

**Novel composite materials as P-adsorption agents and their potential application
as fertilizers**

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Abbreviations

PR: phosphate rock

P-AA: Phosphorus Adsorption Agent

DW: dry weight

HMP: humic metal phosphate

Abstract

The main objective of this study is to review the role of phosphorus in fertilizers, emphasizing in phosphate rock which is the primary source for phosphate fertilizer, with reference to harmful heavy metals as a consequence of their use. Simultaneously, this study examined the use of P-Adsorption agents as a potential application in agriculture, as 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 Phosphorus Adsorption Agent (P-AA) leading to environmental protection and conservation of natural resources. Finally, this study highlighted new aspects that support P bioavailability of Humic-metal-P (HMP) in soils, correlating with novel materials in water purification.

1. Introduction

Eutrophication in natural water systems has recently become a major environmental issue that threatens all kind of living organisms. Phosphate enters the aqueous environment through both natural and anthropogenic activities, such as erosion, mining, agriculture and industry. Cultural eutrophication has been considered as one of the major water pollution issues all over the world, resulting in harmful algal blooms and subsequently in depletion of dissolved oxygen as well as alteration of ecosystem community structure (Kagalou et al., 2008; Pinckney et al., 2001).

Phosphorous, due to its widespread bioavailability, is responsible for the eutrophication of water bodies, resulting in increased aquatic plant and algal growth (Dodds et al., 2009). In addition, P-control is more feasible than that of nitrogen (N) 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 biosphere, including stratified rivers, lakes, reservoirs, estuaries and coastal waters (Smith and Schindler, 2009; Solheim et al., 2008).

In agriculture, phosphorus (P) is an essential macronutrient that can limit normal plant growth if not provided through soil at appropriate quantities of fertilizers. For soils having low concentration of P, this nutrient must be applied in either organic or inorganic forms to optimize crop yield performance. Organic P sources, such as crop residues and animal manure, have low P content, and due to required massive amounts, their use is economically unfeasible (Chien et al., 2011).

In the relevant literature, there are plentiful research studies devoted to regulating ecosystems of high environmental interest via optimum P stewardship. It is particularly noted that chemical lake 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. Recently, the use of several solid adsorbents was considered as a remedy for reducing the P levels (Zamparas et al., 2013). Some of the materials investigated included iron oxides, red mud, fly ash and carbonates (Haghseresht et al., 2009; Huang et al., 2010; Su et al., 2011; Wanchun et al., 2011). While collectively all these materials may have numerous beneficial applications, each one material considered separately 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.

Nowadays, Alum, Calcite, PhoslockTM (lanthanum modified clay) and Modified Zeolite (Z2G1) are those materials commonly used to restore eutrophic water bodies with the latter two constituting the most innovative remediation materials. A recently introduced novel composite humic-acidic material, namely BephosTM, was equally effective with the above materials, bearing as little as possible negative effects for biotic and abiotic factors (Zamparas et al., 2013).

The main objective of this study is to assess the role of phosphorus in fertilizers, emphasizing in phosphate rock which is the primary source for phosphate fertilizer, with reference to harmful heavy metals as a consequence of their use. Simultaneously, this study examined the use of P-Adsorption agents as a potential application in agriculture, as the adsorbed phosphorus can be used as fertilizer or enriching soil conditioners. Finally, this study highlighted new aspects that support P bioavailability of Humic-metal-P (HMP) in soils, correlating with novel materials in water purification.

2. Biogeochemical cycle of P

Phosphorus (P) is the second most important macronutrient for plant growth and nutrition. It is a non-renewable resource and the demand of P in the agricultural production is increasing rapidly. The bioavailability of phosphorus is precisely low due to its high fixation rates and slow diffusion in soils, making phosphorus a limiting nutrient for agricultural production (Damon et al., 2014; Gupta et al., 2014).

As a non-metallic chemical element, P is a key element for plant growth and a series of physiological activities that are related to energy transformations. As a mineral element, the multivalent pnictogen P is almost always present within inorganic phosphate rocks in its maximally oxidized state. Globally, agriculture is the primary user of phosphorus, accounting ~90% of the total world demand. Phosphorus is crucial for food production as all plants need an adequate amount of it (Damon et al., 2014).

