# Application of novel composite materials as sediment capping agents: column experiments and modelling

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# ABSTRACT

The research objective of the study is the estimation of Phoslock™ as a P&N-inactivation agent in the overlying water and sediment cores under oxic and anoxic conditions from a polluted pond. Phoslock<sup>™</sup> was compared with ferrihydrite, unmodified bentonite (N-Bentonite), natural Zeolite (N-Zeolite), Alum and commercial Z2G1<sup>™</sup>. Under oxic conditions, the maximum sorption capacities  $(q_m)$  calculated from the Langmuir model were 14.1, 12.4, 11.2, 9.1 and 3.7 mg g<sup>-1</sup> for ferrihydrite, Phoslock<sup>™</sup>, alum, Z2G1, and natural bentonite, respectively. However, under anoxic conditions the maximum sorption capacities followed the order: Phoslock<sup>™</sup>> alum > Z2G1>ferrihydrite > N-bent onite. Moreover, Phoslock™ as a P-inactivation agent resulted in about ~81% and ~82% reduction of the phosphate flux from oxic and anoxic sediments respectively. Also, the effect of dissolved organic matter (DOM) on phosphate sorption capacity (PAC) of Phoslock™ and Z2G1 was studied experimentally and theoretically, simulating natural eutrophic waters. At both P-sorption agents by increasing the concentration of DOM, the sorption capacity is declined. However, it is noteworthy that in the case of Phoslock<sup>™</sup> application the PAC is retarded, whereas in the case of Z2G1 is sharp. Furthermore, the results unveiled that Phoslock<sup>™</sup> restrained P release from the sediments, therefore a portion of P-mobile is reduced in sediments and undergone transformation to non-reactive species. Finally, in economic terms the research outcomes of this study were verified by literature, where we reported that the concentration of 20.53 mg mobile P kg<sup>-1</sup> can be feasibly treated for \$30.53 kg<sup>-1</sup> of Phoslock<sup>™</sup> applied.

Keywords: Phoslock<sup>™</sup>; Eutrophication; Restoration P-fractions; Sediment

# 1. Introduction

Eutrophication is the enhancement of the natural process of biological production in rivers, lakes, and ponds.

Eutrophication is observed when increasing quantities of phosphorus and nitrogen nutrients (thereafter, they are collectively mentioned as elementary) are disposed at aqueous environments, thus, causing visible cyanobacterial or algal

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blooms, surface scums, floating plant mats, and benthic macrophyte aggregations. Specifically, phosphorus of <0.1 mg L<sup>-1</sup> can cause a cyanobacterial (algal) bloom while the decayed organic matter is releasing bounded phosphorus to oxidized sediment. The oxygen depletion in aqueous environments causes other environmental pollution problems, such as fish kills and the release of toxic substances [1–4].

Lake restoration is accomplished by applying techniques of reducing nutrients inputs from the catchment, including sewage discharge and runoff diffusion from agricultural land. Such a technique can control stock access to lakes while widening riparian buffer zones and constructing wetlands on the main inflow [5,6]. However, this catchment treatment can nurture eutrophic conditions of high in-lakes concentration. Subsequently, the recovery of the waterbody is retarded due to high elementary loads. It is noteworthy that of particular significance nutrient at lakes is phosphorous, in which the low mitigation from the sediment to the lake water necessitates a long time of improving water quality after the incidence of elementary loading [7,8]. In the relevant literature, proposed techniques of reducing nutrient fluxes are that of dredging [9,10], precipitation of phosphorus by aluminum salts [11-13], in-situ chemical injection [14], hypolimnetic oxygenation [15], as well as in-situ capping [16]. Among these literature reported techniques, P-inactivation agents can reduce the rate of sediment nutrient release by blocking the N and P release from the sediments under permanent blocking. Besides, at the in-situ capping technique, a layer is placed at the sediment-water interface to form a barrier between the sediment and the aquatic environment. Such a technique is proven effective to stabilize sediments while preventing re-suspension and diminishing the migration of dissolved contaminants into overlying waters [1,17,18].

Among chemical agents used to lakes, restoration is those of alum, calcite, bentonite, Phoslock<sup>™</sup> (lanthanum modified clay) and modified zeolite (Z2G1). The application of such restoring materials can remediate eutrophic water bodies, while the latter two are novel materials of proven effectiveness to lakes' restoration.

