



Review

Restoration of eutrophic freshwater by managing internal nutrient loads. A review



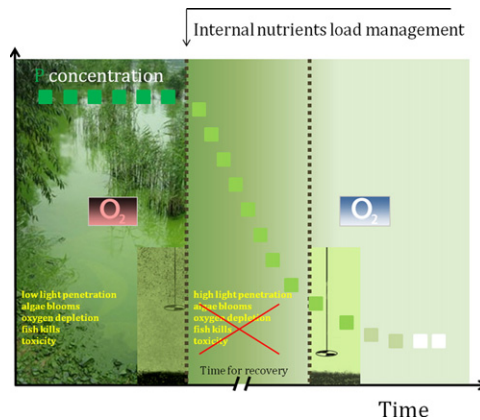
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HIGHLIGHTS

- Restoration methods of internal P loads to control eutrophication were examined.
- Results in areas that inactivate agents have been implemented were also reviewed.
- A conceptual model was developed highlighting the need of an integrated approach.
- Key issues were emerged, pointing out weakness/gaps in the field for future research.

GRAPHICAL ABSTRACT



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ABSTRACT

Eutrophication has become the primary water quality issue for most of the freshwater and coastal marine ecosystems in the world. It is one of the most visible examples of biosphere's alteration due to human activities affecting aquatic ecosystems from the Arctic to the Antarctic. As eutrophication becomes frequent and many eutrophic ecosystems have difficulties meeting the EU Water Framework Directive (WFD) criteria the removal of phosphate and/or ammonium gains great importance, in water treatment. The objective of this paper is to review the restoration methods of eutrophic ecosystems, emphasizing remediation methods of internal nutrient release budget as a major factor to control eutrophication. The use of phosphate inactivation agents as a restoration tool, their capacity and application methods, as well as the individual results (in water quality, algal blooms, flora and fauna) in areas that have been implemented were also examined. Moreover, a conceptual model was conducted as a process to determine remediation technique, highlighting the need of an integrated approach to eutrophication management. The chemical lake restoration methods are not a panacea and their implementation should consist a targeted management approach as a part of an integrated management plan. The longevity of the treatment effectiveness using P-inactivation agents is reduced if not given the necessary importance in managing the external nutrient loads. The successful implementation of internal P management measures requires a site-specific study of a range of factors affecting viability of the method used, in connection with an assessment of the potential adverse effects on humans, livestock, biotic and abiotic factors.

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Contents

1. Introduction	552
1.1. Eutrophication — a worldwide water quality issue	552
2. Policies and protection perspectives. The pressure for immediate effects on water quality	552
3. Catchment remediation works and internal nutrient loads	553
4. Lake sediment release management — overview of restoration procedure	553
4.1. Phoslock™	554
4.1.1. Laboratory and field studies	555
4.2. Modified zeolite	556
4.3. Alum	557
4.4. Calcite	558
5. Discussion	559
6. Future challenges calling for answers	560
Acknowledgments	561
References	561

1. Introduction

1.1. Eutrophication — a worldwide water quality issue

The rapid increase in human activity has substantially accelerated the eutrophication process, altering the geochemical cycles of carbon, nitrogen and phosphorus. In addition to natural sources, nutrients can enter aquatic ecosystems via point and nonpoint sources resulting from anthropogenic origins such as: (a) municipal and industrial sewage discharges, (b) runoff from fertilizers and manure applied to agricultural land, (c) from diffuse sources in catchment areas. Nonpoint sources generally are of greater relevance than point sources since they are larger and more difficult to control (Howarth et al., 2000; Howarth and Paerl, 2008; National Research Council, 2000).

Phosphorous due to its excess bioavailability is the most important nutrient because it is responsible for the eutrophication of water bodies, resulting in increased aquatic plant and algal growth (National Research Council, 2000). Furthermore, phosphorus control is more feasible than that of nitrogen, because, unlike nitrogen, there is no atmospheric source of phosphorus that is bio-available. The proliferation of aquatic plants and the subsequent decomposition of organic matter usually lead to low dissolved oxygen concentrations in bottom waters and sediments with low water renewal rates. High loadings of nutrients from anthropogenic sources resulted in hypoxic/anoxic conditions throughout the world, in stratified rivers, lakes, reservoirs, estuaries and coastal waters (Wetzel, 2001; Howarth and Paerl, 2008; Rabalais et al., 2010; Carvalho et al., 2005; Smith, 2003; Smith et al., 2006; Smith and Schindler, 2009).

Recreational angling and boating activities can be physically impeded by eutrophication-driven macrophyte growth and algal blooms (Dodds et al., 2009). Moreover, water users are less likely to swim, boat, and fish during heavy algal blooms due to health risks, unfavorable appearance, or unpleasant odors. Property values can decrease with declines in water clarity (Dodds et al., 2009). Remarkable is the fact that the potential annual value losses in recreational water usage and waterfront real estate were approximately \$2.2 billion annually as a result of eutrophication in U.S. freshwaters (Dodds et al., 2009). The greatest economic losses were attributed to lakefront property values (\$0.3–2.8 billion per year) and recreational use (\$0.37–1.16 billion per year).

A recent study of over 14,000 lakes <1 ha in size in Great Britain found that 51% are likely to require P-decrease measures to meet the Water Framework Directive to achieve ‘good status’ by the year 2015 (Carvalho et al., 2005; Gibbs et al., 2011). Many shallow eutrophic lakes will have difficulties meeting the EU Water Framework Directive (WFD) criteria without restoration. Therefore, regional water action plans have been adopted to find possibilities for the lakes to meet the criteria of “moderate”, “high”, or “good” ecological condition (Egemose et al., 2010; Solheim et al., 2008; Søndergaard et al., 2005).

In recent years the importance of reducing dissolved P in the water and controlling its release from the sediment in order to counter algal blooms has been recognized (Egemose et al., 2010; Gibbs et al., 2011). The objective of this paper is to review the restoration methods of eutrophic ecosystems, emphasizing remediation methods of internal nutrient release budget as a major factor to control eutrophication. The use of phosphate inactivation agents as a restoration tool, their capacity and application methods, as well as the individual results (in water quality, algal blooms, flora and fauna) in areas that have been implemented were also examined. Furthermore, an attempt is made to assess the role of each inactivation agent on conditions under which it can be used successfully as a restoration tool in eutrophic waters. Based on the study carried out in the context of this review, a conceptual model was conducted as a process to determine remediation technique, highlighting the need of an integrated approach to eutrophication management.

2. Policies and protection perspectives. The pressure for immediate effects on water quality

In Europe, action against eutrophication was brought about by conventions and legislation, which were followed over the past decade by far more comprehensive legislation: the Water Framework Directive (WFD_{2000/60/EC}), which addresses all surface waters and groundwater, and the Marine Strategy Framework Directive (MSFD_{2008/56/EC}), which establishes a framework for marine environmental policy up to the 200 nautical miles limit of the European exclusive economic zone. Similar to this development, additional US legislation was passed to provide protection to coastal water quality (Hypoxia and Harmful Algal Bloom Research and Control Act).

The European Union implemented the Urban Waste Water Treatment Directive (UWWTD) (Commission of European Communities), which required nutrient removal from all sewage treatment works (STW) serving a population equivalent of over 10,000. However, because of the extremely high nutrient loadings that exist in many rivers, nutrient removal from these large STW alone is unlikely to reduce nutrient concentrations, particularly P (Hilton et al., 2002), to the target for good ecological status, as set out in the European Union's Water Framework Directive (2000/60/EC). In order to reverse the eutrophication of lakes, much effort has been made to reduce the external loading of phosphorus (Diederik and Van Der Molen, 1994; Villena and Romo, 2003).

Lake restoration efforts were traditionally focused on reducing nutrient inputs from the catchment, mainly those relating sewage discharges and diffuse runoff from agricultural land. Catchment remediation works including (a) restricting stock access to the lake, (b) enhancing riparian buffer zones and (c) installing constructed wetlands on the main inflow, have been previously used. However, external P-reduction studies in

many lakes have shown a long recovery hysteresis (Hickey and Gibbs, 2009; Villena and Romo, 2003). This is related primarily to the internal sources of nutrient supply and hence is described in detail below.