Besides, phosphorus is essential for life. It is a component of DNA, RNA, ATP, and also the phospholipids that form all cell membranes. Moreover, P is included in a number of cellular processes, including respiration, photosynthesis, energy storage and transfer, cell division and cell enlargement. Ample amount of phosphorus is required for seed formation, root formation, development and plant growth, and improvement of crop quality. Plants uptake P from soils entering it into the food chain and disposing it to soils as decayed organic residue. Most of the phosphates are prevalent in the form of organic compounds, incorporated by living systems and upon their release to the environment, they constitute components of soil organic matter, which is then transformed by soil microorganisms in inorganic forms. P exists in various forms in soils. Nevertheless, three different P pools (that of solution, active and fixed) control the overall P-cycle in nature. Plants take up phosphate from soil solutions, which include P in the inorganic (mainly orthophosphate) form, and small amounts of organic P. Soil solution contains a very small fraction of the total P in soil, which needs to be refilled in time, as growing plants consume the soluble source faster. However, P in the form of the active phosphorus pool is the main available source for plants, released to the soil solutions. It is mostly adsorbed to small particles in the soil along with the chemical elements of Ca, Al, and inorganic P pool easily

mineralizes by the biogenic activities in soil. The fixed P pool contains inorganic phosphate compounds that are very insoluble, as well as organic compounds that are resistant to mineralization by microorganisms in the soil. Phosphate in soils is existent for years without being bioavailable to plants, having thus very poor impact on soil fertility. The inorganic phosphate compounds in this fixed P pool are more crystalline in structure, while less soluble than P compounds of the active P pool. However, some slow conversion between the fixed P pool and the active P pool does occur in soils (Delgado et al., 2002).

3. Phosphorus fertilizers in soil

Phosphorus does not occur in free forms, but it is incorporated in many minerals, such as phosphates. Historically-important but limited commercial sources were organic, such as bone ash and guano. Apatite, the inorganic phosphate rock, is the primary commercial source of this element. The origin of the phosphate is very important, since various heavy metals may enter into the agricultural land along with the fertilizer. Moreover, soil particles may act as sink and source of phosphate to the surrounding water, depending on various physicochemical factors.

The fixed pool of P also includes mostly insoluble inorganic phosphate compounds that are durable to microorganisms into the soil. Although phosphate in this pool may remain in soils for years, a slow transformation between the fixed P pool and the active P pool does occur (Bowsher et al., 2017).

There are some restrictions in P bioavailability in soils predicating plants' development (Bertin et al., 2003; Gupta et al., 2014). The bioavailability of P in most of the soils is in the range of $1\mu\text{mol/L}$. However, plants require $\sim 30\mu\text{mol/L}$ to reaching yield maximum. The concentration within plant cells ($1\text{--}10\text{ mM}$) is 10.000--

fold higher than the concentration of the natural soil solution, which means that P-uptake into plant occurs against a steep concentration gradient (Gupta et al., 2014; Sashidhar and Podile, 2010).

In nature, P is usually present as metal oxide ($P_{\text{inorganic}}$) of phosphate rocks (white phosphorus and red phosphorus) or organic form (P_{organic}) (Hansen et al., 2004). $P_{\text{inorganic}}$ composes almost 35–70% of the total P in soil with apatite, strengite, and variscite being the major phosphate minerals. Nevertheless, release of available P from primary minerals through weathering is too slow for plant life (Sashidhar and Podile, 2010). Secondary P minerals form insoluble chemical complexes, embedding elements like aluminum (Al), calcium (Ca) and iron (Fe) (Gupta et al., 2014; Shen et al., 2011). Nonetheless, dissolution rates of Al, Ca and Fe-salts depend on soil pH and particle size of minerals. Solubility of Al and Fe salts increases invariably with an increase in soil pH and decreases in case of Ca salts. Moreover, oxides and hydroxides of Al/Fe along with the clay minerals adsorb P in soils, due to several adsorption sites in the clay surface (Luengo et al., 2006; Varadarajan et al., 2002).

Fertilizers are essential for plant growth providing nutrients in varying concentrations. It is estimated that 30–50% of crop yields in different parts of the world are attributed to natural or synthetic commercial fertilizers. Fertilizers normally consist of six macronutrients, viz., nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S); and eight micronutrients: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn) and nickel (Ni).