Phoslock<sup>™</sup> (from the words "phosphorus" and "lock") is a composite material of embedding La ions at the interlayer area of nature bentonite. Phoslock<sup>™</sup> is considered a novel and of low-cost material which is developed by Commonwealth Scientific and Industrial Research Organization (CSIRO) in the 90s [8,16,19–21]. Phoslock<sup>™</sup> forms a highly stable mineral known as rhabdophane (LaPO<sub>4</sub>) in the presence of P species such as orthophosphates which are common oxyanions. Phoslock<sup>™</sup> has been classified as not hazardous [8,22]. Leachate experiments showed La release from the material, though, at insignificant quantities of 0.13–2.13 µg L<sup>-1</sup>. In this scenario, Phoslock<sup>™</sup> is applied in a worst-case dose of 250 mg L<sup>-1</sup> [23]. Granular of thick-suspended forms of Phoslock<sup>™</sup> are designed and applied, followed by the development of solid/water slurry through spraying. As it settles through the water column, it permanently binds the orthophosphates and rests on the sediment, acting as a capping material to prevent phosphorus release from the sediment [16,18,23,24].

In addition, a modified zeolite named Z2G1 has been developed by Scion, Rotorua, New Zealand and manufactured

by Blue Pacific Minerals Ltd., (New Zealand) as a new sediment capping agent. Natural zeolite is a porous aluminosilicate material. The properties of such a fine porous-structured material are advantageous since it supports large specific absorptive surface area and satisfactory cation-absorbent performance (e.g.  $NH_4^+$ ). Besides, an Al salt-modified Z2G1 is a sediment capping material to improve P uptake capacity and to effectively remove elementary P and N. The granular form of Z2G1 can improve the settling rate and the overall treatment of the lake bed areas [8]. Moreover, Z2G1 is not causing Al release into the water column. Wood [25] argued that the increased concentration of potentially bioavailable Al in the material can cause adverse environmental effects. However, laboratory assays showed minimal toxicity levels.

This work is part of ongoing research to develop innovative approaches to phosphate removal, supporting the restoration of the currently degraded lake and reservoir systems [6,8,26-30]. The main objectives of the study are the investigation of the efficiency of Phoslock<sup>™</sup> as an active capping agent, which prevents the phosphate release from oxic and anoxic sediments. Specifically, it was examined the effect of Phoslock™ on the fluxes of phosphate and trace metals across the sediment-water interface, through incubation experiments upon polluted sediments. Phoslock™ was compared with ferrihydrite, unmodified bentonite (N-bentonite), natural zeolite (N-zeolite), alum and Z2G1. Furthermore, it was examined the effect of dissolved organic matter (DOM) on phosphate sorption capacity (PAC) of Phoslock<sup>™</sup> and Z2G1, as a critical parameter affecting the sorption of phosphorus in eutrophic water bodies. Also, this study quantified the effects of Phoslock<sup>™</sup> on sediment elemental composition and P fractionation. Finally, a technical and economic evaluation of Phoslock<sup>™</sup> was deployed, thus revealing parameters that are not often mentioned, but they are proven of utmost importance in terms of proper lake restoration.

#### 2. Materials and methods

#### 2.1. Materials

The N-bentonite and N-zeolite samples were supplied by the SB company (Nonantola Town, Province of Modena, Northern Italy) and were extracted from a Bulgarian mining site. The analytical natural zeolite contains 95% klinoptilolit (Ca Si<sub>7</sub> Al<sub>2</sub>O<sub>18</sub>·6H<sub>2</sub>O) with minor amounts of quartz, smectite and natural bentonite, while montmorillonite was the major component. The ferrihydrite (Fh) was synthesized from a stock solution containing 1.0 M Fe(NO<sub>3</sub>)<sub>3</sub> is adjusted to pH 7–8 through the dropwise addition of 1.0 M NaOH, based on the procedure deployed by Cornell and Schwertmann [31]. Centrifugation, dialyze, and freeze-drying of suspension was implemented as rapidly as possible. Then, the dry powder was stored in the refrigerator. The main physicochemical properties of Fh are given by Cornell and Schwertmann [31].

# 2.2. Study site

Sediment samples were collected from a small urban pond (Fig. 1) with area 0.5 ha, near the Lysimachia Lake, located in Western Greece (38° 33' 23" N, 21° 24' 40" E). At first, it was measured the nutrient status and the physicochemical



Fig. 1. General map of study site with Lysimachia Lake and the location of the polluted pond.

parameters of the lake: temperature, conductivity, dissolved oxygen, redox potential, and pH. These parameters are collectively listed in Table 1.

Clear acrylic cylinders with an internal diameter of 4 cm were utilized as sediment samplers. The cylinders were placed vertically onto the lake bed. Intact sediment cores 10 cm in length and 4 cm in diameter were extracted from the lake. The samples were placed vertically and immediately closed in air-sealed screw caps. Water samples for P and trace metals analysis were obtained from the corresponding overlying water above the sediment sampling site. The utilized equipment devices for sample collection, transportation, and preparation were P contaminant–free. Besides, samples were brought to the laboratory in a portable fringe at 4°C within 2 h.