3. Catchment remediation works and internal nutrient loads

Phosphorus release from the sediment into the lake water may be so intense and persistent that it prevents any improvement of water quality for a considerable period after the loading reduction (Søndergaard et al., 2003). Søndergaard et al. (2005) indicate that highly P-saturated lake sediments are often slow to respond to reduced external loads because sedimentary stores of P can act as a buffer to changes in water column P concentrations. According to Kagalou et al. (2008) after an instantaneous reduction of external load leading to an increase in the ratio C_{lake}/C_{in} (where C_{lake} is the internal nutrient concentration in the water column and C_{in} the nutrient concentration of the inflow), a decrease in C_{lake}/C_{in} may be expected again after some years when the P content in the top sediment layer has moved toward equilibrium with the concentrations in the overlying water column. The time needed for this recovery can vary considerably between lakes, and may in some cases take decades.

External nutrient loading, over time, increases the concentration of nutrients in the sediment that can be released back into the overlying water column (Reddy et al., 1998). After receiving elevated external inputs of P for decades, some wetland systems (e.g. Florida Everglades) are greatly impacted by internal P flux, a phenomenon referred to as “phosphorus legacy” (Bostic et al., 2010; Reddy et al., 2011) (Fig. 1).

The sediment plays an important role in the overall nutrient dynamics of shallow lakes. According to Kagalou et al. (2008), a restoration plan in 1995–1996 (Lake Pamvotis, Greece), involving sewage diversion, led to a reduction in external nutrient load and consequently to lower in-lake nutrients and chlorophyll-*a* concentrations. Orthophosphate concentration decreased by about 87%, nitrates fell below 1.20 mg/L, while the total reduction of inorganic N compounds showed a weaker downward trend, fluctuating between 0.39 and 1.24 mg N/l with an average value of 0.76 mg N/l. However, after a short-term recovery, the eutrophication status of the lake Pamvotis can persist up to 8 years later (1996–2004), suggesting the importance of the internal loading process. Internal loading is expected to enhance eutrophication and decrease the lakes' response-time to external decrease in phosphorus load e.g. by a decade or longer.

When entering the sediment, phosphorus becomes a part of the numerous chemically and biologically mediated processes and is ultimately either permanently deposited in the sediment or released by various mechanisms and returned in dissolved form to the water column via the interstitial water.

Numerous mechanisms have been proposed as being responsible for the release of phosphorus from lake sediments. It should be emphasized,

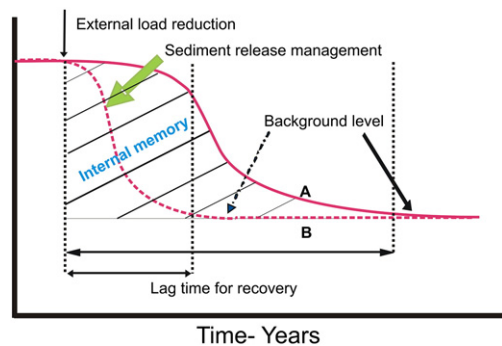


Fig. 1. Line A (solid line) – relationship between water P column and internal P memory due to legacy phosphorus (Reddy et al., 2011), line B (dashed line) – relationship between water P column, internal P memory and implement of sediment release management (by the authors).

however, that lake sediments can be very different and highly variable regarding chemical composition. Parameters such as dry to weight ratio, organic content, and content of iron, aluminum, manganese, calcium, clay and other elements with the capacity to bind and release phosphorus may all influence sediment–water interactions (Søndergaard et al., 2003).

At high internal P-loading, concentrations rise, and phosphorus retention can be negative (Søndergaard et al., 2003). Internal P loading originates from a pool accumulated in the sediment at high external loading, and significant amounts of phosphorus in lake sediments may be bound to redox-sensitive iron compounds or fixed in more or less labile organic forms. These forms are potentially mobile and may eventually be released into the supernatant lake water. Many factors are involved in the release of phosphorus from the sediment to water column. Prolonged external loading may ultimately produce elevated levels of nutrients in bottom sediments that, under certain environmental conditions such as anoxia, are remobilized and returned to the water column (Boström et al., 1988). Thus, sustained high concentrations of water column nutrients have been observed in many lakes despite large reductions in external loads, particularly from point source inputs.

Sediment removal is recommended in cases when the internal nutrient loads need to be reduced for macrophyte control, or to remove toxic substances present in the lake bed (Moss et al., 1996). However, dredging works have practical considerations of how much sediment to remove, where to put contaminated sediment following removal, the feasibility and cost of moving considerable amounts of sediment, and finally the potential for significant disturbance and release of contaminants into lake water during dredging operation (Hickey and Gibbs, 2009). For example, in Alderfen Broad (UK), although the exposed sediment had lower phosphorus concentration than the sediment that was removed, within a year the total phosphorus concentration of the sediment had increased to 80% of its origin value. In other words, phosphorus concentration remained higher than the concentration reported prior to eutrophication (Phillips et al., 1999).

Moreover, hypolimnetic withdrawal is suitable for lakes that are stratified over summer and become anoxic in the layer of hypolimnion. A recognized disadvantage of this restoration technique is its impact on downstream waters, including eutrophication, oxygen depletion and odor development (Nürnberg, 2007). Moreover, this restoration method must take into account the impact that it will have on the downstream environment, as the anoxic discharged water may contain hydrogen sulfide (H_2S). Nürnberg (1987) reported that hypolimnetic withdrawal in 12 lakes is likely to take at least five years and lake water levels have to be maintained preventing erosion of littoral zone. Additionally hypolimnetic withdrawal has a large initial investment and it would be more expensive if the water removed had to be treated to reduce phosphate concentration.

4. Lake sediment release management – overview of restoration procedure

Restoration has been defined as the return of a disturbed system to some predisturbance state that is both self-regulating and integrated into the larger landscape (National Research Council, 2000).

The chemical restoration methods mainly aim at reducing the P release from the sediment by improving the P binding capacity and thus creating P limitation of the phytoplankton. During the recent decade, scientific research has considered a number of different solid adsorbents to be used in reducing the P levels entering the water bodies (Zamparas et al., 2013). Some of the materials investigated included iron oxides, red mud, fly ash and carbonates (De-Bashan and Bashan, 2004; Huang et al., 2008; Wang et al., 2008). While they may have numerous beneficial applications, using each one could have certain disadvantages. For example, the performance of iron oxide and red mud in reducing P is very much affected by the solution pH (Tanada et al., 2003; Zeng et al., 2004). In addition the stoichiometry of the reacting species with the

phosphate anion is greater than 1:1 in most cases. The key drawback of these adsorbents is that the adsorbed phosphate can be released when some of the chemical properties of the solutions such as pH and redox change.

Today, alum, calcite, Phoslock™ (lanthanum modified clay) and Modified Zeolite (Z2G1) are those materials that are commonly used to restore eutrophic water bodies with the latter two constituting the most innovative remediation materials (Table 1). The properties of these materials together with their effectiveness under a range of physicochemical parameters occurring in laboratory and field applications have been described in detail.

4.1. Phoslock™

Melnyk et al. (1974) and Recht and Ghassemi (1970) have reported that phosphate precipitation by lanthanum (a rare earth element) was more effective in a wide pH range (4.5–8.5) than either Fe or Al salts. The molar ratio of La to phosphate anion is 1:1 as resulting from the $\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4$. The solubility product (Ksp) of the La-phosphate complex is particularly low (24.76 and 27.92) in both aqueous and seawater solutions, making it the least soluble of the rare earth–phosphate complexes (Henry Firsching and Brune, 1991; Henry Firsching and Kell, 1993). The complex is known to be so insoluble in low La and phosphate concentrations and low pH conditions (Diatloff et al., 1993). Furthermore, with an increase in temperature the solubility of the La-phosphate complex decreased thus indicating the strength of the La-phosphate bond (Henry Firsching and Brune, 1991). Using

GEOCHEM-PC computer diagrams Diatloff et al. (1993) showed that the complex can be formed in solutions with a pH as low as 4.0. Through their work they established that the reaction of the two components can occur at pH 4 and with very low concentrations of La and phosphate species.