4. Phosphate rock as a primary source for phosphate fertilizer

Phosphate rock (PR) is the raw material used in the manufacture of most commercial phosphate fertilizers on the market. However, properties of the PR vary

extensively according to their source and physicochemical properties. Phosphorus pentoxide (P_2O_5) is the basic constituent of the PR. Grade of PR containing P_2O_5 is around ~25%, with a higher content ~37% to be desirable for commercial production as a phosphate fertilizer.

Sedimentary marine phosphate rock deposits are the main resources (~75%) of world's phosphate budget, followed by igneous and weathered deposits (~15–20%) and biogenic resources (~1–2%). Primary phosphate minerals include Fluor-apatite ($Ca_{10}(PO_4)_6F_2$), found in igneous and metamorphic environments, hydroxy-apatite ($Ca_{10}(PO_4)_6(OH)_2$), found in biogenic deposits, and carbonate-hydroxy-apatites ($Ca_{10}(PO_4, CO_3)_6(OH)$), found in caves, as part of bird and bat excrements (Shen et al., 2011).

However, Ores of the phosphate rock also restrain many toxic metals and radionuclides in varying concentrations that are transferred to phosphate fertilizers or tailings in production processes and eventually to soils. Depending on the source, harmful heavy metals, like cadmium (Cd), arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), and radionuclides, like uranium (U), radium (Ra), and thorium (Th) may be introduced into the soil along with the fertilizer, which are then absorbed by growing crop plants, causing significant health-related issues (Mortvedt et al., 1981). However, the concentration of such contaminants varies considerably especially in the case of metals. It has been noted that application of P fertilizer at a rate of ~20 kg P ha^{-1} in soil heads to an impute of up to ~0.01 g $ha^{-1} y^{-1}$ of Hg and ~25 g $ha^{-1} y^{-1}$ of Cr (Shen et al., 2011). Moreover, contamination of Cd in the environment through phosphate fertilizer is also considered a major issue in several western countries and China. It is estimated that 54–58% of the Cd found in the environment comes from the application of mineral phosphate fertilizers. More refined P-based fertilizers, like

diammonium phosphate (DAP), and triple superphosphate (TSP), are available in the market having a higher price range.

Phosphate rock mining does oppose several concerns over environmental impacts, like landscapes transformation, extraction and pollution of a huge amount of water from adjoining water bodies and contamination with heavy metals and radioactive materials. As a normal constituent of earth's crust, rock phosphate deposits usually contain several million tons of uranium which leads to potential exposure of the environment to radiation.

There is an increasing concern over the use of P fertilizers containing heavy metals, especially cadmium (Cd). Heavy metal uptake by plants is one possible entrance path into the human food chain through consumption. Numerous greenhouse and field studies have been conducted with Cd because it is the heavy metal of most environmental concern in terms of adverse effects from the long-term application of fertilizers. There have also been numerous studies that investigated the Cd impacts from the use of P fertilizers (Chien et al., 2010). Particularly, Grant et al. (1998) noted that Cd concentration of P-based fertilizers, application rate, soil type, and crops growth are all important factors when considering the relationship between added Cd and plant uptake (Grant et al., 1998). Besides, the source of Cd in P fertilizers is PR, thus, depending on the sources of PR, the Cd-associated content with P in apatite minerals can vary widely (Table 1).

Table 1. Cd concentrations of P and Phosphate rock (PR) from various PR sources (adapted from Chien et al., 2010).

Source of PR	mg Cd/kg P	mg Cd/kg PR
Australia (Duchese)	7	50
Australia (Christmas Island)	43	275
Banaba (Ocean Island)	99	563
China (Yuam)	4	35
Egypt (Quseir)	8	61
Israel (Arad)	12	85
Israel (Zin)	32	228
Jordan	6	27
Mexico	8	57
Morocco (Boucraa)	38	240
Nauru	100	641
Peru	11	84
Rusia (Kola)	0.2	1
South Africa	4	23
Tunisia (Gafsa)	38	108
USA (North Carolina)	47	311

5. Materials for Lake Remediation

5.1. 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 $[Al_2(SO_4)_3]$ is a preferable flocculant used in Europe and the United States (Cooke DG, Welch EB, Peterson SA, 1993; JEPPESEN et al., 2005). Because Al hydroxides like iron hydroxides – 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 as an active barrier system that captures and inactivates 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 extent 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. 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 $[Al(OH)_3]$ 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 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 particular application dose ensures the optimal maximum formation of the $[Al(OH)_3]$ -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 DG, Welch EB, Peterson SA, 2005; Zamparas and Zacharias, 2014).

