa) standard of 10.1 $\mu\text{g L}^{-1}$ in surface waters was exceeded in many cases after initial application, but all monitored lakes in the study were later found to comply with the standard a few months after application. Spears et al. (2013) further stated that if exposures to particulate La or total La (TLa) concentrations were accounted for, then the exposure concentration durations may achieve values shown to be adverse to a range of ecological organisms. Similarly, Copetti et al. (2016) concluded that concentrations of FLa from LMB applications may exceed environmental quality standards for some sensitive zooplankton species (i.e., *B. calyciflorus*, *D. magna*, *C. dubia*) during times of application or shortly afterwards (Copetti et al., 2016).

It should also be mentioned that in addition to potential ecotoxicological impacts from exposure to ionic La, several authors noted the potential for adverse effects on some aquatic organisms from the physical presence of LM particles in the water column. This is because LM applications can increase turbidity, and subsequently, potentially

reduce grazing for zooplankton or adversely impact invertebrate filter feeders (e.g. *D. magna*) and/or fish (Álvarez-Manzaneda et al., 2019; Copetti et al., 2016; Kirk, 1991).

To develop ecologically-relevant thresholds limit values, Herrmann et al. (2016) proposed a preliminary pelagic Predicted No Effect Concentration (PNEC) of $4 \mu\text{g La L}^{-1}$ based on a reported NOEC for daphnia (*D. carinata*) and a PNEC for freshwater sediment at 5 mg/kg based on a NOEC value for nematodes (*C. elegans*). For both PNECs, an assessment factor of 10 was used to extrapolate from NOEC to PNEC (European Commission, 2003). To put these values in a broader perspective, one of the most conservative legislations on the maximum allowable concentration of anthropogenic La in the environment is established in The Netherlands, i.e., $10.1 \mu\text{g La L}^{-1}$ of Fla in surface waters (Crommentuijn et al., 2000). Such environmental quality standards and environmental legislations on La in marine environments have not yet been developed, largely due to the lack of sufficient data to draw conclusions regarding La and LM (Copetti et al., 2016; D'Haese et al., 2019; Herrmann et al., 2016; Spears et al., 2013).

3.4. Confounding factors

As mentioned earlier, there has been a wide range of ecotoxicological studies conducted on La and LM, that have spanned test organisms, the type of La or LM used, and other testing conditions. To account for differences in ecotoxicological responses across various studies, some have suggested that confounding factors may have influenced the reported ecotoxicological responses (Copetti et al., 2016; Spears et al., 2013). These include water hardness, alkalinity, pH, and dissolved organic carbon (Herrmann et al., 2016) in addition to the specific test solutions used (Spears et al., 2013). Others have noted challenges in conducting ecotoxicity tests involving La (Copetti et al., 2016; D'Haese et al., 2019), for example, the use of environmental media may result in lower toxicity recorded than if tests are performed in synthetic media due to the complexation and lower availability of La in environmental media (Herrmann et al., 2016), as discussed in previous sections. For this reason, Herrmann et al. (2016) only included studies with measured concentrations of La in their review, as studies with nominal concentrations are expected to underestimate toxicity. More generally, metals that readily reprecipitate also tend to show indirect physical effects which can make laboratory-based ecotoxicity studies difficult to interpret. Known examples include Al and Fe. A greater reliance on field data is normally recommended in these cases (Commission, 2011; Hjorth et al., 2017).

4. Path forward to ensure the development and use of effective and safe La(III)-containing materials

The development and use of LM has received increasing interest in recent years as an effective material for removing phosphate from water, with hundreds of documented *in situ* applications of LMB worldwide. However, at the same time, as with other emerging materials or technologies, there are still areas of research that should be undertaken to help ensure LM is developed and used in a way that is both effective and responsible, by considering environmental, health, and socio-economic implications within innovation and management decisions.