Lanthanum is a rare earth element which fortunately is in relative abundance in the Earth's crust compared to other rare earth elements. In addition, it's very potent when removing P from the water with the previously reported ratio of 1:1, compared to sodium aluminate NaAlO_2 which reached the inefficient ratio of 7:1 in order to achieve similar phosphorous uptake (Douglas and Adeney, 2001). Moreover, the point of zero charge of La oxides is higher than that of other known adsorbents (Wasay et al., 1996; Tokunaga et al., 1997, 1999; Shin et al., 2005), confirming that it is effective in high pH rates.

The research into the use of lanthanum for reducing phosphates has revealed that depending on the concentration and the rate of application, this element can be toxic to aquatic organizations (Douglas et al., 2004). This problem can be overcome by embedding La into the structure of clay minerals, such as bentonite by taking advantage of their cation exchange capacity (CEC). During the manufacturing of Phoslock, lanthanum ions are exchanged with the bentonite internal surface random adsorbed exchangeable cations.

This gave birth to a La-modified bentonite developed by CSIRO (Commonwealth Scientific and Industrial Research Organization) during the 90s (Robb et al., 2003). Phoslock™ forms a highly stable mineral known as rhabdophane (LaPO_4) in the presence of P species such as orthophosphates which are common oxyanions (Table 2). The rare earth

Table 1
P-inactivation materials and implementation actions to natural eutrophic waterbodies. Indicative field applications with Phoslock™, modified zeolite Z2G1, alum and calcite.

Lake/reservoir	Material	Key features	References
De Ploeg urban pond, The Netherlands	Phoslock™	Enclosure experiment was conducted to test the effectiveness of dredging and a Phoslock application in controlling cyanobacterial blooms and toxin production.	Lürling and Faassen (2012)
Clatto Reservoir Dundee, UK	Phoslock™	Short term alterations in sediment La composition and sediment P-fractions before and after the application of Phoslock.	Meis et al. (2012)
Rauwbraken, The Netherlands	Phoslock™	A novel restoration technique "Flock & Lock" was evaluated.	Van Oosterhout and Lürling (2011)
Swan Canning and Vasse Wonnerup estuaries, Australia	Phoslock™	Use of Phoslock in removing dissolved phosphorus (P) from the water column as well as to intercept sediment; explore the effect of reduction of P availability on phytoplankton activity.	Robb et al. (2003)
Lake Okaro, Central North Island, New Zealand	Modified zeolite (Z2G1)	Measuring sub-lethal effects on freshwater crayfish (<i>Paraneohrops planifrons</i>) behavior and physiology of the exposure to modified zeolite.	Parkyn et al. (2011)
Lake Okaro, Central North Island, New Zealand	Modified zeolite (Z2G1)	Effects of a modified zeolite Z2G1 on P and N processes and fluxes across the lake sediment–water interface.	Gibbs and Ozkundakci (2011)
Lake Okaro, Central North Island, New Zealand	Modified zeolite (Z2G1)	Effects of sediment capping on zooplankton and phytoplankton.	Özkundakci et al. (2011a, 2011b)
Lake Okaro, Central North Island, New Zealand	Modified zeolite (Z2G1)	Measuring the in situ health of two finfish species (<i>Oncorhynchus mykiss</i> and <i>Gobiomorphus cotidianus</i>) and crayfish (<i>Paraneohrops planifrons</i>) with respect to a large-scale application of Z2G1.	Landman and Ling (2011)
Lake Okaro, Central North Island, New Zealand	Alum	Impact of the material on the water nutrient concentrations and on the trophic status indicator chlorophyll-a.	Paul et al. (2008)
Lake Süssee, Germany	Alum	Long term effects of phosphorus precipitations with alum in hypereutrophic Lake.	Lewandowski et al. (2003)
Newman Lake, Washington State, USA	Alum	Alum introduction into an oligomictic lake. Whole lake application and microfloc installation.	Moore et al. (2009)
Green Lake Washington State, USA	Alum	Short-term effects of buffered alum treatment on lake sediment phosphorus speciation.	Dugopolski et al. (2008)
Lake Luzin, Germany	Calcite	Dynamic of phosphorus and its binding forms in seston and sediment before and during the whole lake treatment.	Dittrich et al. (2011)
Lake Arendsee (Germany)	Calcite	A failed restoration technique where calcareous mud from the littoral zone was resuspended and distributed over the entire lake surface.	Hupfer et al. (2000)
North Halfmoon Lake and Lofty Lake (Alberta, Canada)	Calcite	The relationships between zooplankton and phytoplankton, together with the effects of lime additions during a 3-year study (1991–93).	Ghadouani et al. (1998)
Eight hardwater lakes monitored in this study: (1) Crooked Lake, (2) Jenkins Lake, (3) Baptist Lake, (4) Nakamun Lake, (5) Lofty Lake, (6) N. Halfmoon Lake, (7) Halfmoon Lake and (8) Figure Eight Lake	Calcite	Effects of single and multiple moderate doses of lime (slaked lime, $\text{Ca}(\text{OH})_2$, and/or calcite, CaCO_3) on eutrophic hardwater lakes.	Prepas et al. (2001)

Table 2
Summary of innovative P-inactivation materials for reducing internal nutrient loads.

Chemical method	Application	Mechanism	Phosphate adsorption capacity (qm) mg P/g material	pH range*	Harmful effects
Phoslock	Applied as a slurry or as granules	$\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4$	10.5	5–8	No toxic effect to <i>Daphnia magna</i> Phoslock™, because it rapidly settles after application.
Modified zeolite	Applied as a slurry or as granules	$\text{Al}_2(\text{SO}_4)_3 + 2\text{PO}_4^{3-} \rightarrow 2\text{AlPO}_4\downarrow + 3\text{SO}_4^{2-}$	12.7	5–7	No discernable changes in plankton species composition when MZ is applied as a coarse-grained material that settled out of the water column rapidly.
Alum	Applied as a liquid	Same as alum $\text{Al}_2(\text{SO}_4)_3 + 2\text{PO}_4^{3-} \rightarrow 2\text{AlPO}_4\downarrow + 3\text{SO}_4^{2-}$	12–13.8	5.5–8.2	Lake water pH reduction–acidification Toxicity
Calcite	Applied as a slurry	$3\text{Ca}^{2+} + 2\text{PO}_4^{3-} = \text{Ca}_3(\text{PO}_4)_2$	6.4	5–6	Settling floc → smothering of the benthos No concerns

* pH range in which the material shows the maximum efficiency.

element in the clay structure can either react with the phosphate anion in the water body or remain in that structure under a great range of environmental conditions (Douglas et al., 1999). Although La ions could be toxic to some aquatic organisms, particularly cladocerans such as *Daphnia* (Barry and Meehan, 2000; NICNAS, 2001), hence the potential liberation of La ions from the bentonite meaning a significant environmental risk (Akhurst et al., 2004), Phoslock has been classified as not hazardous (Martin and Hickey, 2004). A leachate experiment has shown the La could be released from the material, however in only insignificant quantities of 0.13–2.13 µg/L. In this scenario, provided Phoslock™ is applied in a worst-case dose of 250 mg/L (Lurling and Tolman, 2010).

Phoslock™ is applied to the treated water using two main application techniques. Spreading it in a granular form or as a thick suspension, a solid/water slurry through spray is created (Table 2). As it settles through the water column, it binds the orthophosphates permanently and rests on the sediment, acting as a capping material to prevent phosphorous being released from the sediment (Douglas et al., 1999; Robb et al., 2003; Akhurst et al., 2004; Ross and Cloete, 2006; Lurling and Tolman, 2010).

4.1.1. Laboratory and field studies

Vopel et al. (2008) used microelectrodes to measure the apparent gas diffusivity of capping layers derived from different doses of Phoslock™ and their effects on pore water pH and dissolved molecular oxygen. From this study it was revealed that capping material raised the depth of the oxic–anoxic interface and associated pH minimum and altered the sediment O₂ consumption as functions of the capping-layer thickness and apparent diffusivity. Thus, it is proposed that capping layers derived from doses >200 g m⁻² can alter benthic process rates and solute fluxes.