Apart from 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. As far as sediment toxicity is discussed, it can be caused by alum, while a critical issue is the tolerance thresholds for sediment living species between different thicknesses of alum (Gibbs et al., 2010).

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 DG, Welch EB, Peterson SA, 1993). This 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 re-treatment to be necessary (Welch and Cooke, 1999). Nevertheless, an alum treatment may not be effective or have very limited time effectiveness, in cases where lakes are covered with macrophytes which during decomposition release high amounts of P into the water column (Özkundakci et al., 2011; Zamparas and Zacharias, 2014).

5.2. Calcite (ESCal™)

Calcium carbonate (CaCO_3) is an effective natural cleaning process in hardwater lakes that act 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 that 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 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; Ross and Cloete, 2006).

Calcite has a few advantages as a phosphorus binding agent. It is an easily affordable and available non-toxic material and exists naturally in the sediments. Moreover, calcite and P co-precipitation is a natural process. During biogenous calcite precipitation, particulate P attached to the cells ends up to the sediments because of the simultaneous phytoplankton precipitation by calcite precipitating crystals. At the same time, soluble reactive phosphorus (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. 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).

5.3. Modified zeolite (Z2G1)

A modified zeolite named Z2G1 has been developed by Scion, Rotorua, New Zealand and manufactured by Blue Pacific Minerals Ltd as phosphate adsorption 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 able to remove both P and N. Z2G1 does not release Al into the water column. The increased concentration of potentially bioavailable Al in the material could have environmental effects, although, based on a laboratory assay, its toxicity is minimal (Vopel et al., 2008).

A continuous flow incubation system (CFIS) was applied to assess Z2G1 in terms of efficacy and sustainability regarding flux measurements in simulated stratified (anoxic) and mixed (aerobic) conditions. 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 (Vopel et al., 2008). 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 (Gibbs and Özkundakci, 2010; Zamparas and Zacharias, 2014).

In the relevant literature, the Z2G1 modified zeolite was used in an application in Lake Okaro in September 2007. Lake Okaro is a small eutrophic lake (surface area 0.32 km²) and 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. The results showed that modified zeolite Z2G1 was able to completely remove P from the water column of Lake Okaro (Gibbs and Wilson, 2007). The higher dose rate of the 1–3mm grain size material was more effective in removing P than the lower dose rate in natural anoxic lake water. Moreover, from the use of varying grain size 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. This is because of the greater active surface area that a finer material has over a coarser one.

Regarding the metal fluxes in the sampled cores between the sediment and the water, these 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 measured at the time of the core sampling. This could be because of the bottom stir up during the core sampling (Gibbs and Wilson, 2007). Additionally, a shift of the reduction–oxidation (redox) boundary can 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, caused because of the zeolite substrate of the Z2G1, is a good-cation absorber.

In parallel, it was noted 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 this lake, the permanently aerobic littoral zone above 5 m is the only habitable area of the lake bed for most of the year. Hence, for this life-supporting zone to be protected Z2G1 should be applied only below that depth and fortunately, this can be done accurately because of its granular composition and its advantageous settling speed.

From this study, it is established that the Z2G1 modified zeolite is an adequate sediment capping material for sediment phosphorus release blocking in anoxic conditions, at the tested dose rates on the sediment cores. Furthermore, the material absorbed cationic metals which mean that the cation retaining abilities of the zeolite were still in effect and there was an 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 it can be noted that the material is potent in blocking the N and P release from the lake sediments, it remains uncertain to draw general conclusions from these to an actual whole lake trial (Gibbs and Wilson, 2007; Özkundakci et al., 2011). Conclusively, the Z2G1 needs to be tested in that way to give more precise 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.