Table 1Main physicochemical properties of study site

Physicochemical parameters	
Temperature (°C)	13.61
pH	8.1
Conductivity (µs cm <sup>-1</sup> )	316
Dissolved oxygen (mg L <sup>-1</sup> )	9.7
TOC (mg L <sup>-1</sup> )	4.75
TN (mg L <sup>-1</sup> )	1.28
TP (mg L <sup>-1</sup> )	0.47
$PO_4^{-3} (mg L^{-1})$	0.34
NO <sub>3</sub>	0.75
$\mathrm{NH}_4^+$	0.08

#### 2.3. Phosphate sorption batch experiments

Sorption isotherm data of phosphate on Phoslock<sup>TM</sup>, ferrihydrite, N-bentonite, N-zeolite, alum, and Z2G1 were studied under oxic and anoxic conditions using natural aqueous solution. 100 mL of natural water from an urban polluted pond of initial phosphate concentration 0.47 mg L<sup>-1</sup> were added into conical flasks containing 0.02 g of each material. The suspension was separated by centrifugation and the concentration in the supernatant ( $C_o$ ) was measured by the molybdate blue spectrophotometric method. The amount adsorbed ( $Q_o$ ) was calculated from the difference in concentration. Blank samples without any absorbent were perpetrated and monitored as a control. All experiments were carried out in duplicates.

# 2.4. Chemical equilibrium model

The effect of DOM on the P-removal efficiency of Phoslock<sup>™</sup> was examined by chemical equilibrium modeling using the CHEAQS-Pro software [32]. The CHEAQS Pro software calculates speciation of ions and solid saturation conditions based on a given set of total ion concentrations (mg L<sup>-1</sup>), and the solubility products with equilibrium constants issued from the National Institute of Standards and Technology. The program Model V/WHAM-W [33] was chosen to evaluate the formation of complexes of lanthanum with humic acids. Model V/WHAM-W is a discrete site model for humic-ion complexation using carboxylic and phenolic groups as two main types of functional groups [34]. The model was run with the following elementary/chemical concentrations referred to literature: 7.5 mg L<sup>-1</sup>La, based on 150 mg L<sup>-1</sup> Phoslock<sup>TM</sup> as a typical phosphate application rate (mass fraction of 5% La in Phoslock<sup>™</sup>) and 3.6 mg L<sup>-1</sup> Al, based on 150 mg L-1 Z2G1 as a typical phosphate application rate (mass fraction of 2.4% Al in Z2G1), 0.47 mg L<sup>-1</sup> PO<sub>4</sub><sup>-3</sup> (similar to lake phosphate concentration) and varying concentrations of humic substances as dissolved organic carbon (from 10 to 50 mg L<sup>-1</sup> simulating natural eutrophic waters).

## 2.5. P-partitioning in sediments

The determination of total phosphorus (TP) in sediments is not satisfactory predicting the potential ecological damage related to eutrophication. Thus, the long-term contribution of P-bound in sediments can be satisfactorily evaluated based on different P-fractions. P-fractions in sediments were extracted according to Hupfer et al. [35]. 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.

P in each fraction was calculated by:

$$P_{\rm sed} = \frac{P_f \times V_{\rm extract}}{\rm DW} \tag{1}$$

where  $P_{sed}$  is phosphorus in sediment (µg P g<sup>-1</sup> DW);  $P_f$  is phosphorus in fraction (mg P ml<sup>-1</sup>);  $V_{extract}$  is the volume extractant (ml); DW is the dry weight sediment (g)



Fig. 2. Framework of the present study.

#### 2.6. Column experiments

Laboratory sediment incubation experiments were performed by setting up eight columns to assess the effectiveness of sediment capping to reduce the release of phosphorus by using the aforementioned materials studied. The sediment incubation experiments were carried out to estimate the efficiency of natural zeolite (N-zeolite), natural bentonite (N-bentonite), ferrihydrite, alum, Z2G1 and modified bentonite Phoslock<sup>™</sup> as a sediment capping materials to reduce the phosphate fluxes under oxic and anaerobic conditions. Phosphate release measurements were conducted on homogenized wet sediments collected from an urban polluted pond. The collected samples were prepared by mechanical mixing for homogenization, after removal of large debris.