A laboratory study examined the ability of Phoslock™ to adsorb phosphates under the influence of pH and the algal content of the water sample and how these affect its kinetic behavior and moreover what effect the anoxic conditions have on its ability to retain the adsorbed phosphates. In addition, higher Phoslock™ dosages were applied to lake water which had pH above 9 to see if it was possible to achieve a greater phosphorous removal (Ross and Cloete, 2006). It was found that Phoslock™ was most effective at pH values between 5 and 7 (Zamparas et al., 2012) and with a pH increase from 7 to 9, phosphorous removal decreased with any pH above 9 showing large diminution in adsorption capacity (Table 2). This can be explained by the reduction of P binding sites on the surface of Phoslock™ due to the excessive creation of hydroxyl species by the La ions. The precise pH at which La hydroxides begin to precipitate is 8.35 (Dibtseva et al., 2001) so it is subsequent that the adsorption capacity may be decreased above that pH. The sample of lake water which had pH 9, after applying the Phoslock™ had an increased rate of turbidity reduction than that with a pH value of 5. The particle size data collected support this observation. In algae-containing lake water the adsorption capacity was lower than

in prepared reverse osmosis water solutions most likely due to the effect of humic acids. Anoxic conditions did not show phosphorous release from the Phoslock™ modified clay. Some other concluding remarks from this study were: (a) the conductivity of the all water solutions and samples was not affected by Phoslock™. (b) The reduced FRP (filterable reactive phosphorous) adsorption capacity observed at a pH above 9 could not be overcome by increasing the Phoslock™ dosage to a 450:1 treatment ratio (Ross and Cloete, 2006).

According to Liu et al. (2012) the effectiveness of Phoslock™ was tested and evaluated both in laboratory and field trials. The results of static and dynamic simulation experiments under different environmental conditions showed that with the application rate of Phoslock™ at 0.5 kg/m², the orthophosphate (PO₄-P) concentration of the overlying water decreased to a low level (≤0.02 mg/L) within 10 days. Even under anaerobic and high pH (pH = 9.0) conditions, the phosphate release suppression efficiency reached 98.3%, and the P-release rate was –8.20 mg/m² d (negative value indicates P adsorption by Phoslock™). The monitoring data of the field sediments rehabilitation project were consistent with the results achieved in laboratory experiments, thus showing that the application of Phoslock™ could inhibit the internal P release effectively.

One of the first field applications of Phoslock™ was held in the summer of 2001/2002 in the impounded riverine section of two estuaries along the coastal plain of south west Western Australia. Phoslock™ applied in slurry from a small boat reduced dissolved P in the water column to below detection limit in the few hours it took for the clay to settle and substantially reduced P efflux from the sediments during the course of the trial. The effect of P reduction on phytoplankton growth was clearly evident in the phytoplankton dominated Vasse River but was less clear in the alternating phytoplankton to aquatic plant dominated Canning River which is also subject to surface nutrient inputs (Robb et al., 2003).

In addition, a field study was conducted in the Clatto Reservoir in Scotland and were investigated the short term alterations in sediment elemental composition and sediment P-fractions (Table 1). Sediment cores were taken two days before and twenty eight days after the application of 24 tonnes of Phoslock™ in a reservoir of 9 ha (Meis, et al., 2012). The sediment cores taken after the application revealed the substantially increased sediment lanthanum content in the first 8 cm, thereby theoretically increasing the sediment phosphorous binding capacity on the whole reservoir scale by 250 kg. Moreover, the mass balance calculations that were used to estimate the theoretical binding of mobile P (release-sensitive), have shown that the mass of La present in the sediment could potentially bind 42% of P-mobile present in the top 4 cm or 17% of P-mobile present in the top 10 cm. Apart from the significant increase in the fraction of residual P in the top 2 cm, sediment P fractions including P-mobile did not differ noticeably following the Phoslock™ application. After extracting the phosphorous from Phoslock™ in laboratory conditions it was discovered that around 21% of P bound by Phoslock™ could be released easily and the other 79%

was unlikely to be released under pH values of 5 to 9 in shallow lakes. So it is inferred that the application of Phoslock™ is therefore likely to increase the P sorption capacity of sediments under reducing conditions (Meis et al., 2012).

Moreover, at Lake Rauwbraken in the Netherlands, a new way of applying Phoslock™ was used (Table 1). It is called “Flock and Lock” and it’s the combination of a low dose flocculent polyaluminumchloride and Phoslock™ (Van Oosterhout and Lüring, 2011). The new restoration technique “Flock & Lock” involves the inactivation of the water column phosphate, the precipitation of particulate P and the subsequent immobilization of any phosphate released from the precipitated flocks and the sediment. This means that this method is effective in stripping both dissolved (phosphate) and particulate P from the water column, but also counters the internal loading by permanently fixing P released from the sediment. This new technique resulted in the complete removal of P from the water column and a very substantial reduction on the P release from the sediments. In addition, the treatment had very beneficial effects on the water quality as well, filamentous cyanobacteria were removed and chlorophyll-a concentration dropped to 2 µg/L. However, a temporal elevation in the aluminum, lanthanum and suspended clay concentration levels was observed. Following the treatment a grazing phytoplanktonic species (*Daphnia galeata*) disappeared for 3 months from the water column within 1 week after the application. From field observations and additional grazing and survival experiments it was concluded that the disappearance of that species (*D. galeata*) from the lake may have been caused by the combination of the physical effects due to flocks, grazing inhibition by flocks and clay, very low food concentrations and absence of predation refuge. However, effects were temporary and it recovered after the treatment (Van Oosterhout and Lüring, 2011).

These were some of Phoslock’s applications showing its effectiveness regarding phosphorous and its wide application standards regarding pH and other important parameters. Phoslock™ seems to be a very promising material for lake restoration from the P-induced eutrophication.

4.2. Modified zeolite

A modified zeolite named Z2G1 has been developed by Scion, Rotorua, New Zealand and manufactured by Blue Pacific Minerals Ltd. as a new sediment capping agent. Natural zeolite is a porous aluminosilicate material that has a large specific absorptive surface area due to a fine porous structure, and is also a good cation absorbent (e.g. NH_4^+). Z2G1 was modified with an Al salt for improved P uptake capacity, being the only sediment capping material able to remove both P and N. It is designed to be applied in a granular form which improves the settling rate and thus the accuracy of the treatment of the areas at the lake bed (Table 2). Also the Z2G1 does not release Al into the water column. According to Wood (2001) and Klapper (2003) the increased concentration of potentially bioavailable Al in the material could have environmental effects, although, based on a laboratory assay, its toxicity is minimal.

A continuous flow incubation system (CFIS) was applied to assess four agents (alum, Phoslock™, Z2G1 and allophane) in terms of efficacy and sustainability regarding flux measurements in simulated stratified (anoxic) and mixed (aerobic) conditions on the same sediment. An additional objective was the simulation of a summer algal bloom collapse and the following burial of the products and investigation of unwanted effects on nitrification and denitrification processes at the sediment–water interface. (Gibbs et al., 2011). The minimum P removal dose rates were widely different among the products being 190 g/m² for Z2G1, 80 g/m² for alum, 280 g/m² for Phoslock™ and 220 g/m² for allophane for a 2 mm thick coverage and to be effective for at least 4 years. Comparing the Z2G1 modified zeolite with alum, a few advantages over it appeared. First Z2G1 did not require pH buffering of the lake water and it has the high P binding capacity of alum while improving the settling rate (Gibbs and Ozkundakci, 2011). Also unlike alum, modified

zeolite did not acidify lake water following the application, minimizing the potential for aluminum toxicity, which is markedly higher at low pH (ANZEC and ARMCANZ, 2000; Cooke et al., 2005). In addition, Z2G1 was more precise in its application because of its granular nature and it settles more rapidly than the other P inactivation products like alum and Phoslock™. This is an advantage in high turbid lakes where sediment capping is the main priority (Yang et al., 2004; Gibbs and Ozkundakci, 2011).

