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Environmental impacts of selected metal cations for phosphorus capture in natural waters: A synthesis

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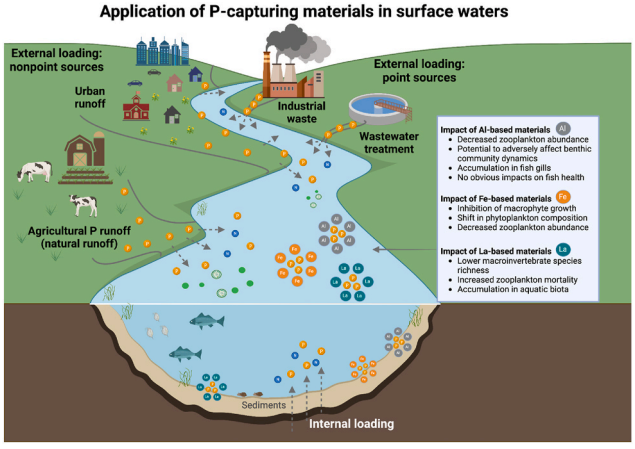
HIGHLIGHTS

- Al-, Fe-, Ca-, La-, and Mg-based P capturing materials show potential for harmful impacts on various macroalgae, zooplankton, macroinvertebrates, and fish taxa.
- Environmental impacts of these materials vary depending on key characteristics of the study design, such as the background conditions, dose(s), and experimental duration.
- The impacts, risks, and uncertainties should be carefully assessed when considering materials for eutrophication management.
- Little is known about environmental impacts of metal-based P capturing materials in freshwaters under eutrophic conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Cultural eutrophication from excessive human-related nutrient (phosphorus, P, and nitrogen, N) inputs is a major concern for water quality. Because P historically was regarded as the critical nutrient in controlling noxious algal/plant growth, P became the focus of "capturing" techniques, with emphasis on removal performance rather than environmental impacts. Here, we synthesize a literature review of known environmental effects linked to use of metal-cation-based P-capturing materials under eutrophic conditions in freshwaters. P-capturing materials with functional cations based on aluminum (Al), calcium (Ca), iron (Fe), lanthanum (La), and magnesium (Mg) were reviewed in terms of their ecotoxicity, persistence, and bioaccumulation-standard criteria used to evaluate environmental risks of chemical substances. We found very few published studies on environmental impacts of

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metal-cation-based P-capturing materials under eutrophic conditions. Available reports indicated that environmental effects vary depending on the selected material, dose, target organism(s), and experimental conditions. The Al-based materials had the potential to negatively impact various biota; several Fe-based materials caused various levels of toxicity in a limited group of aquatic organisms; La-based materials can bioaccumulate and some were linked to various harmful effects on biota; and Mg-based materials also adversely affected various organisms. The limited number of published studies underscores the need for further research to characterize the environmental impacts of these materials. Results can be used to guide future work and can assist resource managers in sustainable management strategies. Among various research needs, future assessments should assess the impacts of chronic exposures on sensitive species under realistic field conditions in eutrophic waters.

1. Introduction

Eutrophication is a natural aging process in aquatic ecosystems that has been greatly accelerated by excessive concentrations of nutrients, particularly phosphorus (P) and nitrogen (N), from human-related activities (Carpenter et al., 1998; Dodds and Smith, 2016; Kakade et al., 2021). The accelerated process caused by human-induced pollution, sometimes called cultural eutrophication (Burkholder and Glibert, 2024), is a major concern for water quality and ecosystem health worldwide (Goyette et al., 2018). Excessive P and N result in noxious overgrowth of the primary producers, algae (here, including cyanobacteria) and macrophytes (Wetzel, 2001; Burkholder and Glibert, 2024). Eutrophication can adversely affect aquatic ecosystems in an array of direct and indirect ways, including development of hypoxia/anoxia that can cause "dead zones" and kill aquatic life (Burkholder and Glibert, 2024). Harmful algal blooms, stimulated by the high P and N supplies and a shift in the N:P balance, can harm aquatic animal health via poor food quality and habitat degradation (e.g., hypoxia). In freshwaters, some strains (populations) of harmful algae (cyanobacteria, euglenophytes) produce toxins that can cause disease and death of fish and other aquatic life (Burkholder et al., 2018a and references therein). Humans commonly are adversely affected as well, through drinking water quality compromised by algal taste-and-odor substances and toxins, loss of aesthetics in recreational waters, and other impacts (Wurtsbaugh et al., 2019). Economic impacts from cultural eutrophication were conservatively estimated to be ~$2 billion per year in the U. S. as of 15 years ago (Dodds et al., 2009) and harmful freshwater algal blooms linked to nutrient pollution have since escalated in frequency and extent (Burkholder et al., 2018b; Kibuye et al., 2021).

Excess nutrient enrichment can be caused by both external loading from surface runoff, shallow groundwater inputs, atmospheric deposition, and internal loading of legacy nutrients that accumulate in sediments over time (D. Chen et al., 2018; Kibuye et al., 2021). Both nonpoint sources, such as urban and agricultural stormwater runoff (Paul and Meyer, 2001; Barcala et al., 2021), and point sources such as partially treated sewage from wastewater treatment plants (Thornton et al., 2013), are main drivers of eutrophication in lakes, reservoirs, and rivers (Smith, 2003). Aquatic ecosystems are extremely sensitive to small amounts of nutrient inputs because the dominant algal primary producers that mostly consist of very small cells with high surface area-to-volume ratio that are effectively immersed in a nutrient broth. Cropland farmers consider nutrients in kilograms of fertilizer; yet it requires a P concentration of only ~80–100 μg L^{-1} to push an aquatic ecosystem into eutrophic (highly productive, nutrient enriched) conditions and stimulate noxious algal blooms (Dodds et al., 1998; Wetzel, 2001). Runoff from agricultural fields after fertilizer or manure applications can add ~1000-fold higher P concentrations, although much of it is particulate (Jarvie et al., 2006; Burkholder et al., 2007). Most U.S. sewage treatment plants still have only secondary treatment without limits on P, leaving highly bioavailable P in the discharged effluent (Metcalf et al., 2013; USEPA, 2016). Even when external watershed and airshed external loading is decreased, partial recovery of eutrophic freshwaters can require a decade or more due to the underlying internal loading of P from sediments (Powers et al., 2016; M. Chen et al., 2018; Kibuye et al., 2021).

To date, numerous strategies have been developed and used to limit the amount of P that can leach or run off into aquatic systems, and to capture excessive P already present. Here, P capture refers to the ability to capture, sequester, and ultimately decrease or remove P from nutrient-rich waters, relying on mechanisms such as precipitation, flocculation, and adsorption (Langer et al., 2017). Various approaches have been developed to capture P from the water column in freshwaters, including physical (e.g., filtration, aeration, UV radiation), biological (e. g., microbial remediation), and chemical techniques (e.g., alum, copper sulfate, flocculation) (Teixeira and Rosa, 2006; Wang et al., 2012). These approaches help manage P to mitigate the negative effects of eutrophication. For instance, aeration facilitates the growth of aerobic bacteria, enabling them to absorb and eliminate P via biological processes. UV radiation can support the breakdown of organic matter that might bind with P. Copper sulfate is commonly used to kill cyanobacteria but lyses the cells (Jančula and Maršalek, 2011), which can enhance P recycling from cyanobacterial biomass (Lee et al., 2022). This study focuses on chemical P-capture techniques, which involve the use of metal salts as coagulants to precipitate P from the water column (Drewek et al., 2022; Zahed et al., 2022).

Several groups of chemical substances have been used for P capture, including polyaluminum chloride (PAC), aluminum sulfate, calcium nitrate, magnesium sulfate and chloride, ferric chloride, magnetic iron particles, and lanthanum-modified bentonite (LMB). The most commonly used groups of substances to date, aluminum- and iron-based, have been described as effective in controlling eutrophication in lake restoration based on a decrease in algal blooms (Lürling and Oosterhout, 2013; Gołdyn et al., 2014; Drewek et al., 2022). Yet, these substances also have caused adverse impacts on aquatic biota in some cases (Jančula et al., 2011; Gagnon et al., 2013; Álvarez-Manzaneda and De Vicente, 2017; Del Arco et al., 2021). In addition, La-based materials have demonstrated effectiveness at capturing P in waters under a range of conditions and have relatively low to moderate impacts on aquatic organisms (Van Oosterhout and Lurling, 2011; Yamada-Ferraz et al., 2015), although researchers have also noted that these effects vary across studies and testing conditions and more research is needed to fully understand the impacts of La materials (Zhi et al., 2020). Ca- and Mg-based materials have shown potential for P capture as well, although these substances can also affect microbial communities and aquatic ecosystems (Kleinhenz et al., 2019; Wang et al., 2019).