The sediments (5 cm of thickness) were placed in 14 glass cylinders (1 L) (8 under oxic conditions and 8 under anoxic conditions) with an internal diameter of 4 cm. Then, 700 mL of deionized water was added into each column. To maintain uniform conditions, columns was capped securely with plastic cap and sealed tightly with paraffin film. Aeration tube was placed in the cap of each column (only in oxic columns), and the tube was connected to 0.45  $\mu$ m polytetrafluoroethylene syringe filter to maintain redox potential gradient without microbial contamination. Besides N<sub>2</sub> was introduced, so that the dissolved oxygen from anaerobic columns to be removed. 1 g of each material carefully introduced into

columns and layered at the top of the sediments. Untreated sediments acted as control columns simulating phosphate flux from sediments under oxic and anoxic conditions. The columns were allowed to reconstitute for 5 d before starting the experiment. The experiments were conducted at room temperature ( $25^{\circ}$ C ± 1^{\circ}C). The columns were monitored for 92 d and within this period samples were taken for the determination of phosphate concentration contained.

The flux of phosphate release from sediments was calculated by [36]:

$$F_{D} = \frac{\sum_{i=1}^{n} \left[ V_{i-1} \times \left( C_{i} - C_{i-1} \right) \right]}{A \times t_{n}}$$
(2)

where  $F_D$  is the flux of phosphate release from the sediments during the experimental incubation period (mg m<sup>-2</sup> d<sup>-1</sup>);  $C_{i-1}$  and  $C_i$  are the phosphate concentrations (mg L<sup>-1</sup>) at time  $t_{i-1}$  and  $t_i$  (d); n is the number of sampling;  $t_n$  is the time of exposure (d); A is the surface area of the sediment (m<sup>2</sup>).

Having the  $F_D$  under uncapped and capped conditions, the capping efficiency can be calculated as [37]:

$$CE = 100\% \left( \frac{1 - F_{D_{capped}}}{F_{D_{uncapped}}} \right)$$
(3)



Fig. 3. Adsorption isotherms of phosphate by Phoslock<sup>TM</sup>, ferrihydrite, alum, Z2G1, and N-bentonite under oxic conditions.



Fig. 4. Adsorption isotherms of phosphate by Phoslock<sup>TM</sup>, ferrihydrite, alum, Z2G1, and N-bentonite under anoxic conditions.

# 3. Results and discussion

# 3.1. Effect of DOM on PAC of Phoslock<sup>TM</sup> and Z2G1

While the concentration of DOM increases from 10 up to 40 mg L<sup>-1</sup> the behavior of P-sorption onto Z2G1 is slightly declined (~20% reduction). At higher concentrations of DOM, the sorption capacity of Z2G1 shows a striking drop ~86% (comparing to initial DOM concentration of 10 mg L<sup>-1</sup>) (Fig. 5).

Additionally, while the concentration of DOM increases from  $10 \text{ mg } \text{L}^{-1}$  up to  $30 \text{ mg } \text{L}^{-1}$  the behavior of P-sorption onto Phoslock<sup>TM</sup> is relatively stable (~15% reduction). At higher concentrations of DOM, the sorption capacity of Phoslock<sup>TM</sup> shows a remarkable drop ~50% (comparing to initial DOM concentration of 10 mg L<sup>-1</sup>) (Fig. 6).



Fig. 5. Comparison between measured phosphate concentrations (black symbols, mg L<sup>-1</sup>) and those predicted from chemical equilibrium modeling (red symbols) in water with different humic acid concentrations incubated for 24 h in the presence of 3.6 mg La L<sup>-1</sup> (from 150 mg L<sup>-1</sup> Z2G1 containing 2.4% La).



Fig. 6. Comparison between measured phosphate concentrations (black symbols, mg L<sup>-1</sup>) and those predicted from chemical equilibrium modeling (red symbols) in water with different humic acid concentrations incubated for 24 h in the presence of 7.5 mg La L<sup>-1</sup> (from 150 mg L<sup>-1</sup> Phoslock<sup>TM</sup> containing 5% La).

#### 3.2. P-fraction sediment analysis

The proportion of loosely sorbed P (labile P, the P present in pure water) was about 4% of the TP, the proportion of reductant soluble P was 12%, the proportion of labile organic P together with metal oxide bound Fe was 36%, and the proportion of hardly bioavailable apatite P (P-bound to carbonates and apatite P) and residual P was 23% and 25% respectively (Fig. 7). Therefore, the sequential extraction indicated that the P-fractions can be shorted out at the following descending order: organic P > apatite P > Residual P > reluctant soluble P > labile P. The proportion of bio-available P – that has been defined as the sum of labile P, reluctant soluble P and labile organic P – was 52%.



Fig. 7. P-Fractions of sediment (%) before the incubation experiments.

# 3.3. Effects on sediment P-binding properties with Phoslock $^{\rm TM}$ treatment

The Phoslock<sup>™</sup> restrained P-release from the sediments and the proportion of P mobile in sediments was reduced, the majority of which was transformed into non-reactive species (Fig. 8). The application of Phoslock<sup>™</sup> caused an increase in the mass of P-present in the more refractory "apatite bound P" fraction compared to P mobile (sum labile P, reluctant-soluble P and organic P fractions) of which is likely to permanently reduce the magnitude of P cycling between the sediment and the water-column. Besides, its was noted an increase of P-storage at the residual P-fraction of sediment post-application. Similar conclusions were reported at the studies of Zamparas et al. [19] and Gibbs and Hickey [38].