The Z2G1 modified zeolite was used in an application in Lake Okaro in September 2007 (Table 1). Lake Okaro is a small eutrophic lake (surface area 0.32 km²) with a maximum depth of 18 m and was formed by a hydrothermal explosion crater. It is seasonally stratified for 8 months and it is mixed fully for 4 months every year. Located in the central region of the North island of New Zealand within the Taupo Volcanic Zone it suffers frequent cyanobacterial blooms caused by high nitrogen and phosphorus inputs from the catchment and significant internal P loading released from the sediments during summer stratification. This application was deemed a ‘whole lake’ trial to test the effectiveness of the product in reducing the internal load of P from the sediments and, additionally, to assess if the Z2G1 could be used in a potential treatment of the much bigger lake Rotorua (81 km²) and other lakes in the region. The purpose of the study was to determine if the product is efficient in blocking the P release before undertaking the whole lake trial. The CFIS technique was used in the sediment core testing in this trial. The P removal efficacy was examined by treating sediment cores with two grain sizes and dose rates of Z2G1 under aerobic and anoxic conditions. Additionally, different layer thicknesses of the capping material were used to examine the effects on the microbial processes of nitrification and denitrification and the potential release of arsenic (As) and mercury (Hg) from the geothermally influenced sediments of Lake Okaro under aerobic and anoxic conditions.

The CFIS results from the comparisons between control and treatment fluxes under aerobic and anoxic conditions showed that, at the trialed dose rates, a thin layer of the modified zeolite Z2G1 was able to completely block the release of P from the sediments of Lake Okaro. The higher dose rate of the 1–3 mm grain size material was more effective in removing sediment P than the lower dose rate in natural anoxic lake water and, as expected, had a better coverage of the sediment surface. Interestingly however, the lower dose rate of Z2G1 at <1 mm and 1–3 mm grain sizes removed significantly more P from the water column than the higher dose rate when the phosphate concentration was increased under anoxic conditions. In relation to the unused material, the increase in Phosphorus content of the Z2G1 recovered from the sediment cores confirmed that it was removing P, and that it was not the passive action of the granular material on the sediment surface. Also from the use of different grain sizes it was shown that the <1 mm grain size absorbed about 45% more P than the 1–3 mm grain size in both the natural and phosphate-enriched water incubation trials for the same period of sediment exposure. This is because of the greater active surface area that a finer material has over a coarser one.

Now regarding the metal fluxes in the sampled cores between the sediment and the water, they were generally low, and even when the incubation tubes were made anoxic, the metal concentrations were generally much lower than those just above the sediment that we measured at the time of the core sampling. This could be because of the bottom stir up during the core sampling (Gibbs and Ozkundakci, 2011). Additionally a shift of the reduction–oxidation (redox) boundary could cause the release of metals with sensitivity and mobility under anaerobic conditions (Himmelheber et al., 2008). Although the small layer thickness of the Z2G1 had the potential to enhance metal mobilization from the sediments there was very low or no metal fluxes from the sediments in aerobic or anaerobic conditions. The very few changes in metal concentrations in the water above the sediment particularly under anoxic conditions could be because the zeolite substrate of the Z2G1 is a good cation absorber. The products absorbed Al from the sediments since in the used one we found higher amounts

than those in the new. Finally, apart from P, other metals were retained too such as Fe, As, Hg and K.

What is more, it was found that Z2G1 can inhibit nitrification and denitrification under aerobic conditions. This means that Z2G1 could increase N retention in the lake if it was applied in the permanently aerobic zones for instance the littoral zone of Lake Okaro. In the lake the permanently aerobic littoral zone above 5 m is the only habitable area of lake bed for most of the year. Hence, for this life supporting zone to be protected we should apply the Z2G1 only below that depth and fortunately this can be done with great precision because of its granular composition and its settling speed.

From this study it is established that the Z2G1 modified zeolite is an effective sediment capping material for sediment Phosphorus release blocking in anoxic conditions, at the tested dose rates on the sediment cores. Also, the material absorbed cationic metals which means that the cation retaining abilities of the zeolite were still in effect and besides that there was absorption of NH_4^+ from the overlying water and the stopping of $\text{NH}_4\text{-N}$ release from the sediment. Consequently we infer that the Z2G1 is the only known sediment capping agent that inactivates both P and N.

Nonetheless, while from the reported results of the core incubation study we see that the material is potent in blocking the N and P release from the lake sediments, we cannot extrapolate with certainty from these to an actual whole lake trial. Conclusively the Z2G1 needs to be tested in that way in a lake to give more clear conclusions about its usability as a lake restoration method as well as for its long term effects after several or many years of usage in lake restoration.

4.3. Alum

Aluminum salts are very common in water treatment and have been used in water clarification and lake water restoration as flocculation agents for a long time. Alum or aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) is the most preferable flocculant used in Europe and the United States (Cooke et al., 1993; Jeppesen et al., 2005). Because Al hydroxides like iron hydroxides – which are present in lake sediments are natural P adsorbents and because unlike aluminum-bound phosphorus, iron-bound P is soluble in reducing sediments, the Al hydroxides are preferred for P binding and as a long-lasting sink for bioavailable P. This means that aluminum acts an active barrier system capturing and inactivating the potentially mobile P from the lake bottom sediments (Jeppesen et al., 2005).

Alum is at its optimal performance at pH values above 6 and up to 8, effective in precipitating suspended particulates and to a lesser extend in absorbing and removing soluble forms such as phosphorus fractions. Moreover alum is effective under anoxic conditions adsorbing the dissolved reactive phosphorus (DRP) and then the resulting floc settles on the bottom sediment (Jeppesen et al., 2005).

Alum is applied to the lake water as an acidic solution, thus, it must first be buffered, usually with sodium bicarbonate, to maintain pH above 6.5 (Table 2). If the water has low alkalinity, the result will be a pH drop below 6 and highly toxic Al^{+3} species will be formed (toxic Al^{+3} species are formed by reverse hydrolysis of the $[\text{Al}(\text{OH})_3]$ which is toxic to the lake fish). This step has to be taken in order to facilitate the flocculation process. Additionally, in high pH water values, flocculation cannot be achieved; however this requires the use of a low concentration alum solution. The wind can also disrupt the floc formation due to of the surface mixing effect (Hickey and Gibbs, 2009).

As alum is added to the water column, the formation of aluminum hydroxide reduces alkalinity, so the maximum dosage of the added material is often determined as the maximum amount of Al than can be added until the lake water pH decreases to a value of 6 (Jeppesen et al., 2005). This specific application dose ensures optimal maximum formation of the $[\text{Al}(\text{OH})_3]$ -P floc with minimal occurrence of the toxic Al^{+3} . An alternative way to calculate alum dose is based on the amount of internal phosphorus from the sediment and is calculated as five times

the average summer internal phosphorus load (Cooke et al., 1993; Jeppesen et al., 2005).

Besides the aforementioned potential alum toxicity and acidification, another non-target effect is caused by the settling of the floc, which is the smothering of the lake bed (Table 2). As far as sediment toxicity is discussed, there are no published data that show it can be caused by alum and also provide information on tolerance thresholds for sediment living species between different thicknesses of alum (Hickey and Gibbs, 2009). In 1990, a study on five alum-treated lakes discovered increases in faunal density and diversity in almost each one of them (Narf, 1990).

Given the correct implementation of an alum application, meaning that pH and application rates have to be carefully considered, the material can sequester enough DRP with effectiveness and create a P limitation in the water which can remediate eutrophication by eliminating toxic cyanobacterial blooms in favor of harmless phytoplanktonic species like diatoms (Downing et al., 2001). Alum can also be used for sediment capping except for its primary use as a flocculant (Cooke et al., 2005). The material should be applied toward the end of the summer stratification when the bottom lake water is anoxic and the accumulation of DRP is maximum. As to the duration of an implementation action, alum has an expected duration of effectiveness for 5 to 20 years, before a repeat treatment is necessary (Welch and Cooke, 1999). Nevertheless, an alum treatment may not be effective or have a very limited time effectiveness if a significant part of the lake is covered with macrophytes which during decomposition release high amounts of P into the water column (Özkundakci et al., 2011a, 2011b).