Overall, a growing body of literature indicates that while there is potential for metal-based materials to capture P from water to help remediate cultural eutrophication of freshwaters, a comprehensive understanding of these materials is needed to ensure their sustainable use in aquatic ecosystems. This study contributes a synthesis of the available peer-reviewed science on the potential environmental risks of a subset of P-capturing metal-based materials in natural waters under eutrophic conditions. Note that it does not aim to investigate potential risks of the selected metal-based materials used or proposed for use in drinking water or wastewater treatment systems or processes. Environmental risks are evaluated here using criteria of ecotoxicity, bioaccumulation, and persistence. Results from this work not only provide a timely review of the potential environmental risks of select metal-based P-capturing

materials, but can also help inform future research priorities and support decision-making on the development and use of these materials in future remediation efforts. This point is particularly important given that most published studies on P-capturing materials (including metal-based materials) have focused on documenting their performance and effectiveness at capturing P from water, while few studies exist on their environmental impacts.

To the best of the authors' knowledge, no published research has investigated the environmental risks and implications of the selected set of metal cations used for P absorption in eutrophic conditions. While other review articles have focused on the performance, mechanism(s) of absorption, recovery, and effectiveness of P-capturing materials in water and wastewater (e.g. Loganathan et al., 2014; Liu et al., 2018; Bacelo et al., 2020), we could not find published studies that have focused on their potential environmental impacts for in situ applications. In addition to filling a gap in the literature, this research is the first to document the scarcity of studies published on environmental impacts of the selected metal cations relevant to eutrophic conditions in surface freshwaters.

2. Methods

Five metal-based, P-capturing materials were selected for this synthesis based on their performance for coagulating phosphate in eutrophic conditions (Liu et al., 2022). These included materials with functional cations based on aluminum (Al), calcium (Ca), iron (Fe), lanthanum (La), and magnesium (Mg). Three criteria were used to investigate environmental risks of the selected P-capturing materials, including ecotoxicity, bioaccumulation, and persistence. These are standard criteria for assessing environmental risks of chemical substances (Zhong et al., 2022). Searches were conducted to identify peer-reviewed studies that investigated environmental impacts of the selected P-capturing materials, if possible, under eutrophic conditions. Retrieved studies addressed at least one of the two criteria-either ecotoxicity or bioaccumulation. However, most of the studies selected did not cover bioaccumulation; and there was no study found on persistence. Common article retrieval databases were accessed. Keywords included eutrophication, phosphorus capturing materials/inactivation agents, ecotoxicity of phosphorus capturing materials, bioaccumulation of phosphorus capturing materials, persistence of phosphorus capturing materials, metal-based salts, oxides, hydroxides used for phosphorus capturing, etc. Studies that predominantly focused on the overall efficacy of capturing P using the selected metal-cation-based materials, with little or no assessment of environmental impacts, were excluded.

More than 100 published studies were initially identified and screened. Of these, 43 studies were assessed as relevant for this synthesis. These studies specifically investigated ecotoxicity, bioaccumulation of the selected P-capturing materials or included other relevant data for this review. The remaining studies were used to obtain a broader understanding of cultural eutrophication, its impacts on aquatic systems, and the general importance of capturing P in remediation efforts. Information from the 43 key studies were reviewed and compiled into a spreadsheet, including the P-capturing material and dose(s); type of experiment (laboratory, outdoor mesocosm, in situ mesocosm, or field (e.g. in a lake, pond, or reservoir); exposure duration and biota assessed; results on ecotoxicity, bioaccumulation, and persistence of P-capturing materials; and notes on other relevant findings.

3. Review of environmental impacts of metal-based P-capturing materials

Excessive nutrients in water can have multiple negative consequences, including detrimental effects on the productivity of commercial fisheries, decreased recreational value of waterbodies, increased costs for drinking water treatment, and potential risks to human health (Shortle et al., 2020). The environmental impacts of metal-cation-based P-capturing materials in surface waters under eutrophic conditions are complex (Fig. 1). For example, these materials can raise metal ion concentrations that can concentrate or bioaccumulate in food webs and pose risks to human health (Su et al., 2016). In the absence of a proper treatment system, such chemical methods can cause secondary pollution and residues, making them suitable only for emergencies (Zhang et al., 2020). Alkaline conditions can decrease the efficacy of metal-based P-capturing substances through the presence of dissolved organics and competing anions (Chen et al., 2014). These substances also can increase sediment P release into the overlying water depending on the environmental conditions such as the dissolved oxygen concentration (Chen et al., 2014). Other potential risks include the release of toxic metal ions and sudden pH changes, influenced by water hardness and organic content. Addressing these complex environmental impacts and controlling influences for effective management of eutrophication in natural waters requires comprehensive evaluation, adequate monitoring of environmental conditions before and after in situ use, and implementation of appropriate measures to mitigate potential adverse effects.

3.1. Al-based materials

A total of 14 studies investigated environmental impacts of Al-based P-capturing materials (Table 1). Many of them focused on acute aquatic toxicity; and the studies were conducted in lab bench scale for shorter duration of time compared to the lifespan of the majority of the organisms. Across the 14 studies, the range of materials used included polyaluminum chloride (PAC), aluminate, aluminum sulfate, aluminum-amended zeolite, and dried alum sludge. The studies additionally varied substantially in the type of experiment (lab bench, mesocosm, etc.),

the duration, material concentrations and application rates. Target organisms spanned trophic levels from decomposers (bacteria) to primary producers (algae and macrophytes = higher plants with vascular tissue), to multiple trophic levels of consumers (microfauna, macroinvertebrates, and fish) with, however, sparse information on each. The studies also considered very different endpoints: weight or body mass, length, somatic index, survival rate, feeding rate, tissue or cell damage, immobilization, mortality, and (rarely) metal accumulation.

The studies that reported ecotoxicity effects of Al-based materials for P capture described a range of impacts. Dawah et al. (2015) found that application of 10 mg/L alum in eutrophic waters suppressed noxious cyanobacterial blooms without apparent water quality degradation, based on physical/chemical characteristics such as temperature, dissolved oxygen, nitrate, and total ammonia. However, the same study showed that prolonged use (14 d) of alum in fishponds led to a decline in zooplankton and other beneficial aquatic life, suggesting potential implications across trophic levels. Other authors reported that alum + sodium aluminate (applied as a buffer) affected N cycling by increasing the nitrogen oxide (N_2O) concentration in surface water, indicating that benthic ecosystem dynamics may be affected by rising levels of Al and sulfate (Nogaro et al., 2013). Gagnon et al. (2013) reported that residual alum leachates exceeded the ecological risk threshold of 0.03 mg/L Al, indicating potential for chronic/sublethal toxicity effects in fish. Toxicity levels did not, however, exceed the threshold for lethal effects. In contrast, Duranceau et al. (2016) observed that application of dried alum sludge did not cause apparent immediate toxicity to bacteria.

According to Landman and Ling (2011), application of Al-modified zeolite (Z2G1) in a temperate lake did not appear to affect fish health in general observations over a 3-month duration, indicating that the Al in Z2G1 was not readily accessible. Yet, exposure to Z2G1 altered the hematology, blood and tissue chemistry, and particular tissue histology of rainbow trout (*Oncorhynchus mykiss*), the common bully (*Gobiomorphus cotidianus*), and the crayfish (*Paranephrops planifrons*). Moreover, an unexplained osmoregulatory stress not attributed to Z2G1 Al exposure was documented in the trout, as evidenced by elevated ion concentrations in blood plasma. Other work indicated no apparent influence of high alum doses (3.44 g/m^2) on growth and survival of fish, crayfish,