#### 3.4. Release of phosphate from sediments

The average flux of phosphate from the sediments, under oxic and anoxic conditions respectively, was calculated using Eq. (2). Moreover, the obtained results are shown in Fig. 9. The concentration of P in the overlying of control was estimated at ~1,1 and ~1,7 mg m<sup>-2</sup> d<sup>-1</sup> under oxic and anoxic conditions, respectively. The use of Phoslock<sup>TM</sup> as a P-inactivation agent resulted in about 81% reduction of the phosphate flux from the sediments under oxic conditions, and 82% reduction from sediments under anoxic conditions. Moreover, the applications of modified zeolite (Z2G1), alum and ferrihydrite as capping materials resulted in about 73%, 68% and 84% reduction of the phosphorus flux from the oxic sediments (Fig. 9), and 71%, 75% and 59% reduction of the phosphorus flux from the anoxic sediments respectively (Fig. 9).

Passive capping agents –such as sand, gravel, and clay– can reduce the diffusion rate of nutrients into the overlying water. The thickness and finesse of the layer of passive material, can lower the diffusion rate and enhance the reduction at the sediment-water exchange. Typical sediment capping



Fig. 8. P-Fractions of sediment (%) after Phoslock<sup>™</sup> application.



Fig. 9. Phosphate fluxes from treated sediments with Phoslock<sup>TM</sup>, ferrihydrite, alum, Z2G1, and untreated columns under oxic and anoxic conditions.

thicknesses higher than 5 cm is limiting the applicability of the technique to smaller ponds and reservoirs, owing to the large quantities of capping material required. Phoslock<sup>TM</sup> with small quantity requirements could serve as an active capping agent enabling to reduce the diffusion rate of phosphates from the sediments without unbalancing the equilibrium of biotic and abiotic environment.

## 3.5. Technical and cost evaluation of Phoslock<sup>TM</sup>

According to Table 2 and based on the study of Lewtas et al. [39], it was considered that the variables of "surface area" and "mean depth" are analogously contributing to Phoslock<sup>TM</sup> load and concentration, thus, the representative weighted Phoslock<sup>TM</sup> loads and concentrations were derived from the corresponding weighted values. These weighted values were derived by the combined calculation of [surface areas] and [mean depth] for 15 lakes, which were allocated at the four countries of the United Kingdom, the Netherlands, Germany, and New Zealand, respectively (Table 2). Taken into consideration the aforementioned study of Lewtas

Country	No. of lakes	Weight: [Surface area (ha)] × [Mean depth (m)]	Phoslock load range (tons ha <sup>-1</sup> )	Weighted Phoslock load (tons ha <sup>-1</sup> )	Weighted Phoslock concentration (mg L <sup>-1</sup> )
United Kingdom (UK)	3	9.9–25.2	1.6-3.0	40.6	1,865.4
The Netherlands (NL)	2	28.0-35.2	4.5-5.9	108.1	1,986.7
Germany (G)	9	2.1-150.8	1.9-6.4	303.5	5,550.9
New Zealand (NZ)	1	680.0	0.06	0.06	0.29
Greece (GR), own study	1	1.1	_	3.7 (estimation)	_

Table 2 Phoslock<sup>™</sup> load and concentration upon 15 literature-selected lakes at four countries worldwide

et al. [39] and the fact that at this study the artificial pond covers an area of 0.5 ha of mean depth 2.1 m, it is literature estimated that for mean depth lake of 2.4 m the Phoslock<sup>TM</sup> load can achieve a strong P-binding efficiency. Specifically, it is estimated at application range of 150–200 mg L<sup>-1</sup> (mean value 163 mg L<sup>-1</sup>), and estimated application requirement of 3.5–4.0 tons ha<sup>-1</sup> (mean value 3.7 tons ha<sup>-1</sup>) of Phoslock<sup>TM</sup>, as opposed to natural materials N-Zeolite and N-Bentonite which are requiring multiple amounts without even achieving such P-binding efficiency, as Phoslock<sup>TM</sup> is achieving.