There are a few notable cases of alum field applications. Alum was applied to Lake Okaro on December 2003 with the objective of documenting the impact of the material on the water nutrient concentrations and on the trophic status indicator chlorophyll-a. In two days, 13 m^3 of alum solution was added to the lake by spraying from a boat producing a concentration of 0.6 g/m^3 of Al in the epilimnion. (Paul et al., 2008). The results has shown a decrease in total P and an increase in Chl.-a. This indicates the possible flocculation of P by the alum application and that the phytoplankton may not be P-limited, perhaps as a result of sufficient internal P load or limitation by N. Also, the low dose rate of the alum application was in response to the low alkalinity of lake Okaro and because there was a risk of substantial decrease of pH and alkalinity with the application. Low buffering capacity and high assimilation of inorganic carbon from phytoplankton production in the lake resulted in a pH over 9 in the epilimnion before and after the dosing. At high pH values, floc formation is highly unlikely, P sorption capacity is reduced and soluble Al may be more persistent in the water. In contrast, pH in the hypolimnion was below the lower limit for adsorption of pH 6. After dosing soluble Al concentrations were above the recommended guidelines for protection of freshwater species for at least 3 months and there was potential for fish kills, however, no fish deaths were observed. Still there were decreases in most nutrient species in the hypolimnion after dosing albeit temporary possibly due to the exhaustion of Al adsorption capacity, burial of the floc layer on the bottom sediments (Lewandowski et al., 2003) or bioturbation. Following the alum dosing there was a decrease in phosphate concentration in the epilimnion; however, at the time of dosing phosphate concentrations were low and representing only a small proportion of the total P pool. Most P near the surface was present in phytoplankton or associated with other organic particulate matter in less easily adsorbed forms by the alum floc, than free phosphate ions (Cooke et al., 1993). As to N species, a substantial increase of ammonium in the epilimnion was noticed after the dosing. Mineralization of dead organisms like zooplankton by heterotrophic bacteria might explain the increase in ammonium, though mortality of heterotrophic bacteria from alum dosing should not be discounted. The increase in the surface ammonium which coexisted with the decrease in phosphate the day after the dosing may have led to a reduction in N limitation of phytoplankton. Paul et al. (2008) infer that alum applications require careful

consideration of the abundance and availability of different P forms and their adsorption capacities.

Another restoration attempt using alum was conducted in Newman lake in Washington State starting in 1989 (Table 1). Newman lake is oligomictic with medium depth (30 m) and sustains a stable thermal summer stratification beginning mid- to late May and remains until mid August or early September. Two main alum applications were conducted, one whole lake application in 1989 and one microfloc in 1997. Annual average growing season TP ranged from 43 to 77 $\mu\text{g/L}$ with an increasing trend prior to restoration. The first alum application lasted for 6 days in September 1989 using an aluminum dose of 2.8 mg/L (Moore and Christensen, 2009). In 1998, the year following the lake treatment TP dropped to 33 $\mu\text{g/L}$, however in the next two years, phosphate concentration increased to pre-restoration levels, showing the limited effectiveness of the treatment. Aeration technique at the same time with the alum application may be responsible for the limited treatment longevity because increased oxygen demand associated with phosphates precipitated by alum, could have heightened internal P loading, overwhelming the retention capability of the floc (Moore and Christensen, 2009).

The alum microfloc installation was put in place in April 1997 and it was deemed operational at mid-summer of that year. The key difference from conventional whole lake alum treatments is that these form large aluminum hydroxide flocculants, which because of their size settle rapidly and effectively remove particulates and solute P. Obviously the main objective of this kind of treatment is to inactivate P by chemically bonding it with the sediments (Moore et al., 2009). This method has been successful in reducing nutrients and algae and in improving water clarity. Lower settling velocities compared to whole lake treatments offer increased opportunities for $\text{Al}(\text{OH})_3$ to react with particulate and dissolved phosphorus. For lake managers, microfloc alum provides an important new opportunity by providing capability of a due time response to alterations in water quality conditions. This system offers great flexibility for dosing and timing, which can allow the manager to gain maximum benefit from limited resources by applying alum when, where, and at concentrations to achieve greatest efficacy. On the other hand, for small lakes or small scale implementations, alum injection may be sufficient in accomplishing water clarity on its own, as well as achieving algae and nutrient reduction goals. Although such systems have not been used as direct replacements for whole-lake treatments, especially in large lakes, they do offer a long-term and flexible tool for lake managers. The successes so far indicate that additional deployment and continued evaluation of microfloc alum injection systems for lake restoration is appropriate (Moore et al., 2009).

Green Lake, Washington, was treated with a dose of 24 mg Al/L aluminum sulfate (alum) during March–April 2004 to ameliorate a variety of eutrophication-related problems (Dugopolski et al., 2008). Four sediment cores collected six months after the alum treatment in Green Lake were used to examine the short-term effects of alum on sediment phosphorus speciation. By comparing this ratio of Al to Al–P (112:1) to the average ratio of $\sim 11:1$ found in other alum-treated Washington lakes, it can be inferred that approximately 10% of the binding capacity of the added Al had been utilized. The added Al has the potential capacity to bind a total of 21.6 g/m^2 of P. The amount of sediment inorganic P (Fe–P and labile-P) that supports internal loading was determined to be 2.8 g/m^2 . Therefore, the quantity of alum added to Green Lake was sufficient to inactivate the remaining inorganic mobile-P and to control future P mobilization from the pool of organic sediment P (Dugopolski et al., 2008).

Almost all the controlled variables improved with treatment, especially nutrient concentrations such as soluble reactive phosphorus (SRP) and transparency. In spite of low SRP in the water column, the treatment did not prevent appearance of *Microcystis* sp. colony (> 10 colony per ml) approximately 30 days after alum application. Although, aluminum sulfate was not added in sufficient quantity to reduce the total phosphorus content, SRP concentration was significantly

increased in the long-term. In addition, external loading of phosphorus was high and not taken into account by the in-lake treatments. Resuspension of sediment removed the alum layer on the sediment surface, which reduced treatment effectiveness (Van Hullebusch et al., 2002).

Many studies about short-term effects are reported, but little is known about long-term effects. To reduce this lack of knowledge Lewandowski et al. (2003) investigated the German hardwater lake, Süsser See, which was treated almost annually from 1977 to 1992 with aluminum sulfate. Pore-water profiles of SRP taken in situ and in sediment core experiments, as well as sorption batch experiments, illustrate that the $\text{Al}(\text{OH})_3$ sorption capacity is still not exhausted with further P sorption. The internal P load was affected by the magnitude of the downward flux into the P sorbing layer (Lewandowski et al., 2003).

4.4. Calcite

Calcium carbonate (CaCO_3) natural precipitation is an effective natural cleaning process in hardwater lakes that acts against eutrophication trapping dissolved P and algae cells as it occurs. During algal blooms the increase of pH promotes the forming of CaCO_3 . Calcium cations and hydrogen carbonate anions which have elevated concentration at the time, form carbon dioxide and CaCO_3 which precipitate and co-precipitate P to the sediment in the process. Calcite or lime is a very stable CaCO_3 polymorph and it is used for artificially induced CaCO_3 precipitation for removing P and for algae flocculation in order to improve water quality in the long term (Dittrich et al., 2011).

The co-precipitation of dissolved P in the form of PO_4^{3-} with calcite occurs upon the beginning of crystallization of calcite in the water. The interaction happens at the surface of the material and some surface bound P can be incorporated in the calcite crystalloid structure upon its formation. In fact in many cases the P and calcite co-precipitation can be linearly described. The resulting product is a complex mixture of CaCO_3 and forms of calcium phosphate with the most frequently occurring final form being the mineral hydroxyl apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$], which has a very low solubility product (Hart et al., 2003).