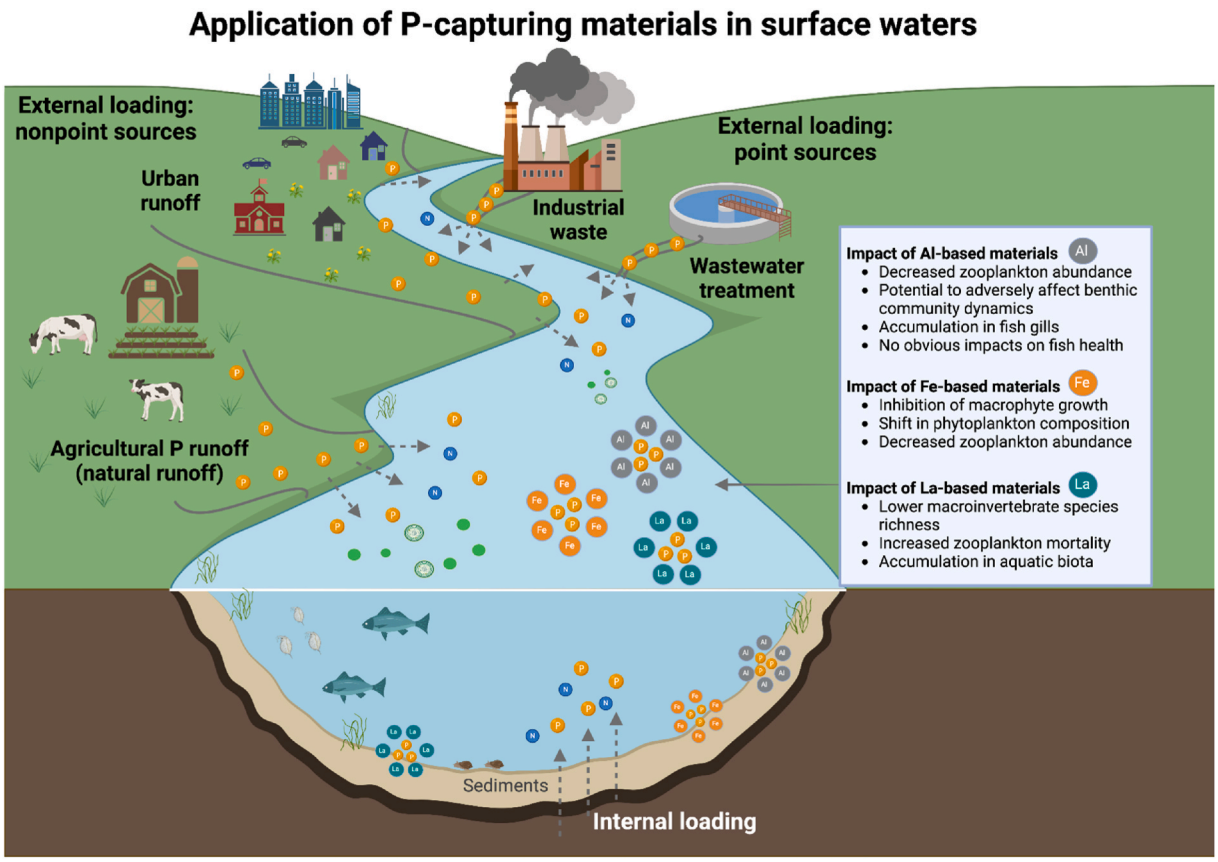

Fig. 1. Environmental impacts of metal-based P-capturing materials in surface water. The figure shows P sources, both point and nonpoint, as well as introduction of P through external loading and internal loading from the bottom sediments. Applied P-capturing materials (such as Al-, Fe-, and La-based materials) inactivate P to varying extent and also have impacts on the surrounding environment. These materials as well as others (e.g., Ca- and Mg-based materials) need substantially more research to understand their impacts on freshwater ecosystems. Visual created with BioRender.com.

and mussels, but sublethal effects on clams that could make them less active and thus more susceptible to predation (Clearwater et al., 2014).

Fish gills accumulated Al in a species-specific manner after Al treatment when aluminate was applied. In most cases, the amount of Al in the gills was not high enough to cause fish death (perch, roach, beam) (Wauer and Teien, 2010). There was a strong correlation between Al bioavailability in the water column and its toxicity. For example, the amount of Al accumulated in freshwater snails appeared to be inversely proportional to the Al lability (Walton et al., 2009). Pacioglu et al. (2016) reported that aspen leaves (*Populus tremula*) and gammarid amphipods (which use the leaves as a food source) from a eutrophic hardwater lake had lower C/N and C/P ratios than control leaves and amphipods without Al exposure, suggesting that the stoichiometric balance between food and consumers was altered by exposure to PAC. Pacioglu et al. (2016) also observed direct toxic effects on invertebrates. In other work, daphnids exposed to PAC were immobilized, particularly when the PAC Al concentration was 9 mg/L or higher (Jančula et al., 2011). Steinman and Ogdahl (2008) reported lower macroinvertebrate abundance in a eutrophic north temperate lake following 8 months of PAC application. Other work has shown that Al addition can temporarily inhibit *Daphnia* grazing (Reitzel et al., 2003).

Charophycean macroalgae known as stoneworts (e.g., *Chara hispida*) are considered especially vulnerable to adverse effects of Al. Al has been shown to enter and accumulate in their primitive "plant body" or thallus. Bioaccumulation in *C. hispida* has been inhibited at $> \sim 2.0$ mg/g Al dw, indicating that this organism is a poor Al accumulator. Nevertheless, as concentrations of Al coagulants increase, a shift in the chlorophyll *a*/chlorophyll *b* ratio has been observed, which in turn slows thallus regeneration in damaged areas (Rybak, 2016). The severity of thallus damage (e.g., chlorosis, necrosis, flaking of cortical cells, thallus "softening") has been directly related to the coagulant concentration (Rybak et al., 2017b).

Thus, overall, Al-based P-capturing materials have been shown to depress cyanobacterial blooms. These materials were used as solids or granulates, dissolved solutions, flocs, or slurries at doses ranging from 2 to 350 g/m^2, 0.5–1000 mg/L, 50–200 ml/m^3. The EC_{50} values for Al^{3+} vary from 9.89 to 54.29 mg/L, depending on the water conductivity (Jančula et al., 2011). Since Al solubility, bioavailability, and toxicity are controlled by the chemical form, the chemical speciation of Al in drinking water is critically significant (Krupińska, 2020). Adding Al salts to water can increase the concentration of low-molecular-weight Al species, which are more readily absorbed by humans and exhibit chemical reactivity (Krupińska, 2020).

Furthermore, the longevity of Al treatment is closely related to the amount and frequency of Al doses, the Osgood index (a morphological index), the watershed-to-waterbody surface area ratio (which, in turn, is related to hydraulic residence time), the sediment P content-to-Al dose ratios, and the abundance of benthic-feeding fish (Huser et al., 2016). Other morphometric features can be important; for example, Huser et al. (2016) reported that shallow, polymictic urban lakes had a mean longevity of improved water quality (decreased TP and suspended microalgal biomass as chlorophyll *a*, and increased water transparency) for 5.7 years post-Al treatment, while in deeper, stratified lakes water quality improvements lasted up to 21 years. However, depending on the dose used, these materials have also been shown to adversely affect beneficial aquatic life across trophic levels, with effects ranging from depressed growth to death of some biota.

Table 1
Overview of published studies investigating environmental impacts of Al-based materials for P capture.