Since the weights are not considered as measured variables, but as relative weights to each other, no normalization was made (since the numerator and denominator coefficients are mutually canceled out). Moreover, it has been literature denoted that the cost of Phoslock<sup>™</sup> treatment depends on various aspects including the application dosage, the amount of monitoring, the biologically available P immobilized, the data analysis, as well as the labor and the equipment costs associated with lake size [39]. At the study of Lewtas et al. [39] it was argued that the calculation of Phoslock<sup>TM</sup> cap material per m<sup>2</sup> it is related to dosage of 100 g Phoslock<sup>TM</sup>/g mobile sediment P. Assuming that the quantity of mobile P in top 5 cm ranges at 50–400 mg kg<sup>-1</sup>, then, the cost ranges at \$0.75–6.02 (showing a linear pricing behavior) respectively [39]. Therefore, at the lake studied in this study (of 0.5 ha surface area, top 10 cm depth, and 203.53 mg mobile P kg<sup>-1</sup>), its dimension equals to 250 m<sup>3</sup> volume of sediment-layer, or 250,000 kg of sediment-layer, and 50.88 kg of mobile sediment P. Then, since the literature-based proper dosage applied is 100 g Phoslock<sup>™</sup>/g mobile sediment P [39], the quantity of Phoslock<sup>™</sup> applied is 5.088 tons (that is 50.88 kg × 100) and the price of  $Phoslock^{\rm TM}$  applied is \$30.53 kg^-1  $Phoslock^{\rm TM}.$ Specifically, this price is literature-verified by Lewtas et al. [39] who argued that the dosage of Phoslock<sup>TM</sup> applied is 100 times higher than the quantity of mobile sediment P treated under the conditions of 50-400 mg mobile P, and costs range \$7.5-60.2, respectively. Therefore, the quantity of 5.088 tons Phoslock<sup>™</sup> applied costs 155.34 thousand dollars.

## 4. Conclusions

In this study, the efficiency of Phoslock<sup>™</sup> as an active capping agent –to prevent the phosphate and ammonium release from anaerobic sediments– was investigated. Phoslock<sup>™</sup> was compared with unmodified bentonite (N-bentonite), natural zeolite (N-zeolite), ferrihydrite, alum, and Z2G1. The application of Phoslock<sup>™</sup>, as a P-inactivation agent, resulted in about ~81% reduction of the phosphate flux from the sediments under oxic conditions. Moreover, the applications of the capping materials resulted in a reduction of the phosphorus flux materials from the sediments at oxic conditions (given in percentages, below): N-bentonite 45%, N-zeolite 9%, alum 68%, ferrihydrite 84%, and Z2G1 73%. In addition, the application of Phoslock<sup>™</sup> resulted in about ~82% reduction of the phosphate flux from the sediments under anoxic conditions. Moreover, the applications of the capping materials resulted in reduction of the phosphorus flux materials from the sediments at anoxic conditions (given in percentages, below): N-bentonite 50%, N-zeolite 4,7%, alum 75%, ferrihydrite 59%, and Z2G1 71%.

At the P-sorption agents Z2G1 and Phoslock<sup>TM</sup>, by increasing the concentration of DOM, the sorption capacity is declined. However, it is noteworthy that in the case of Phoslock<sup>TM</sup> application the sorption capacity is retarded, whereas in the case of Z2G1 the sorption capacity is sharp.

Moreover, Phoslock<sup>™</sup> restrained P release from the sediments and the proportion of P mobile in sediments can be diminished, enabling the transformation of the majority of phosphorus into non-reactive species. The experimental examination of different P-forms co-presented in sediments showed their vital contribution to the P-loadings of the ecosystem, as well as the pronounced role of P-inactivation agent on P-binding properties of sediments. It is also noteworthy that knowing the TP at sediments, it does not forecast the potential ecological damage related to eutrophication. Instead, it was proven the utmost important issue to evaluate the bio-available sediment fractions transported at the water column, which are intensifying eutrophication. Therefore, the long term contribution of P-bound in sediments can be more effectively determined based on different P-fractions. The sum of labile P, reluctant-soluble P, and organic P fractions, is determining the bio-available P (P mobile) and represents the potential release-sensitive P. Subsequently, the reduction of the excess of P-inactivation agents into the water column and sediment, it can prevent the disturbance for filter feeders and benthic fauna respectively. However, it has to be stressed out that the P-reduction goals cannot outmatch potential adverse effects on the aquatic fauna. Another important remark to assess P-fractions in sediments is that these P-forms are strongly influenced by the physicochemical parameters of eutrophic waters; thereby enabling researchers to assess the most appropriate time for water treatment. This targeted timeframe of aquatic environments' remediation can achieve highly efficient removal of P-fractions.

Finally, in economic terms the research outcomes of the study were verified by literature [39], since the concentration of 203.53 mg mobile P kg<sup>-1</sup> falls in the concentration range of 50–400 mg mobile P kg<sup>-1</sup>, while the estimated cost of Phoslock<sup>TM</sup> applied \$30.53 falls in the cost range of \$7.5–60.2.