More specifically, long-term studies that investigate La release from LM (such as LMB) in diverse environments are needed, particularly in environments with high NOM and low phosphate concentrations. This will not only help LM developers in terms of achieving high performance materials for phosphate removal, but it will also elucidate mechanisms for La bioavailability from the use of LM on a long-standing basis. Second, there is a need for long-term exposure studies (Waaen et al., 2017a) that investigate potential ecological effects of primary producers including macrophytes or algae as well as sediment-dwelling (benthic) micro- and macroorganisms (Spears et al., 2013). Third, more studies are needed on the potential for bioaccumulation of La and the

mechanism in which La may be incorporated into the tissues of aquatic organisms (Copetti et al., 2016), as well as the ability for trophic transfer (Waaen et al., 2017b). Fourth, site-specific environmental monitoring is needed to evaluate potential impacts of LMB applications on abiotic and biotic systems, including the monitoring of zooplankton, benthic plants, and sediment-dwelling organisms during and post-LM applications (Lürling and Tolman, 2010). After *in situ* applications, regular (e.g., monthly) monitoring in surface and bottom waters may be effective in determining TLa and Fla concentrations (Spears et al., 2013). Finally, material developers and water quality managers may benefit from incorporating a broad range of societal and ethical parameters, including stakeholder perceptions, in addition to technical performance, cost, and environmental and human health considerations within decision-making processes to select the best remediation strategy(ies) for phosphate removal in waters. Among other benefits, this will help ensure that diverse perspectives and needs are included in environmental management decisions while also adhering to best practices for responsible research and innovation (Stilgoe et al., 2013).

5. Conclusions

Through a review and evaluation of the literature, we find that the main benefits of LM for phosphate removal include its ability to strongly (and often irreversibly) bind to phosphate under diverse environmental conditions, including a wide pH range and in the presence of diverse constituents in environmental matrices. There also appears to be a very low risk of adverse effects for use in freshwater bodies for both ecological organisms as well as humans at the intended doses and under proper environmental conditions (i.e., in waters with pH above 7 and moderate-to-high bicarbonate alkalinity). Key parameters involved in LM performance include the maximum phosphate uptake capacity (q_m), which appears to be most directly related to La content, and reaction kinetics, which may be influenced by LM formulation and ambient environmental conditions (e.g., pH, co-existing ions, ligands, NOM). Our analysis has also identified that $\text{LaPO}_4(s)$ precipitation is the dominant mechanism of phosphate sequestration. However, due to the insoluble nature of $\text{LaPO}_4(s)$, recovery and reuse of phosphate from $\text{LaPO}_4(s)$ will pose significant challenges, and therefore LM may be more suitable for preventing P recycling in lakes and reservoirs.

The main factors involved in understanding impacts of LM on ecological systems include the potential for La release, bioavailability, bioaccumulation, and ecotoxicity of La. Increased La release can occur under some environmental conditions, including moderately acidic (i.e., $\text{pH} < 4.5\text{--}5.6$), highly saline conditions, and in the presence of organic matter. At the same time, released La will likely undergo hydrolysis, bind to organic matter, and combine with P to form rhabdophane, all of which reduce bioavailability of La in aquatic environments. In terms of bioaccumulation, La has been found to accumulate in some aquatic species, with high bioaccumulation factors in aquatic plants, mollusks, and fish organs. In addition, there has been a wide range of ecotoxicological studies conducted on La and LM across diverse test organisms and under differing testing conditions. The results of these various studies have produced divergent conclusions. Nonetheless, across most studies, LM use appears to present a very low risk of adverse effects in water above pH 7 and with moderate-to-high bicarbonate alkalinity.

Moving forward, we recommend additional research dedicated to understanding La release under diverse environmental conditions, long-term exposures on ecological organisms and particularly primary producers and benthic organisms, as well as potential for bioaccumulation and trophic transfer of La. Further, site-specific monitoring is needed to evaluate potential impacts of LMB applications on both biotic and abiotic systems. Overall, these findings may be helpful for material developers as well as water quality managers to ensure the overall sustainability of LM for phosphate removal in natural water and wastewater systems.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: We would like to avoid Dr. Irene M. C. Lo from Louisiana State University. Dr. Liping Fang from Hong Kong University of Science and Technology as reviewers, as we are studying the same topic.

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Disclaimer

Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the Danish Environmental Protection Agency.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2020.106115>.

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