P-capturing material	Dose, form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Bioaccumulation	Other findings	Reference
Polyaluminum chloride (PAC)	Low: 6.1 g Al/m^3 Medium: 12.2 g Al/m^3 High: 24.5 g Al/m^3; solid	Mesocosms (in situ)	3 d	Macroalga *Chara hispida* (charophycean)[a]	Damage of cells, tissues	Chlorosis, softening of thallus.	Poor accumulator of Al in the macroalgal thallus.	The authors suggested that the dose should not exceed 5.0 g Al/m^3.	Rybak et al. (2017b)
PAC	2 and 20 g Al flakes per m^2; solution	Laboratory	18 d	Amphipod *Gammarus pulex*	Survival, body mass, feeding rate	No apparent effect.	Al accumulated in body tissue.	A high dose of Al flakes was added, but below lethal levels.	Pacioglu et al. (2016)
PAC	50 ml/m^3, 100 ml/m^3 and 200 ml/m^3; solution	Mesocosms (in situ)	2 months	Macroalga *Chara hispida*	Photosynthetic pigments	Degradation of branchlet and cortex cells by chlorosis and necrosis.	–	Negative impact on general health.	Rybak (2016)
Dried alum sludge	Maximum concentrations of dilution, 45% or 81.9% by volume; solution	Laboratory	15 min for EC_{50}	Bacteria (*Vibrio fischeri*)	Bacterial bioluminescence inhibition	No significant acute toxic effect.	–	Dried alum sludge caused little or no apparent toxicity.	Duranceau et al. (2016)
Aluminum Sulfate (Alum)	10 mg/L; solution	Field	14 d	Fish *Oreochromis niloticus*	Fish growth (body weight)	No negative effect on fish growth.	–	Application of alum in fish ponds suppressed zooplankton (Cladocera, Copepoda, Rotifera, Ostracoda), which could affect natural communities.	Dawah et al. (2015)
Aluminate	137 g Al/m^2; solution	Field (in lake)	5 years	Fish (*Perca fluviatilis*, *Rutilus rutilus, Abramis brama, Hypophthalmichthys molitrix*)	Accumulation in gills	–	Al (100 μg Al/g dw) accumulated in perch gills, but apparently not in the gills of roach, bream, and silver carp.	High Al concentration in gills.	Wauer and Teien (2010)
Alum	57–344 g alum/m^2; solid	Laboratory	2 months	Benthic macroinvertebrates - crayfish, mussels, common bullies, fingernail clams	Respiration measurements, weight, length	The high alum application rate decreased clam survival (there was 23% survival).	No significant Al accumulation as water-column Al concentrations significantly decreased.	No significant effect on growth or survival of mussels, fish, and crayfish.	Clearwater et al. (2014)
Alum	38, 47, and 58 g/m^2; solid	Field	2 months	–	–	–	–	Potential to alter benthic community dynamics.	Nogaro et al. (2013)
Dried alum residual	24 mg/L; solid	Laboratory	30 d	Fish (*Salvelinus fontinalis*, *Oncorhynchus mykiss)*	Percent mortality, changes in typical behavior	Exceeded the ecological risk threshold (0.03 mg/L) for chronic and sublethal toxicity effects, but did not exceed the threshold for acute toxicity.	–	Residual alum has the potential to cause chronic/sublethal toxicity threat to sensitive fish species.	Gagnon et al. (2013)
Aluminum amended zeolite (Z2G1)	350 g/m^2; solid	Field (in lake)	3 months	Fish (*Oncorhynchus mykiss*, *Gobiomorphus cotidianus*); crayfish (*Paranephrops planifrons*)	Body weight, length, somatic index, hematological variables	Increased blood plasma ion concentrations in *O. mykiss*.	Al from Z2G1 was not readily bioavailable.	No obvious negative impacts on fish health.	Landman and Ling (2011)
PAC	1–1000 mg/L Al^{3+}; solid	Laboratory	24 h, 48 h	Cladocerans (*Daphnia magna*)	Immobilization	EC_{50} values 9.89–54.29 mg/L Al^{3+}; toxicity mostly depended on treated water conductivity.	–	The authors hypothesized that Al > 3–20 mg/L (typically used for water treatment in reservoirs) may be harmful to some zooplankton, such as daphnids when Al^{+3} is ≥ 9 mg/L	Jančula et al. (2011)
Aluminum nitrate	500 μg/L; solid	Laboratory	30 d	Freshwater snails (*Lymnaea stagnalis*)	Metal accumulation in snail tissues	Lability of Al^{+3} in the water column was a good predictor	Exposure to Al + P resulted in more Al	Metal accumulation in the same organism might vary to	Walton et al. (2009)

(*continued on next page*)

Table 1 (*continued*)

P-capturing material	Dose, form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Bioaccumulation	Other findings	Reference
						of toxicity. The degree of Al lability and its toxicity appeared to be inversely related to the amount of Al accumulated.	accumulation in snails than Al exposure alone.	different degrees without clear correlation to the level of behavioral effect.	
Alum	80 g Al/m^2; liquid slurry	Field (in lake)	8 months	Benthic macroinvertebrates -oligochaete worms, chironomid midge larvae, phantom midge *Chaoborus*, and biting midge larvae (ceratopogonid nematomorphs)	Abundance (densities - organisms/m^2)	Reductions in overall macroinvertebrate abundance, and in some populations (*Chaoborus* and oligochaetes).	–	Lake pH from 7.5 to 8.5 was high enough to minimize Al toxicity.	Steinman and Ogdahl (2008)
PAC/Al hydroxides	26 m^3 PAC Al: P mobile (molar ratios of 4:1 and 8:1); floc	Mesocosms (in situ)	39 d	Zooplankton - cyclopoid copepods, cyclopoidans, *Bosmina* spp. and *Daphnia* spp.	Abundance	Negative effect on abundance of *Daphnia* spp. while *Bosmina* spp. and cyclopoidans became more abundant.	–	*Daphnia* abundance decreased after Al addition, with little or no change in abundance of the other zooplankton. In Al-treated mesocosms, cyclopoid copepods and *Bosmina* spp. dominated, whereas *Daphnia* spp. dominated in controls.	Reitzel et al. (2003)

EC_{50} means the concentration of a substance at which 50% of the test organisms exhibit a biological response after exposure to a certain dose.
[a] Algal taxonomy here and throughout followed Graham et al. (2016) and references therein; dw = dry weight.

3.2. Ca-based materials

Various Ca-based P-capturing materials have long been used in attempts to mitigate cultural eutrophication, such as calcium oxides, hydroxides, and calcium salts (Cooke et al., 1993). However, the available peer-reviewed science on environmental impacts of Ca-based P-capturing materials under eutrophic conditions consisted of only three publications that describe acute toxicity laboratory bench, field mesocosm, or field experiments (Table 2). The experiments were conducted from 10 to 145 d and assessed impacts from various forms and doses of Ca-based materials including salts, oxides, and hydroxides. The focus spanned from the sediment bacterial consortium to plankton (phytoplankton assemblage response; zooplankton community structure, abundance, and mortality). One study included information on one benthic macroinvertebrate species.

Lake application of calcium oxide sprinkle effectively controlled water-column P (and N) concentrations, apparently by altering the availability of dissolved oxygen and the sediment microbial consortium (Wang et al., 2019) (Table 2). In field mesocosms, calcium hydroxide significantly decreased phytoplankton production (biovolume) and promoted a shift in the zooplankton community from smaller rotifers to larger microcrustaceans (cladocerans, copepods) (Frau et al., 2019). The third study, a lab bench experiment, assessed acute toxicity of calcium nitrate to zooplankter *Ceriodaphnia silvestrii* and benthic macroinvertebrate *Chironomus xanthus* (Yamada et al., 2012). High concentrations of nitrate and nitrite in interstitial sediment water (up to 2300 mg/L and 260 mg/L, respectively) caused mortality of both organisms, expected since the concentrations of the N forms are known to be extreme and highly toxic (Camargo and Alonso, 2006) and indicating that calcium nitrate should not be used as a P-capturing material.

Ca-based P-capturing materials were used in both solid and solution at doses ranging from 125 to 200 g/m^2. When calcium nitrate was applied, the concentration of nitrate and nitrite in the sediment interstitial water reached as high as 2.3 g/L and 0.26 g/L, respectively, and was the principal cause of zooplankton and benthic macroinvertebrate mortality (Yamada et al., 2012). Overall, these sparse findings suggest that although Ca-based P-capturing materials may perform well in P capture, they can adversely influence beneficial biota in eutrophic freshwaters.

3.3. Fe-based materials

A total of 9 peer-reviewed studies identified that investigated the environmental impacts of Fe-materials under eutrophic conditions. These studies all focused on acute aquatic toxicity; none of them investigated bioaccumulation or chronic effects. Most were conducted on a laboratory scale and investigated a range of materials including Fe salts, magnetic particles (MPs), and natural clay-modified salts. The experimental duration ranged from 24 h to 10 months, with target organisms including algae, microorganisms, and macroinvertebrates (Álvarez-Manzaneda and De Vicente, 2017; Álvarez-Manzaneda et al., 2019; Del Arco et al., 2021; Ren et al., 2021).

The studies described various outcomes, with impacts spanning from organism to community scales (Table 3). For example, some authors reported a decrease in cyanobacterial dominance and decreased bloom toxicity based on microcystin concentrations, even at low doses of Fe (Orihel et al., 2016). Phytoplankton assemblage composition shifted across a range of doses from 2 to 225 g/m^2 Fe (Orihel et al., 2016). In other work, Fe-based P-capturing material such as red soil-based flocculant resulted in a significant decrease in zooplankton, particularly rotifers (Peng et al., 2019). In contrast, no discernible change in sediment microbiota was observed after adding Fe-700-BC (Ren et al., 2021).

Álvarez-Manzaneda and De Vicente (2017) assessed the potential for short-term (24-h), acute lethal and sublethal toxicity of iron magnetic particles (MPs) on the rotifer *B. calyciflorus*. Iron MPs negligibly affected

Table 2
Overview of published studies investigating environmental impacts of Ca-based materials for P capture.