#### References

- J.W. Lin, Y.H. Zhan, Z.L. Zhu, Evaluation of sediment capping with active barrier systems (ABS) using calcite/zeolite mixtures to simultaneously manage phosphorus and ammonium release, Sci. Total Environ., 409 (2011) 638–646.
- [2] A.L. Solheim, S. Rekolainen, S.J. Moe, L. Carvalho, G. Phillips, R. Ptacnik, W. Ellis Penning, L.G. Toth, C. O'Toole, A.-K.L. Schartau, T. Hesthagen, Ecological threshold responses in European Lakes and their applicability for the Water Framework Directive (WFD) implementation: synthesis of lakes results from the REBECCA project, Aquat. Ecol., 42 (2008) 317–334.
- [3] S.W. Nixon, Coastal marine eutrophication: a definition, social causes, and future concerns, Ophelia, 41 (1995) 199–219.
- [4] E. Union, Directive 2006/7/EC of the European Parliament and of the Council of 15 February 2006 Concerning the Management of Bathing Water Quality and Repealing Directive 76/160/EEC, Official Journal of the European Union, 2006.
- [5] C.W. Hickey, M.M. Gibbs, Lake sediment phosphorus release management-decision support and risk assessment framework, N. Z. J. Mar. Freshwater Res., 43 (2009) 819–856.
- [6] M. Zamparas, I. Zacharias, Restoration of eutrophic freshwater by managing internal nutrient loads. A review, Sci. Total Environ., 496 (2014) 551–562.
- [7] M. Søndergaard, J.P. Jensen, E. Jeppesen, Role of sediment and internal loading of phosphorus in shallow lakes, Hydrobiologia, 506–509 (2003) 135–145.
- [8] M. Kasprzyk, M. Gajewska, Phosphorus removal by application of natural and semi-natural materials for possible recovery according to assumptions of circular economy and closed circuit of P, Sci. Total Environ., 650 (2019) 249–256
- [9] G.D. Cooke, E.B. Welch, S. Peterson, S.A. Nichols, Restoration and Management of Lakes and Reservoirs, 3rd ed., CRC Press, LLC, US, 2005.
- [10] W.M. Bishop, R.J. Richardson, Influence of Phoslock® on legacy phosphorus, nutrient ratios, and algal assemblage composition in hypereutrophic water resources, Environ. Sci. Pollut. Res., 25 (2018) 4544–4557.
- [11] K. Reitzel, J. Ahlgren, A. Gogoll, E. Rydin, Effects of aluminum treatment on phosphorus, carbon, and nitrogen distribution in lake sediment: a <sup>31</sup>P NMR study, Water Res., 40 (2006) 647–654.
- [12] S. Egemose, G. Wauer, A. Kleeberg, Resuspension behaviour of aluminium treated lake sediments: effects of ageing and pH, Hydrobiologia, 636 (2009) 203–217.
- [13] A. Afsar, S. Groves, Comparison of P-inactivation Efficacy and Ecotoxicity of Alum and Phoslock®, PWS Report Number: IR 015/09, Phoslock Water Solutions Limited, Australia, 2009.
- [14] G. Wauer, T. Gonsiorczyk, K. Kretschmer, P. Casper, R. Koschel, Sediment treatment with a nitrate-storing compound to reduce phosphorus release, Water Res., 39 (2005) 494–500.
- [15] M.W. Beutel, Inhibition of ammonia release from anoxic profundal sediments in lakes using hypolimnetic oxygenation, Ecol. Eng., 28 (2006) 271–279.
- [16] G. Ross, T.E. Cloete, Phoslock® Field Trial at K'shani Lake Lodge, Hartbeespoort Dam January - December 2006 Summary of Results, University of Pretoria, South Africa, 2006, pp. 1–15.
- [17] R. Galvez-Cloutier, S.K. Saminathan, C. Boillot, G. Triffaut-Bouchet, A. Bourget, G. Soumis-Dugas, An evaluation of several in-lake restoration techniques to improve the water quality problem (eutrophication) of Saint-Augustin Lake, Quebec, Canada, J. Environ. Manage., 49 (2012) 1037–1053.
- [18] B.M. Spears, M. Lürling, S. Yasseri, A.T. Castro-Castellon, M. Gibbs, S. Meis, C. McDonald, J. McIntosh, D. Sleep, F. Van Oosterhout, Lake responses following lanthanum-modified bentonite clay (Phoslock®) application: an analysis of water column lanthanum data from 16 case study lakes, Water Res., 47 (2013) 5930–5942.