5.4. Phoslock™

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. Moreover, the molar ratio of La to phosphate anion is 1:1, as resulting from the chemical reaction of: $\text{La}^{3+} + \text{PO}_4^{-3} \rightarrow \text{LaPO}_4$. The solubility product (K_{sp}) 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. The complex is known to be so insoluble in low La and phosphate concentrations and low pH conditions (Diatloff et al., 1993).

The research into the use of lanthanum for reducing phosphates has revealed that, depending on the concentration and the rate of application, this component can be toxic to aquatic life. 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 mechanism enabled the development of a La-modified bentonite 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 that are common oxyanions. The rare earth element in the clay structure can either react with the phosphate anion in the water body or remain in that structure under a vast range of environmental conditions (Zamparas et al., 2015b). Although La ions could be toxic to some aquatic organisms, particularly cladocerans such as *Daphnia* (Barry and Meehan, 2000), hence the potential liberation of La ions from the bentonite implies a significant environmental risk (Akhurst et al., 2004), Phoslock™ has been classified

as not hazardous (Martin and Hickey, 2001). A leachate experiment showed La could be released from the material, but in only insignificant quantities of 0.13–2.13 $\mu\text{g/L}$. In this scenario, provided Phoslock™ can be applied in a worst-case dose of 250 mg/L (Lürling and Tolman, 2010).

According to Liu et al. (Liu et al., 2009) 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 0.5 kg/m² application rate of Phoslock™ 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/m²d, where negative values indicate P adsorption by Phoslock™.

Table 2. Comparison of phosphate adsorption capacity (q_m) of tested material with some literature values (adapted from Zamparas et al., 2013).

Material	qmPhosphate (mg/g)	pH range*
Alum	12–13.8	5.5–8.2
Ferric hydroxide	16.9	5.5–8.2
Phoslock™	10.5	5–7
Al-bentonite	12.7	3–5
Fe-bentonite	11.2	5–7
Iron oxide tailing	8.6	3.2
Goethite	6.4	5–6

Red mud	0.8	2
Modified fly ash	9.1	4–10
Bephos™	26.5	5–9

* pH range under which the maximum efficiency was measured.

5.5. Bephos™

Bephos™ (nomination is originated from the words “Bentonite” and “phosphorus”) is a novel low-cost composite material embedding Fe, Cu ions and humic acid in the interlayer space of a natural bentonite. This material is derived from a novel precursor material Zenith/Fe (Zamparas et al., 2012) that it is absent upon the addition of humic acids. Its properties have been studied in detail elsewhere (Miltiadis Zamparas et al., 2013). The point of zero charge (PZC) of the material is pH 8.8. This means that the positive charges of bound Fe^{3+} , Cu^{2+} , and the clay surface groups counterbalance the negative charges of the HA. From the functional point of view, the existence of both positively-charged sites, e.g. Fe^{3+} , Cu^{2+} , surface (+) groups as well as negatively charged sites (e.g. due to HA) render Bephos™ the capability to bind both anionic species e.g. PO_4 , as well cationic species, e.g. NH_4^+ . In addition, the important information from XRD data (Zamparas et al., 2013) is that Fe and Cu ions have been incorporated in solid crystalline phases, while other phases have been depleted from the pristine clay. Humic acid is rich in carboxylates which act as strong anchoring sites for Fe and Cu ions. Thus, the formed COO-Fe, COO-Cu sites behave as coordination sites for P and N due to the known strong affinity of Fe and Cu to coordinate P and N atoms. Bephos™ is a novel composite material where Fe, Cu, HA and clay lamellas are strongly interconnected (Zamparas et al., 2015a).

Moreover, the modified clay was highly efficient for simultaneous phosphorus removal from water at the wide range of pH value 5 to 9. Its efficiency is maintained at alkaline pH (pH 8–9) in contrast with most materials, whose ability in adsorbing phosphorus drops dramatically under these conditions. This is of particular importance as in eutrophic waters the pH value ranges between 8 and 9. In addition, the adsorption capacity for phosphate and ammonium followed the order: Fresh water > brackish > marine water (Zamparas et al., 2013).