P- capturing material	Dose; form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Other findings	Reference
Calcium oxide	75 kg/ 600 m^2; solid	Field (in lake)	2 months	Bacteria	Abundance, consortium structure	Species richness of bacteria strains was affected; for example, the bottom sediment in the test zone had higher relative abundances of *Acidobacteria* and *Planctomycetes*, at 2.39% and 2.08% of the total bacterial abundance, respectively, compared to the control zone where the corresponding values were 2.08% and 1.11%, respectively, of the total abundance.	When sediment pH is acidic, organic materials formed by sediment decomposition interact more easily with metal ions than phosphate, which prevents insoluble phosphate precipitation.	Wang et al. (2019)
Calcium hydroxide	200 g/ m^2; solid	Mesocosms in situ	10 d	Phytoplankton (58 species), zooplankton (30 species)	Phytoplankton assemblage response, zooplankton community structure	Total phytoplankton biovolume decreased.	Promotion of herbivorous zooplankton development.	Frau et al. (2019)
Calcium nitrate	141 g N/ m^2; solution	Laboratory	145 d	Zooplankter *Ceriodaphnia silvestrii*; benthic macroinvertebrate *Chironomus xanthus*	Mortality	High nitrate and nitrite in sediment pore water caused mortality.	Mortality of *Ceriodaphnia silvestrii* and *Chironomus xanthus* was primarily attributed to elevated of nitrate and nitrite in the sediment interstitial water, which reached concentrations as high as 2300 mg/L and 260 mg/L, respectively.	Yamada et al. (2012)

*There were no bioaccumulation data in the three studies.

the rotifer egg bank and the LC_{50} (1.63 g MP/L) indicated minimal mortality for adults (Table 3). The phytoplankter *Chlorella* sp. also appeared to be minimally affected by iron MPs. Over a longer duration (70 d), iron MPs did not affect total abundance of

zooplankton (rotifers, copepods), species richness, or metabolism (Álvarez-Manzaneda et al., 2019). In contrast, chronic toxicity studies of MPs with zooplankter *D. magna* revealed that parthenogenetic reproduction was significantly affected by dissolved Fe, whereas there was no significant effect on larval or pupal mortality or adult emergence for benthic *Chironomus* sp. (Álvarez-Manzaneda et al., 2017; Fjällborg et al., 2006 evaluated the acute toxicity of $FeCl_3$ on *Daphnia magna* in a 48-h laboratory experiment. The EC_{50} value for immobilization was 8800 μg/L. In a lake restoration effort, exposure of the macroalgal charophycean *Chara hispida* to iron sulfate (21.6 g/m^3) decreased growth and oospore production (Rybak et al., 2017a,b).

Fe-based P-capturing materials were used in solid and solution forms, with doses ranging from 2 to 225 g/m^2 and from 0.312 to 5000 mg/L. The EC_{50} values for Fe^{3+} were 8.8 mg/L, with a tendency of decreasing toxicity with increasing pH from 6 to 9 (Fjällborg et al., 2006). A second study reported an EC_{50} value for Fe^{+3} of 2760 mg/L (Álvarez-Manzaneda et al., 2019). Treatment efficacy was primarily influenced by redox conditions. When redox conditions were low, Fe-bound P was readily released due to the Fe reduction dissolution effect (Kleeberg et al., 2013). According to Kleeberg et al. (2012, 2013), the release of Fe and P from sediments caused their co-precipitation in the overlying lake water, helping to promote effective Fe treatment control. Organic matter and soluble sulfides were described as potentially confounding factors that can impair the efficiency of adsorption sites on Fe compounds by competing with P for these sites (Kleeberg et al., 2012, 2013).

In summary, application of Fe-based P-capturing materials has generated dose-dependent responses in various aquatic organisms. Negative impacts largely depended on the dose and the type of experiment. Most available studies were carried out at a laboratory scale. The environmental persistence of Fe-based P-capturing materials, potential for bioaccumulation, and other impacts from long-term exposure remain unknown.

3.4. La-based materials

Lanthanum-modified bentonite (LMB) is a P-capturing material that has been increasingly used in efforts to mitigate eutrophication. LMB is a modified bentonite clay containing 5% (by weight) La incorporated into the clay matrix. It is produced by a process of ion exchange wherein lanthanum ions are loaded into clay material. La-embedded P is absorbed by the formation of rhabdophane, then transformed into monazite ($LaPO_4$) (Dithmer et al., 2016). LMB can reduce P availability in both the water column and sediments, potentially mitigating eutrophication. When tested in a water column, LMB use reduced 80% of the soluble reactive phosphorus (SRP) present (Yamada-Ferraz et al., 2015). Also, application of LMB into sediments resulted in a significant decrease in the levels of bioavailable sediment P (Lin et al., 2020).

All 13 peer-reviewed studies that investigated potential environmental impacts of La-based materials under eutrophic conditions focused on acute toxicity from various doses. For example, (Lürling and Tolman, 2010) used a range of doses in laboratory experiments, whereas a single dose was applied in the other selected LMB studies. In general, invertebrates, benthic organisms, macrophytes, and algae were the organisms tested, usually with several P-capturing substances. The test organisms were tracked for growth, mortality, and bioaccumulation of La, survival, and response rate. Species diversity, evenness, and abundance, as well as community structure, were also evaluated where data permitted.

The environmental impacts of La-based P-capturing materials are summarized in Table 4. Across the studies focused on LMB, biota responded in diverse ways (Table 4). For example, LMB inhibited the growth of the exotic invasive macrophyte *Myriophyllum spicatum* and led to a decrease in aboveground biomass while their belowground biomass was significantly larger (Lin et al., 2021). As a result, the root-to-shoot ratio of *M. spicatum* in the LMB treatment was much higher than in

Table 3
Overview of published studies investigating environmental impacts of Fe-based materials for P capture.

P-capturing material	Dose; form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Other findings	Reference
Magnetic particles (MPs) - carbonyl Fe particles (97.5% Fe, 0.9% C, 0.5% O and 0.9% N)	1.4 g MP/L; aqueous dispersion	Microcosms (outdoor)	70 d	64 phytoplankton species -Cyanobacteria, Heterokontophyta, Chlorophyta, Cryptophyta	Species composition of phytoplankton assemblage	MPs apparently did not cause adverse species-specific effects.	No strong evidence to infer that MPs caused an effect on the phytoplankton assemblage.	Del Arco et al. (2021)
Fe-700-BC (Nano-zero-valent iron modified reeds prepared at 700 °C)	23 mg/L; solution	Laboratory	40 d	Sediment microbial consortium, using sequence data (operational taxonomic units based on the 16S rRNA gene)	Abundance	No significant effect on diversity or species richness.	No significant change in the relative abundance of most microorganisms.	Ren et al. (2021)
Red soil flocculant (RSBF): Red soil, chitosan and $FeCl_3$	15, 25, 35 mg $FeCl_3$/L; solid	Mesocosms (in situ)	2 months	Zooplankton - rotifers, cladocerans, copepods	Abundance	Rotifer populations rapidly decreased.	Decreased abundance of zooplankton, especially rotifers; copepods and cladocerans recovered quickly so that species composition was unchanged.	Peng et al. (2019)
MPs	1.4 g MP/L; aqueous dispersion	Microcosms (outdoor)	70 d	Zooplankton - rotifers, copepods	Zooplankton community structure	The experimental conditions (temperature, pH, O_2 concentrations) were within the tolerance ranges of these zooplankton.	Did not promote significant direct or indirect effects on zooplankton composition or structure.	Á lvarez-Manzaneda et al. (2019)
MPs	0.01–5 g MP/L; solution	Laboratory	30 d	Zooplankter *Daphnia magna*, benthic macroinvertebrate *Chironomus* sp.	Immobilization, offspring production, mortality of larvae and pupae, and adult emergence	EC_{50} for immobilization was notably lower in *Chironomus* sp. than in *D. magna*, suggesting that the benthic species was more sensitive than the plankter.	No apparent toxic effect on this population of *D. magna* or this population of *Chironomus* sp.)	Á lvarez-Manzaneda et al. (2017)
MPs	0.01–5 g/L MPs; solution	Laboratory	24 h	Phytoplankter *Chlorella* sp. (chlorophyte), zooplankter *Brachionus calyciflorus* (rotifer)	Growth, mortality	The EC_{50} for *Chlorella* sp. was 0.15 g/L. The LC_{50} for *B. calyciflorus* was 1.63 g/L.	The authors inappropriately extrapolated to whole-lake applications and asserted that addition of MPs in a whole-lake application may cause minor lethal and sublethal effects on all populations of both the phytoplankter and the rotifer.	Á lvarez-Manzaneda and De Vicente (2017)
Iron sulfate	Low, Medium, High 5.4, 10.8 and 21.6 g/m^3, respectively; solid	Laboratory	30 d	Macroalga *Chara hispida* (charophycean)	Growth and production of oospores	*C. hispida* grew more slowly and produced fewer oospores.	Growth and reproduction efficiency were inhibited. The authors hypothesized that if multiple doses are added, iron sulfate impact would be cumulative, likely promoting *C. hispida* decline.	(Rybak, et al., 2017a,b)