- [19] M. Zamparas, M. Drosos, Y. Deligiannakis, I. Zacharias, Eutrophication control using a novel bentonite humic-acid composite material BephosTM, J. Environ. Chem. Eng., 3 (2015) 3030–3036.
- [20] M. Zamparas, G. Gavriil, F.A. Coutelieris, I. Zacharias, A theoretical and experimental study on the P-adsorption capacity of Phoslock<sup>™</sup>, Appl. Surf. Sci., 335 (2015) 147–152.
  [21] M. Zamparas, M. Drosos, Y. Georgiou, Y. Deligiannakis,
- [21] M. Zamparas, M. Drosos, Y. Georgiou, Y. Deligiannakis, I. Zacharias, A novel bentonite-humic acid composite material Bephos<sup>™</sup> for removal of phosphate and ammonium from eutrophic waters, Chem. Eng. J., 225 (2013) 43–51.
- [22] M.L. Martin, C.W. Hickey, Determination of HSNO Ecotoxic Thresholds for Granular Phoslock<sup>™</sup> (Eureka 1 Formulation) Phase 1: Acute Toxicity, NIWA Project: PXL05201, National Institute of Water & Atmospheric Research Ltd. (NIWA), New Zealand, 2004.
- [23] M. Lurling, Y. Tolman, Effects of lanthanum and lanthanum-modified clay on growth, survival and reproduction of *Daphnia magna*, Water Res., 44 (2010) 309–319.
  [24] D. Akhurst, G.B. Jones, D.M. McConchie, The application
- [24] D. Akhurst, G.B. Jones, D.M. McConchie, The application of sediment capping agents on phosphorus speciation and mobility in a sub-tropical dunal lake, Mar. Freshwater Res., 55 (2004) 715–725.
- [25] H. Klapper, Technologies for lake restoration, J. Limnol., 62 (2003) 73–90.
- [26] M. Zamparas, A. Gianni, P. Stathi, Y. Deligiannakis, I. Zacharias, Removal of phosphate from natural waters using innovative modified bentonites, Appl. Clay Sci., 62–63 (2012) 101–106.
- [27] M. Zamparas, V.C. Kapsalis, A.E. Kanteraki, E. Vardoulakis, G.L. Kyriakopoulos, M. Drosos, I.K. Kalavrouziotis, Novel composite materials as P-adsorption agents and their potential application as fertilizers, Global Nest J., 21 (2019) 48–57.
- [28] M. Zamparas, M. Drosos, I.K. Kalavrouziotis, Sorption of phosphate from innovative composite material focusing on physicochemical interactions, Desal. Wat. Treat., 151 (2019) 212–218.
- [29] A. Gianni, M. Zamparas, I.T. Papadas, G. Kehayias, Y. Deligiannakis, I. Zacharias, Monitoring and modeling of metal concentration distributions in anoxic basins: Aitoliko Lagoon, Greece, Aquat. Geochem., 19 (2012) 77–95.
- [30] M. Zamparas, Y. Deligiannakis, I. Zacharias, Phosphate adsorption from natural waters and evaluation of sediment capping using modified clays, Desal. Wat. Treat., 51 (2013) 2895–2902.
- [31] R.M. Cornell, U. Schwertmann, The Iron Oxides: Structure, Properties, Reactions, Occurences and Uses, Wiley-VCH, New York, 2003.
- [32] W. Verweij, Manual for CHEAQS Next, A Program for Calculating CHemical Equilibria in AQuatic Systems, PRO Version 2013.1, 2013.
- [33] E. Tipping, M.A. Hurley, A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances, J. Soil Sci., 39 (1988) 505–519.
- [34] J.E. Sonke, Lanthanide--humic substances complexation. II. Calibration of humic ion-binding model V, Environ. Sci. Technol., 40 (2006) 7481–7487.
- [35] M. Hupfer, R. Gächter, R. Giovanoli, Transformation of phosphorus species in settling seston and during early sediment diagenesis, Aquat. Sci., 57 (1995) 305–324.
- [36] Y. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.
- [37] E. Eek, O. Godøy, P. Aagaard, G.D. Breedveld, Experimental determination of efficiency of capping materials during consolidation of metal-contaminated dredged material, Chemosphere, 69 (2007) 719–728.
- [38] M.M. Gibbs, C.W. Hickey, Flocculants and Sediment Capping for Phosphorus Management, Chapter 7, D.P. Hamilton, K.J. Collier, J.M. Quinn, C. Howard-Williams, Eds., Lake Restoration Handbook: A New Zealand Perspective, Springer Nature, Switzerland, 2018, pp. 207–266.
- [39] K. Lewtas, M. Paterson, H.D. Venema, D. Roy, Manitoba Prairie Lakes: Eutrophication and In-Lake Remediation Treatments Literature Review, International Institute for Sustainable Development (IISD), Available at: https://www.iisd.org/sites/ default/files/publications/manitoba-prairie-lakes-remediationliterature-review.pdf.