Calcite has a few advantages as a phosphorus binding agent. It's an easily affordable and available non-toxic material and exists naturally in the sediments (Table 2). Also, as stated, calcite and P co-precipitation is a natural process and during biogenous calcite precipitation by super saturation caused by the use of CO_2 from photosynthesizing phytoplankton, particulate P attached to the cells ends up to the sediments because of the simultaneous phytoplankton precipitation by calcite precipitating crystals. At same time SRP is stripped from the water by adsorption on the calcite surface. Moreover adding calcite, as seed to promote P precipitation, lowers the interfacial energy of Ca-phosphate interaction and the precipitation of calcite bound P is faster (Berg et al., 2004). An alternative way to induce CaCO_3 precipitation is by adding calcium hydroxide [$\text{Ca}(\text{OH})_2$] which reacts with the CO_2 in suitably saturated lake water. $\text{Ca}(\text{OH})_2$ dissolves and facilitates the formation of CaCO_3 mainly by increasing pH, however this has the obvious drawback of creating very high alkalinity water which is toxic for the majority of aquatic organisms (Dittrich et al., 2011; Mehner et al., 2008; Berg et al., 2004).

The most widespread way to apply calcite in water is with an active barrier system (ABS). It is recommended especially for application on anaerobic sediment–water interface and for efficiently adsorbing the excess P that is released. Despite that the idea that it is known that calcite cannot counter N release, particularly the usual NH_4^+ species, and because of that inability, natural zeolites may very well and possibly be used in a calcite mixture to address both the P and N fluxes from anaerobic sediments (Lin et al., 2011).

The difference in the interaction with P of precipitated calcite and that used in ABS, is the very much faster adsorption of orthophosphates that is achieved with the calcite in an ABS. Additionally, the created calcium phosphate is slowly incorporated into the calcite crystal matrix.

Nevertheless, the mechanism of this adsorption is no different from what that the surface precipitated calcite presents (Hart et al., 2003).

Lime treatment has been used on a number of lakes in Alberta (Table 1), and on small drinking water supplies (Ghadouani et al., 1998; Prepas et al., 2001). It was shown that these lake treatments improved the water quality with respect to phosphorus and chlorophyll concentrations. The high pH of approximately 11 resulted in the death of some invertebrates in a pond. In lake treatments in Alberta, for which pH has been kept at 10 (Prepas et al., 2001), measurements before and after the treatments did not detect any change in the invertebrate or fish populations (Prepas et al., 2001).

The attempt to restore the highly eutrophic Lake Arendsee (Germany) by means of artificial resuspension of calcareous mud (Seekreide) and capping of the natural bottom sediments in 1995 did not show the expected effects of decreasing the phosphorus (P) content in the water body (Table 1). The partial removal of SRP by this treatment was not due to apatite formation or sorption of SRP to calcite, but very likely to its sorption to Fe-hydroxides associated with the Seekreide particles. Hupfer et al. (2000) note that resuspension of autochthonous calcareous mud (Seekreide) that appeared as a promising low-cost approach to decrease phosphorus in eutrophic hard-water lakes, turned out as only insignificantly effective in whole-lake-experiment.

5. Discussion

Based on a thorough review, the basic features of material behavior in natural aquatic ecosystems are summarized in Table 3. With this attempt we can assess the role of each inactivation agent on conditions under which it can be used successfully as a restoration tool in eutrophic waters. In fact we focus on the shortcomings in each material in order to select the optimum method during implementation actions.

In general, the overall effectiveness of an alum treatment can be assessed from the reduction of DRP concentration in the water, duration of P inactivation and immobilization, potential adverse effects on phytoplankton community and possible toxicity from high Al^{+3} concentrations (Paul et al., 2008). The main advantages of the material are the low cost, and the fact that apart from a lake surface application, it can also be applied directly to the hypolimnion as a slurry with the benefit of minimizing the whole lake benthos exposure to the floc. As for the disadvantages we can list the aluminum (Al^{+3}) toxicity, the lake water pH reduction which requires buffer dosing, the low floc stability mainly because of wind mixing and the adverse effects on the littoral benthos from an application to the epilimnion, smothering of the benthos by the settling floc, potential resuspension of the floc if the material is applied in shallow lakes and a restriction period for drinking, irrigation and stock water use after an application.

Phoslock has great efficiency in SRP removal, and effective capacity of sediment capping of the bottom, avoiding the P release. From the field applications demonstrated exciting results on eutrophic water purification. With Phoslock, the eutrophic water could be turned into good water quality, with variously healthy aquatic plants growing. Moreover, Phoslock could eventually purify the eutrophic water, thus, it was an

effective way for water eutrophication prevention. In addition, in a recent study, most La was recovered in the HCl extract, indicating that P became strongly bound to La in the Phoslock matrix (Reitzel et al., 2013).

As far as the efficacy and the terms of sediment capping are concerned we have a fast reduction of phosphate concentration in the sediment pore water present inside the calcite active barrier. This is due to the fact that the higher the P concentration the faster is the precipitation of calcium phosphate. Hence the rich in P sediment–water interface is highly recommended for ABS application. Furthermore the use of an ABS particularly with calcite, a relatively novel ecotechnology, definitely is an ecological application mainly because $CaCO_3$ is a natural sediment component. The survival of macrozoobenthic organisms has been proven by Berg et al. (2004) after applying a calcite ABS for sediment capping. Still there is disadvantage in the stability of an active barrier that being a few in-lake conditions, such hydrodynamics and bioturbation. These two factors can significantly diminish the efficiency and sustainability of this sediments capping technology.

Modified zeolite and Phoslock settle rapidly and this is an advantage in highly turbid lakes where sediment capping is the main priority. For example, Phoslock increased the sediment stability threshold by 265% whereas Al had no stabilizing effect (Egemose et al., 2010). However, it could be a disadvantage in lakes with high inputs as the Z2G1 and Phoslock capping layer would become buried. In addition more rapid settling may allow less time for binding phosphate as it sinks into the water column.

Recently, there have been renewed arguments to suggest that P removal alone may not alleviate eutrophication and to recognize the importance of simultaneous control of P and N (Conley et al., 2009). It has been observed that controlling only phosphorous (P) inputs to freshwaters and ignoring the large anthropogenic inputs of Nitrogen (N) can reduce algal uptake of N and thus allow more N to be transported downstream where it can exacerbate eutrophication problems in estuarine and coastal marine ecosystems (Conley et al., 2009). Based on this fact, improvements in the water quality of many freshwater and most coastal marine ecosystems require a decrease in both nitrogen and phosphorus inputs. Thus, the capacity of modified zeolite for adsorption of both phosphorus and ammonia is an important advantage against other materials used to restore eutrophic water bodies. Moreover, in cases where one of the two factors e.g. P or N, is the limiting nutrient of a natural water ecosystem, the use of Z2G1 is appropriate without requiring additional use of other materials.

Today there are many examples of lakes that have recovered after the reduction of phosphorus discharge to the lakes and their tributaries. On the other hand, there are also many examples of no effect of an advanced wastewater treatment due to the presence of diffuse pollution sources, which were not reduced. It is therefore necessary to consider all sources of nutrients and organic matter in our efforts to solve the pollution problems properly. A eutrophication model of a lake or reservoir should always be developed with an indication of all sources of nutrients and organic matter and with possibilities to predict the effect of a certain reduction of the nutrient discharge from all sources. Fig. 2 shows a conceptual model as a process to determine the optimal remediation technique, highlighting the need of an integrated approach to eutrophication management.

Before the decision to proceed to a restoration method, simultaneous monitoring of external and internal nutrient loads should initially be carried out. In this way we will define the reference conditions of the ecosystem and will choose which method to use in order to have the desired results. For example, if we avoid to consistently monitoring external P & N sources, underestimating their part in eutrophication and following a chemical restoration method, positive results in water quality will be negligible. Moreover, the conceptual model suggests that, to achieve our goals that we have set regarding water quality, a P-inactivation agent should be applied, followed by simultaneous and continuous monitoring of catchment and sediment nutrient loads,

Table 3

Basic features of P-Inactivation agents in natural water bodies, evaluating the effectiveness in relation to morphological and physicochemical characteristics of a eutrophic ecosystem.