(*continued on next page*)

Table 3 (*continued*)

P-capturing material	Dose; form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Other findings	Reference
Iron	2–225 g/m^2; solid	Mesocosms (in situ)	10 months	Phytoplankton and benthic microalgae - Cyanobacteria, Heterokontophyta (diatoms), Dinophyta, Euglenophyta, and Chlorophyta	Biomass	Phytoplankton and periphyton biomass decreased, and phytoplankton composition shifted.	From these data and other work, the authors suggested that Fe is an important influence on the trophic state of freshwaters.	Orihel et al. (2016)
Ferric chloride	312-20,000 μg/L; solution	Laboratory	24, 48, 96 h	Zooplankter *Daphnia magna*	Immobility	EC_{50}: 8800 μg/L.	The toxicity of Fe to *D. magna* was reduced by pH increase from 6 to 9.	Fjällborg et al. (2006)

the control group, suggesting that an increase in root biomass may help inhibit sediment resuspension and P release (Lin et al., 2021). Similarly, LMB adversely affected growth of *Vallisneria denseserrulata*, especially clonal shoot growth, resulting in a 35% decrease in biomass and a 27% decrease in plant density, whereas the effect on individual weight was minimal (Zhang et al., 2021). In contrast, in other work LMB did not result in apparent adverse impacts on macroinvertebrate communities (Yin et al., 2018).

In bioassays with zooplankter *Ceriodaphnia silvestrii*, LMB treatment resulted in significant mortality throughout the water column, particularly at intermediate depths (65% mortality) and at the sediment-water interface (85% mortality) (Yamada-Ferraz et al., 2015). Likewise, "Flock.

& Lock" (LMB + $FeCL_3$) application to a north temperate lake eliminated a population of zooplankter *Daphnia galeata*. This population may have disappeared due to Flock physical effects, clay-induced grazing inhibition, very low food quantities, and/or lack of refuge from predation (Van Oosterhout and Lurling, 2011). Similar effect of "Flock & Lock" application was observed for macroinvertebrates (snails; oligochaetes; water lice and other malacostracans; arachnids; and larvae of biting midge, dipteran flies, stoneflies, and mayflies) in a nearby lake, all of which disappeared for 1–2 months (Waajen et al., 2017). In another study, LMB caused increased immobilization of the zooplankter *Daphnia magna* as concentration and contact time increased; the 48-h EC_{50} value for *D. magna* immobilization was 2.14 g/L (Álvarez-Manzaneda et al., 2019a). Nevertheless, the authors speculated that accumulation or long-term impacts of P adsorbents in the pelagic phase were unlikely. (Lürling and Tolman, 2010) exposed juvenile *D. magna* to up to 5000 mg/L LMB and reported EC_{50} values for growth rates based on the weight and length at 871 and 1557 mg/L, respectively. There was a negative correlation between exposure to La and animal growth, maturity, and reproduction.

Waajen et al. (2017) conducted a five-year field (within-lake) experiment in control vs. LMB-treated areas to assess whether the submersed macrophyte *Elodea nuttallii*, chironomid larvae, and several species of fish accumulated La. Fish tissues bioaccumulated La at high concentrations for up to five years after LMB application, suggesting that the fish continued to take up La from food resources and the surrounding environment. Other work showed an increase in La concentrations in the ovaries, hepatopancreas, and abdominal muscles of crayfish after exposure to LMB, indicating that La is bioavailable and is taken up by crayfish (Van Oosterhout et al., 2014). In another investigation, Lürling and Oosterhout (2013) examined how LMB affected population growth of the rotifer *Brachionus calyciflorus*. Their data suggested that LMB depressed population growth of rotifers at $\geq$ 0.2 g/L and may adversely affect planktonic grazers, especially cladocerans. This finding was attributed to the fact that cladocerans do not have a specific diet and consume both food (algal) particles and clay particles. Other authors have suggested that direct effects on chironomid larvae may be unlikely, but the larvae could act as vectors for LMB or La to other organisms (Van Oosterhout et al., 2020). Su et al. (2016) noted that La and Al concentrations were negligible after phosphorus-inactive clay treatment in a laboratory bench study, which superficially might suggest the possibility of minimal ecological risk. However, the authors pointed out that additives used to deactivate P could increase metal ion concentrations in aquatic ecosystems, which could eventually lead to the accumulation of these ions in food webs and subsequent risks to human health.

In summary, LMB has been used in solid, solution, slurry, spray form with doses ranging from 0.005 to 5 g/L and 26.91–584 g/m^2. The toxicity values varied depending on the context of the studies. For instance, the EC_{50} values were found to be 871 mg/L, 1557 mg/L, for concentrations up to 5000 mg/L of LMB (Lürling and Tolman, 2010) and 2.14 g/L (Álvarez-Manzaneda et al., 2019a). The available studies collectively support the premise that application of LMB causes discernible short-term toxic impacts on aquatic organisms, and that La also has the potential to bioaccumulate—which could translate into long-term impacts to exposed biota and the organisms that consume them or their remains.

3.5. Mg-based materials

Only four peer-reviewed, published studies were identified that investigated environmental impacts of Mg-based materials under eutrophic conditions (Table 5). They focused on acute aquatic toxicity (similar to the other materials) and were conducted in both field (mesocosms) and laboratory experiments. None of the studies investigated bioaccumulation. The experimental duration ranged from 24 h to 7 weeks, with different doses applied as Mg-based salts. The studies focused on phytoplankton (biomass, assemblage composition) growth rates, community metabolism, and macroinvertebrate drift.

Available information is limited on the underlying mechanisms of Mg toxicity (Hogan et al., 2013). Mooney et al. (2020) estimated Mg concentrations in an in-situ stream mesocosm experiment for EC_{01} values $<$ 3 mg/L, including microalgae cryptomonads, diatoms, dinoflagellates, and chlorophytes or green algae. Overall, when Mg concentrations increased, there was a loss of zooplankton functional feeding groups (copepods, cladocerans) (Table 5). Other work described an increase in Mg toxicity with exposure duration among biota ranging from phytoplankton to fish, but the magnitude of the toxicity increase varied considerably among taxa (Hogan et al., 2013). Various macroinvertebrate taxa exhibited an array of responses such as decreased biomass, decreased abundance, and shifts in community composition. Freshwater mussels *Velesunio angasi* and *Velesunio* sp. were moderately sensitive to Mg in comparison to other tropical species (Kleinhenz et al., 2019). Moreover, natural benthic communities from a low-conductivity stream were especially sensitive to aqueous Mg (Clements and Kotalik, 2016).

Mg-based P-capturing materials were applied as solutions with doses ranging from 2.5 to 12000 mg/L. Multiple studies have reported different toxicity levels on various organisms, such as EC_{01} ($<$3 mg/L)

Table 4
Overview of published studies investigating environmental impacts of La-based materials for P capture.