6. The role of humics in agriculture

Humic acids are complex organic molecules that are formed by the breakdown of organic matter. They influence soil fertility through their water-holding capacity effect on soil, making important contributions to soil stability and fertility, leading to exceptional plant growth and nutrient uptake. Plant growth is also improved by the ability of the plant to uptake and receive more nutrients. Humic acid is especially beneficial in freeing up nutrients in the soil to become available to the plants. Organic acids such as citric, malic, and oxalic—being released as exudates— can form complexes with the Fe or Al phosphates, and thereby enhance the uptake of plant available phosphates. It is predicted that these chelators are more effective in P mobilization comparing to other elements. Even, P adsorption sites on the soil particle may be blocked by forming complexes with cations on soil mineral surfaces (Urrutia et al., 2014). For instance when an aluminum and a phosphorous are bounded together, humic acid detaches them, making the phosphorus available for the plant (Fig 1). Humic acid is also especially important because of its ability to chelate micronutrients increasing their bio-availability (Delgado et al., 2002).

In the relevant literature there are also numerous studies that co-evaluated several humic and fulvic substances, metals and P, that reported the formation of

HMP in solution, as well as their presence in lakes, freshwaters, and soil solutions (Delgado et al., 2002; Leytem and Westermann, 2003; Urrutia et al., 2014).

Regarding the availability of HMP-complexed P for plant uptake, a number of tests showed that diverse plant species can acquire P from HMP, at least at the same level as that can be uptaken from conventional P sources (monopotassium phosphate, KH_2PO_4) (Urrutia et al., 2014). Although plants receiving HMP are developing similar or higher dry matter than control plants fed with KH_2PO_4 , the concentration of P in the leaf of HMP-treated plants is significantly lower than that of control plants fed with KH_2PO_4 . This fact indicates that the physiological utilization efficiency of plants for HM-P was higher than for KH_2PO_4 -P.

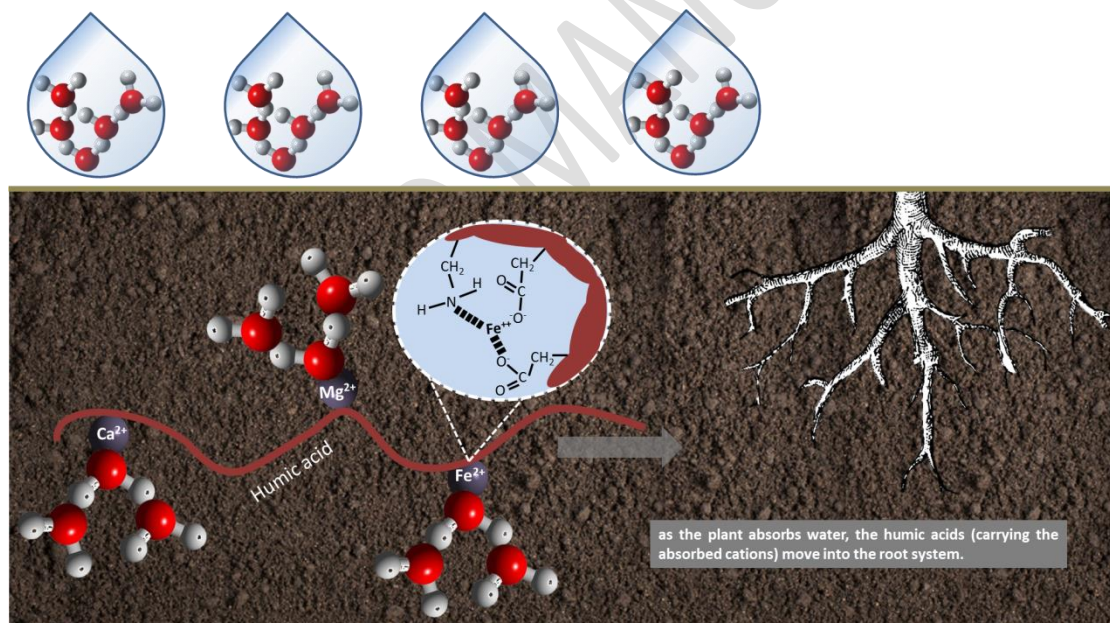


Figure 1. Humic acid transport nutrients close to the plant roots.