	Alum	Phoslock	Modified Zeolite
Wind exposed lakes	NR	R	R
Deep lakes	R	R	R
Highly turbid lakes	NR	R	R
High sedimentation	R	NR	NR
Low alkalinity and poor buffering capacity	NR	R	R
Long period of stratification and anoxia	NR	R	R
High ammonium concentrations	NR	NR	R

NR = not recommended, R = recommended.

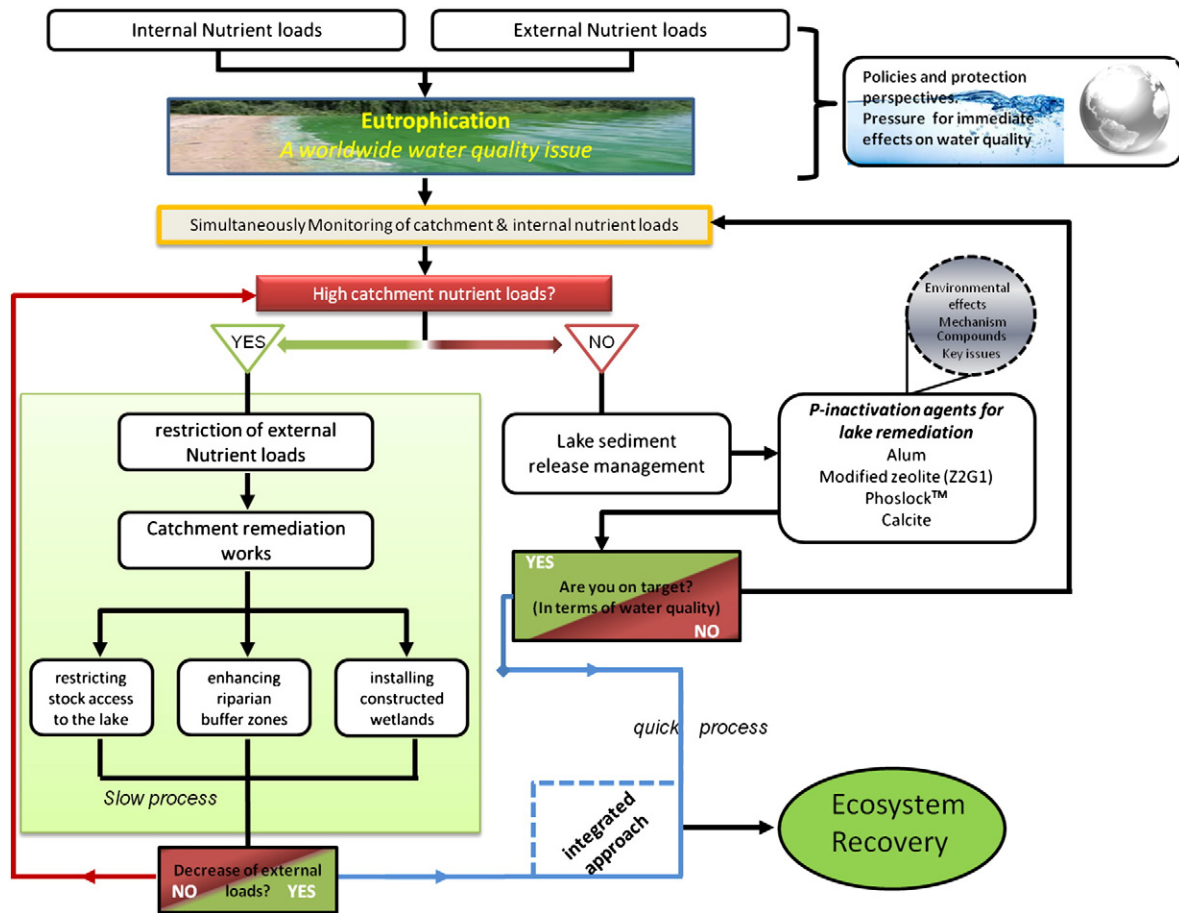


Fig. 2. Conceptual model of an integrated approach to eutrophication management.

until the requirements in water quality are fulfilled. The basic features of P-inactivation agents in natural water bodies should be taken into account, evaluating the effectiveness in relation to morphological and physicochemical characteristics of a eutrophic ecosystem.

6. Future challenges calling for answers

Nutrient reduction, as part of a lake/pond/reservoir management plan, needs to be a highly customized process. Much preliminary work needs to be done before developing a restoration plan in order to ensure success and not bring about unintended harmful effects. It is recommended that prior to any chemical lake treatment a series of parameters should be taken into account and quantified in order to get the desired outcomes. The use of chemical methods may be viewed as a treatment for mitigating eutrophication and not a solution for the factors begetting eutrophication. The calculation of the amount of P-inactivation agent required for restoration should take into account the speciation of P-sediment forms. An important purpose is to investigate the different P-forms present in sediments, their contributions to the P-loadings of the ecosystem and also the effect of P-inactivation agent amendment on P-binding properties of sediments. The determination of total phosphorus (TP) in sediments cannot predict the potential ecological danger related to eutrophication. More specifically, the bio-available sediment fractions transported in the water column intensifying eutrophication should be evaluated. Thus, the long term contribution of P bound in sediments can be more effectively determined on the basis of different P-fractions. P-fractions in sediments were extracted according to Hupfer et al. (1995). The sum of *labile P*, *reluctant-soluble P* and *organic P* fractions was defined as bio-available P (*P mobile*) and represent the potential release-sensitive P. In this way, it will be reduced the excessive

amounts of P-inactivation agents into the water column and sediment preventing the disturbance for filter feeders and benthic fauna respectively. It is therefore recommended that the P-reduction goals should not outmatch any possible adverse effects on the aquatic fauna.

The stability and thus the efficacy of an equitable sediment capping layer are correlated with a number of processes occurring in the lake sediments. Gas effervescence, advection and bioturbation may contravene the sediment stability and disturb the capping layer. For this reason, these factors must be evaluated before any whole lake experiment with P-adsorbents. The particle size and the specific weight of each P-adsorbent must be taken into account as the aforementioned parameters can vary in magnitude between lakes/ponds/reservoirs and across trophic gradients.

Moreover, many studies about short-term effects are reported, but little is known about long-term effects. Most of publications provide short-term studies representing a small part of what really happens in a natural eutrophic ecosystem and they don't provide comprehensive information about the sources of potentially bioavailable P in sediments. According to Özkundakci et al. (2011b) the transformation and degradation of biogenic P into dissolved inorganic P, which in turn is released from the sediment, may provide a long-term supply of orthophosphate to water column. In addition, ^{31}P NMR (nuclear magnetic resonance) analysis gives more knowledge about the origin of P compounds in lake sediment and provides information about the sources of P into the lake (Özkundakci et al., 2011b). This knowledge will help us to evaluate initial restoration targets, as the reduction of external nutrient loads, before following any chemical method. The chemical lake restoration methods are not a panacea and their implementation should consist a targeted management approach as a part of an integrated management plan. The longevity of the treatment effectiveness using

P-inactivation agents is reduced if not given the necessary importance in managing the external nutrient loads. The successful implementation of internal P management measures requires a site-specific study of a range of factors affecting viability of the method used, in connection with an assessment of the potential adverse effects on humans, live-stock, biotic and abiotic factors.

The properly designed application of chemical restoration methods may reduce the concentration of nutrients and improve the water quality in eutrophic ecosystem. However, the demand of the burial of phosphorus into sediment layers is not a sustainable aspect. Nowadays, the demand for fertilizer is increasing worldwide related to the global phosphate supply shortage (Neset and Cordell, 2012). It seemed that the application of such chemical restoration methods has reached its limits and it is necessary to be transformed in a sustainable way. The use of magnetic nanocomposites (Ramashayam et al., 2012; Liu et al., 2013) might be an alternative method of sediment remediation as it can be reused and the adsorbed phosphorus can be used as fertilizer or enriching soil conditioners. Therefore it is generated a sustainable cycle taking into account a renewable resource-based P-inactivation agent leading to environmental protection and conservation of natural resources. Renewable resource-based magnetic nanoparticles for removal and recovery of phosphorus from contaminated sediments are a promising technique but require further study to be used in natural eutrophic ecosystems.

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