P-capturing material	Dose; Form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Bioaccumulation	Other findings	Reference
LMB	La^{3+}: PO_4^{3-} = 1:1; solid	Laboratory	28 d	Macrophytes (submersed exotic invasive *Myriophyllum spicatum*)	Growth, morphological characteristics	Significant decrease in total biomass, aboveground biomass, and relative growth rate	The root-to- shoot ratio with LMB was significantly higher than in the controls.	Decrease in total biomass (aboveground and below-ground), may increase risk of sediment resuspension/ nutrient release.	(Lin et al., 2021)
LMB	LMB: *P mass ratio of 100:1; slurry	Mesocosms (in situ)	12 weeks	Macrophytes (submersed *Vallisneria denseserrulata*)	Clonal growth	LMB negatively affected growth, with 35% less biomass and 27% fewer ramets.	–	Significant negative impacts on the plant population	Zhang et al. (2021)
LMB	810 kg LMB on 30092 m^2; solid	Field (in lake)	3 years	Macrophytes (floating-leaved *Nymphaea alba*; emergent *Phragmites australis* (exotic invasive), *Scirpus lacustris, Typha latifolia)*; and macroinvertebrates (chironomid larvae)	La concentration in macrophytes, chironomid larvae	–	In chironomid larvae, La increased from 1.7 μg/g dw before application to 1421 μg/g dw one month after application. After 3 years tissues still contained 277 μg/g dw. In floating-leaved and emergent macrophytes, La tissue concentrations ranged from 22.6 to 136 mg/kg dw.	The authors suggested that emergent and floating-leaved macrophytes, as well as chironomid larvae, may be vectors for La in freshwater food webs.	Van Oosterhout et al. (2020)
Two magnetic (HQ and Fe_3O_4); two non-magnetic (CFH-12® and LMB)	0.05, 0.1, 0.5,1 and 1.5 g/L for HQ and Fe_3O_4; 0.02, 0.04, 0.1, 0.24 and 0.6 g/L CFH-12®; 0.1, 0.5, 1, 1.5 and 2 g/L LMB; solution	Laboratory	24 h	Phytoplankter *Raphidocelis subcapitata* (chlorophyte), cladoceran zooplankter *Daphnia magna*	Growth rate inhibition, immobilization	No apparent inhibition with Fe_3O_4 or LMB. *D. magna* had comparable EC_{50} values for the four adsorbents.	–	The authors speculated that neither accumulation nor longer-term effects of P adsorbents may occur in pelagic *D. magna*, based only on this population. They recommended that the potential for unacceptable impacts should be evaluated on a case-to-case basis.	Á lvarez-Manzaneda et al. (2019a)
LMB, thermally modified calcium-rich attapulgite (TCAP)	LMB: Mobile P at a 100:1 ratio; TCAP: Mobile P at a 200:1 ratio; spray	Mesocosms (in situ)	7 months	Tubificid and chironomid macroinvertebrates	Diversity, species evenness	Did not result in ~~a~~pparent adverse impacts.	–	The authors suggested that bioturbation by invertebrate fauna may promote more mixing/transport of these P adsorbents deeper into the sediments.	Yin et al. (2018)
LMB, $FeCl_3$, LMB + $FeCl_3$	LMB (584 g/m^2), $FeCl_3$ (64.9 mL/ m^2); solids.	Laboratory	12 h	Macroinvertebrate fauna -Gastropoda, Oligochaeta, Diptera, Malacostraca, Hirudinea, Trichoptera, Ephemeroptera, Arachnida, Coleoptera, Odonata, Turbellaria, Bivalvia, and Heteroptera	Macroinvertebrate assemblages, relative species abundance, response rate	Significant decline in the number of taxa and the number of specimens during the first month after Flock Lock treatment.	–	Apparent short-term (1–2 months) adverse impact on the macroinvertebrate community.	Waajen et al. (2017)
P-inactive clay (PIC): Al-modified	10, 20, 30, 40 mg/ L; solid	Laboratory	15 d	Microalgae - Cyanobacteria, Cryptophyta,	Phytoplankton abundance, assemblage structure	Minimal ecological or health risks were	–	The authors noted a general need for careful monitoring and assessment after practical	Su et al. (2016)

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Table 4 (*continued*)

P-capturing material	Dose; Form	Type of experiment	Exposure	Biota	Parameter(s) of focus	Ecotoxicity	Bioaccumulation	Other findings	Reference
bentonite clay, $^{+}$LMB				Heterokontophyta (diatoms), Chlorophyta, Euglenophyta		inferred from this lab. bench study.		application in potable source-waters.	
LMB	Microcosms: 13.6 g. Mesocosms: 1.1 kg; slurry	Mesocosms (in situ)	Microcosm: 41 d; Mesocosm: 25 d	Zooplankton (*Ceriodaphnia silvestrii*), benthic macroinvertebrates (*Chironomus xanthus*)	Mortality	Mortality of *C. silvestrii* was 65.1% at EC_{50} values.	–	There were negative impacts of LMB addition to the water column based on acute toxicity tests.	Yamada-Ferraz et al. (2015)
LMB	1 g/L or 67.3 g/m^2; slurry	Laboratory	28 d	Crayfish *Procambarus fallax* f. *virginalis*	Accumulation of La in body tissues	–	La from LMB is bioavailable and was taken up by the crayfish.	The authors recommended thorough study on potential side effects, due to bioavailability of La.	Van Oosterhout et al. (2014)
LMB	0.0, 0.005, 0.05, 0.1, 0.5 and 5.0 g/L; solution	Laboratory	48 h	Zooplankter *Brachionus calyciflorus* (rotifer)	Population growth	Population growth was depressed at $\geq$ 0.2 g/L.	–	Field application of LMB may negatively affect rotifers (*Brachionus calyciflorus*).	Van Oosterhout and Lürling (2013)
Flock: flocculent (PAC); Lock: LMB	9 mg/L flocculent, 67 mg/L modified clay; slurry + dilution	Field (in-lake)	3 years	Zooplankter *Daphnia galeata*	Survival, abundance, grazing	*D. galeata* was not found in water samples for at least 3 months after application, followed by population recovery.	–	*D. galeata* disappearance may have been caused by physical effects due to Flock, inhibition of grazing by Flock + clay, very low food availability (chlorophyte *Scenedesmus obliquus*), and/or absence of refuge from predation.	Van Oosterhout and Lurling (2011)
La and LMB	100 mg/L; spray	Laboratory	5 d	Zooplankton (*D. magna*)	Life history traits	Smaller size, delayed maturity, depressed reproduction; lower population growth rates.	–	Lanthanum, up to the 1 mg/L tested, exhibited no impact on the life-history characteristics of *D. magna* in P free medium.	Lürling and Tolman (2010)

$^{+}$Separately applied, *Porewater P; dw = dry weight.

(Mooney et al., 2020) and LC_{50} (300 mg/L) (Kleinhenz et al., 2019). Field applications of these materials are limited, which prevents a comprehensive understanding of their environmental impacts.

4. Implications of findings for safe use of P-capturing materials

Sustainable P management is critical to protecting freshwater resources and ensuring water and food security (Elser and Bennett, 2011; Withers et al., 2014). Although many studies have detailed the application of P-capturing materials to help mitigate eutrophication in freshwaters, scientific understanding of the full array of potential environmental impacts associated with their use is extremely limited. We found 43 peer-reviewed publications that addressed one or more of the three major environmental risk criteria. The extent and severity of negative effects were shown to depend on environmental conditions such as pH, temperature, and settling period, and on substance form, bioavailability and lability (Gagnon et al., 2013; Van Oosterhout et al., 2014; Zhi et al., 2020). The data, although sparse, indicate that use of metal-based P-capturing materials to mitigate eutrophication has associated adverse impacts and environmental risks that may outweigh their potential benefit in some cases.

Based on the available studies, Al-, Fe-, Ca-, La-, and Mg-based P-capturing materials show potential for harmful impacts on various macroalgae, zooplankton, macroinvertebrates, and fish taxa. Toxic effects of Al include depressed microbial activities that could potentially disrupt biogeochemical processes (Nogaro et al., 2013). Fe-based P-capturing materials have limited the growth of some phytoplankton, benthic microalgae, and macrophytes which, in turn, would be expected to adversely influence higher trophic levels. Direct effects on aquatic fauna from Fe-based materials have also included depressed parthenogenic reproduction in *Daphnia magna* (Fjällborg et al., 2006; Álvarez-Manzaneda et al., 2017). Varied outcomes have been reported from tests of La-based P-capturing materials such as LMB—as examples, decreased clonal growth, depressed biomass and reduced density for some macroalgal and submersed macrophyte taxa (Lin et al., 2021; Zhang et al., 2021); reduced size, delayed maturity, depressed reproduction, and lower population growth rates for zooplankter *Daphnia* (Lürling and Tolman, 2010); and depressed species richness in benthic macroinvertebrate communities (Lürling and Tolman, 2010; Yamada--Ferraz et al., 2015). Only one study indicated that La accumulation in tissues of macrophytes, chironomid macroinvertebrates, and fish tissues was not linked to apparent negative effects (Copetti et al., 2016). These organisms nevertheless may act as vectors for La to fauna that rely upon them as food. Very sparse information about Ca- and Mg-based P-capturing materials suggests that those materials have also negatively affected some planktonic and benthic organisms (Clements and Kotalik, 2016; Mooney et al., 2020).

This paper is the first known effort to synthesize the peer-reviewed literature pertaining to the ecotoxicity, bioaccumulation, and persistence risks of using these five selected metal cations for P-capturing materials to mitigate eutrophication. A major finding is that very few studies have investigated impacts of these materials on freshwater biota. In fact, data were remarkably sparse for environmental impacts of any of the five selected metals in P-capturing materials. Some studies described acute toxicity, but only for few substances and very few targeted freshwater taxa. Most studies were done indoors on a lab-bench scale, which severely limits inferences that can be extrapolated to freshwater environments. And also the majority of research was not conducted under eutrophic conditions or did not indicate the background nutrient regime at all, making it challenging to identify the actual background nutrient conditions. Further, most studies used only a single application rather than applying multiple doses that would have simulated practical

Table 5
Overview of published studies investigating environmental impacts of Mg-based materials for P capture.