This case is also based on the fact that the nutrient-uptake efficiency, which is the ratio between the nutrient taken up by the plant and the nutrient available in the

rhizosphere, is higher in those plants receiving $\text{KH}_2\text{PO}_4\text{-P}$. P-included in HMP is not in a free form but in complexed form. Therefore, plant roots have to compete with HMP to uptake HMP-complexed P. It also might involve the activation of stress responses under conditions of P deficiency, with the exertion of additional energy. In order to reduce this energy-intensive demand, plants can activate specific mechanisms to optimize the physiological and metabolic utilization of P-presented in the shoot (Urrutia et al., 2014).

This explains why plants receiving P from HM-P have the same shoot DW as those fed with P from KH_2PO_4 but having a lower P concentration in the leaf. Therefore, P-utilization efficiency is higher in plants fed with HMP complexes, while P-uptake efficiency is higher for plants fed with monopotassium phosphate (KH_2PO_4). The aforementioned results suggest that fertilizers containing HMP support higher P efficiency of plants than those based on water-soluble P.

7. Potential usefulness of lake restoration materials in agriculture

In the previous sections, P-adsorption materials have been studied only for lake restoration. However, there is the possibility to recycle these materials for agricultural use. Most of these materials are clay-based, so their addition to soil may not disturb the ecosystem but improve its cation exchange capacity (CEC). Materials like BephosTM contain also monovalent iron and copper that could act like micro-nutrients. However, their most advantageous feature is their ability to retardedly adsorb phosphorous and, then, to slowly release it. Specifically, it has been reported that BephosTM can uptake 26.5 g kg^{-1} phosphate, gradually releasing 5.3 g kg^{-1} every 6 months (Zamparas et al., 2013). Considering the need of phosphorous in crop fields that is $\sim 50\text{ kg ha}^{-1}$ per year (for the crops of wheat, maize, and tomato), the need of

5tn ha⁻¹ of BephosTM is estimated, that would retardedly release the necessary phosphorus over a period of more than 3 years. BephosTM is not just a modified clay, but it can be considered as a modified organo-mineral clay since it contains humic acid (Zamparas et al., 2013). The application of 5tn ha⁻¹ BephosTM in the field would result in the addition of 6 kg ha⁻¹ humic acid. However, the aforementioned results are obtained for BephosTM, because there is lack of information about other P-adsorption derivatives. Moreover, the P-release ratio can be measured in water, not in soil. It is also noteworthy noting the need for lowering the cost of these materials since these are proven effectively recyclable in agriculture after being used in lake restoration. However, further research is needed to estimate the actual release of bound phosphorous of these materials in soil and their interaction mechanisms with mycorrhizal (Cozzolino et al., 2013).

8. Conclusions

Humic-metal-phosphate complexes can decrease phosphate fixation in soils and increase plant growth and phosphate uptake. Phosphorus fertilizers, containing humic-metal-phosphate complexes, are proven effective to improve plant growth and P uptake with respect to conventional fertilizers, such as single superphosphate. The values of parameters related to plant phosphorus-utilization efficiency (PUt E) suggest that the regulation of root acquisition of phosphate from these complexes could introduce a controlling system for the optimization of metabolic P utilization in the shoot, and another controlling system that involves stress responses of roots under phosphorus deficiency.

The properly designed application of chemical restoration methods can reduce the concentration of nutrients and improve the water quality in eutrophic ecosystems.

However, the demand for fertilizer is increasing worldwide, contrarily to the global phosphate supply shortage (Cozzolino et al., 2013). It seemed that the application of phosphate fertilizers has reached its limits and it is necessary to be transformed in a sustainable way. Moreover, phosphate fertilizers losses not only reduce nutrients efficiency, resulting in low plant yields, but also create adverse impacts on the environment (Chen et al., 2018). Thus, the use of P-adsorption agents (Behrens and Appel, 2016; Ramasahayam et al., 2012) can prove alternative methods in which 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 Phosphorus Adsorption Agent (P-AA) leading to environmental protection and conservation of natural resources. P-AA for removal and recovery of phosphorus from eutrophic water bodies are a promising technique but require further study in its feasible scaling up to the agricultural sector worldwide.

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