P-capturing material	Dose; form	Type of experiment	Exposure	Biota	Parameter (s) of focus	Ecotoxicity	Other findings	Reference
Magnesium sulfate	2.5, 7.5, 23, and 68 mg/L; solution	Mesocosms (in situ)	4–7 weeks	Phytoplankton (Cyanobacteria, Heterokontophyta (diatoms), Dinophyta, Euglenophyta, and Chlorophyta); Zooplankton (ostracods, cladocerans, copepods)	Phytoplankton biomass, zooplankton taxa richness	Mg EC_{01} values were <3 mg/L.	Decrease in phytoplankton biomass, taxa richness.	Mooney et al. (2020)
Magnesium sulfate	0–500 mg/L; solution	Laboratory	Acute 24 h	Mussels (*Velesunio angasi*, *Velesunio* sp.)	Growth rate, survival	Mean lethal (LC_{50}) toxicity 284 mg/L for *V. angasi*; mean LC_{50} 300 mg/L for *Velesunio* sp.	The authors identified a major lack of available acute or chronic toxicity data regarding Mg in freshwater mussels.	Kleinhenz et al. (2019)
Magnesium sulfate	0–1000 mg/L; solution	Mesocosms (in situ)	30–40 d	Macroinvertebrate communities	Community composition, survival, and metabolism; and macroinvertebrate drift	Across all endpoints, mean EC_{20} values were considerably lower for $MgSO_4$ indicating greater toxicity.	Mayfly drift, abundance of baetid and heptageniid mayflies, total mayfly abundance, and community metabolism were adversely affected at specific conductance ≤300 μS/cm.	Clements and Kotalik (2016)
Magnesium sulfate, Magnesium chloride	0–12000 mg/L; solution	Laboratory	4, 8, and 24 h	Phytoplankton (chlorophyte *Chlorella* sp.); macrophytes (floating *Lemna aequinoctialis*); zooplankter *Moinodaphnia macleayi*; macroinvertebrates (mollusc *Amerianna cumingi*, cnidarian *Hydra viridissima*), and fish (trout *Mogurnda mogurnda*)	Growth, survival	Mg toxicity increased with exposure duration for all species, but the magnitude of the increase varied considerably among species.	The authors noted that there is very little available information about underlying mechanisms of Mg toxicity.	Hogan et al. (2013)

use of these substances; only Lürling and Tolman (2010) applied multiple doses in laboratory trials with LMB. In general, very little information was available about safe limits (e.g., predicted no-effect or maximum allowed concentration) for metal-based P-capturing materials (Herrmann et al., 2016; Sneller et al., 2000). Beyond the dearth of information about the various substances within each of the five groups of metal-based P-capturing materials, almost no practical information is available about the fate of the potentially toxic metals in aquatic food webs, interactions of these substances with other chemical environmental contaminants, and the influences of environmental conditions (low pH, hypoxia/anoxia, high free ammonia, high sulfide, etc.) typical of eutrophic waters at night or at depth (Wetzel, 2001; Wang et al., 2016; Burkholder and Glibert, 2024). Such conditions are known to stress and kill sensitive aquatic life without addition of metal-based P-capturing materials or other chemical environmental contaminants and would be expected to exacerbate the negative impacts of these substances.

In addition to the limited studies focusing on environmental impacts, substantial differences in experimental design make it challenging, at best, to compare environmental impacts indicated by the data that do exist. Environmental risks of metal-based P-capturing materials are known to vary in major ways depending on key characteristics of the study design, such as the background conditions, dose(s), and experimental duration. The use of P-capturing materials to mitigate eutrophication in freshwater ecosystems realistically involves a complex web of interrelated factors including the intended use, operational performance, and sustainability of the P-capturing materials in meeting water quality goals like ecosystem health and public health regulations. As such, thorough evaluation of potential risks and negative environmental impacts should be completed before attempting to apply P-capturing materials (Douglas et al., 2016). The impacts, risks, and uncertainties should be carefully assessed by water resource managers, fish and wildlife managers, scientists, and public health officials when considering the use of metal-based P-capturing materials among other options for mitigating eutrophication.

Future ecotoxicity and environmental impact studies would benefit from investigating a greater diversity of species across trophic levels to gain understanding of the full suite of impacts from P-capturing materials in eutrophic waters. The absence of established water quality criteria based on threshold values for P-capturing materials creates additional challenges in understanding their environmental influences. Research is needed to establish the optimal concentrations and threshold dose values for different P-capturing materials used in situ. Future studies should also investigate the long-term fate and transport of these materials within aquatic ecosystems. In addition to single-dose applications, multi-dose studies should be performed with a suite of species across trophic levels, including microbial decomposers, to characterize the short-term and long-term cumulative environmental impacts of these materials. The dose and exposure duration of P-capturing materials are crucial factors to consider in the restoration process, as higher dose and longer exposure times can promote elevated metal toxicity levels.

While acute ecotoxicity data were more abundant than information on bioaccumulation and persistence, chronic ecotoxicity studies have not been conducted for most of these metal-based P-capturing materials. Much more information on long-term bioaccumulation and environmental persistence is needed before scientists can understand their fate and transport. Insofar as possible, such studies should be conducted in situ to provide more realistic data that can be used to support improved management decisions to mitigate impacts of cultural eutrophication.

This synthesis will hopefully inspire safe-by-design practices for scientists' use in developing new materials for effective P capture that minimize known environmental impacts (European Commission, Joint Research Centre et al., 2022). Societal perceptions and needs can be included through inclusive participatory approaches when selecting the best mitigation strategy for eutrophic waters (Roque et al., 2022). Overall, risk evaluation and tradeoff analysis should be considered essential prior to application of metal-based P-capturing materials, to ensure efficiency and minimize unintended adverse consequences.

5. Conclusions

Cultural eutrophication, caused by excessive phosphorus (P) and nitrogen (N), is a major environmental concern worldwide that can lead to negative impacts on aquatic life and water quality. Efforts to restrict cyanobacterial growth have traditionally centered on capturing P, using various metal-based materials that may have their own impacts on aquatic ecosystems. For these reasons, this review was conducted on the environmental impacts of P-capturing materials containing Al, Ca, Fe, La, or Mg. Synthesis of the peer-reviewed literature revealed that surprisingly little is known about environmental impacts of metal-based P-capturing materials in freshwaters under eutrophic conditions. We identified major gaps even in information about the full suite of short-term acute effects, and found very little about chronic effects, especially regarding species known to be sensitive to chemical contaminants. Comparison among studies was challenging due to variations in experimental settings, doses, periods, and type of biota. Nevertheless, the sparse available data indicate that, as an expected outcome, application of metal-based P-capturing materials can promote various adverse, unintended consequences. This synthesis emphasizes the importance of conducting studies of these materials in eutrophic conditions to inform improved management strategies for eutrophying waters. Based on a review of available studies, we find that these materials may pose environmental risks in some cases, such as increased metal mobility in the environment, bioaccumulation, alteration to sediment chemistry, toxicity to aquatic life, and sustainability issues, although much more research is needed to confirm any adverse effects.

This study also underscores a critical need for comprehensive screening of metal cation-based P- capturing materials for environmental risks before continuing their common use in freshwaters to mitigate cultural eutrophication. Laboratory experiments should be conducted under realistic conditions that simulate eutrophic environments. In field settings, carefully designed monitoring of water quality and biota (including early life history stages of sensitive species across trophic levels) should be imposed prior to, during, and following applications to strengthen insights about impacts and reduce the uncertainty associated with use of these materials in situ. Site-specific research can then be designed to customize application of the most appropriate P-capturing material to mitigate eutrophication while also protecting beneficial aquatic life (Zamparas and Zacharias, 2014). Such studies, alongside sustainable material and technology development for P capture, may help ensure a more robust and comprehensive understanding of various metal-based materials proposed for P capture for eutrophic waters.

CRediT authorship contribution statement

Mumtahina Riza: Conceptualization, Data curation, Writing – original draft, Writing – review & editing. **Khara D. Grieger:** Conceptualization, Funding acquisition, Project administration, Supervision, Visualization, Writing – review & editing. **Madison D. Horgan:** Visualization, Writing – review & editing. **JoAnn M. Burkholder:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Jacob L. Jones:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

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