



KTH Architecture and  
the Built Environment

**PHOSPHORUS RECYCLING FROM  
WASTEWATER TO AGRICULTURE USING  
REACTIVE FILTER MEDIA**

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Victor Cucarella  
Stockholm, May 2007



## LIST OF PAPERS

This thesis is based on the following papers, which are referred to in the text by their Roman numerals and can be found in Appendix 1-3.

- I. Cucarella, V., Zaleski, Z., Mazurek, R., 2006. Phosphorus sorption capacity of different types of opoka. *Journal of Polish Agricultural Universities* (accepted for publication).
- II. Cucarella, V., Zaleski, Z., Mazurek, R., 2007. Fertilizer potential of calcium-rich substrates used for phosphorus removal from wastewater. *Polish Journal of Environmental Studies* (accepted for publication).
- III. Cucarella, V., Zaleski, Z., Mazurek, R., Renman, G., 2007. Effect of reactive substrates used for phosphorus removal from wastewater on the fertility of acid soils. Submitted to *Bioresource Technology*.

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## ABSTRACT

This thesis focused on testing the suitability of reactive filter media used for phosphorus (P) removal from wastewater as fertilizers, thus recycling P to agriculture. The work compared the P sorption capacity of several materials in order to assess their suitability as a source of P for plants. The selected materials (Filtral P, Polonite and wollastonite) were saturated with P and used as soil amendments in a pot experiment. The amendments tended to improve the yield of barley and ryegrass compared with no P addition. The amendments also increased soil pH, P availability and cation exchange capacity in the studied soils. The substrates studied here can be of particular interest for acid soils. Of the materials studied, Polonite appears to be the most suitable substrate for the recycling of P from wastewater to agriculture.

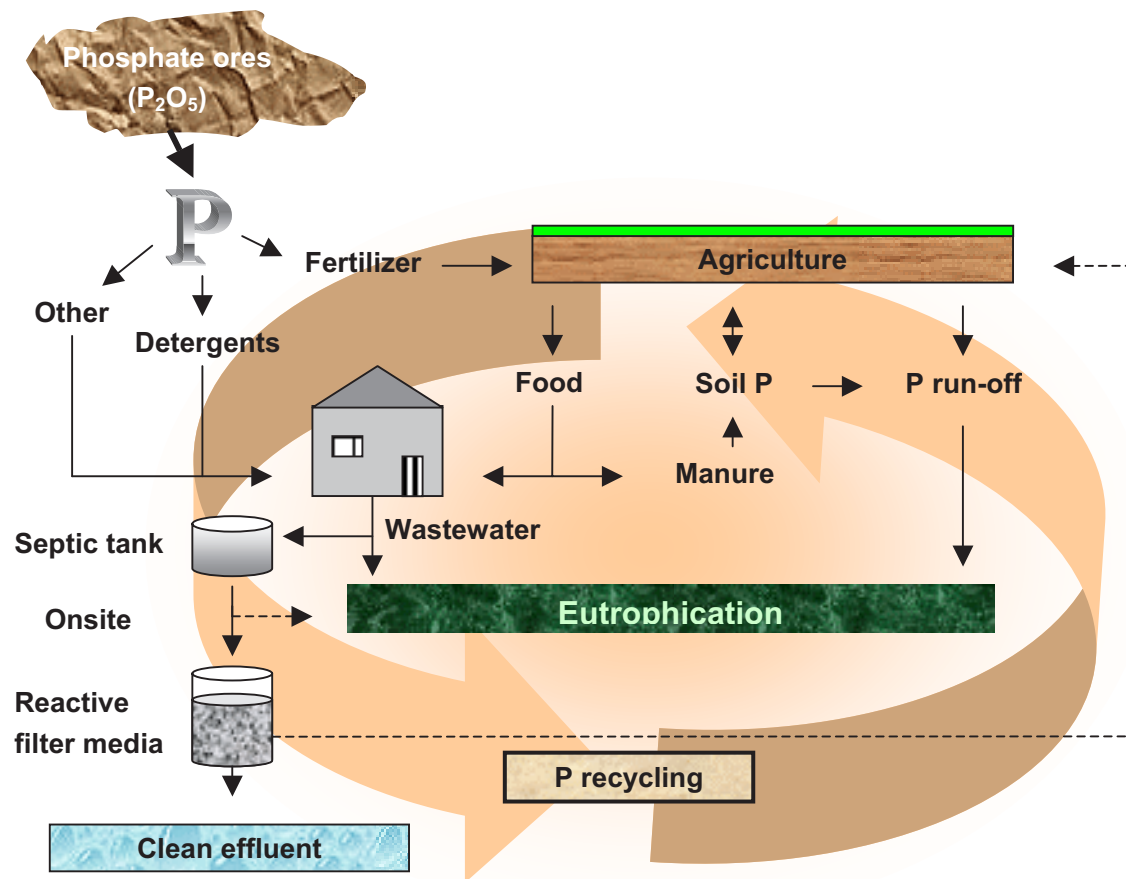
**Keywords:** Filtral P, phosphorus, Polonite, recycling, sorption, wollastonite

## 1 INTRODUCTION

In a sustainable society, the existing resources must be managed appropriately, in particular, those that are finite and non-renewable. This is the case for phosphorus (P), which is a key element in all living forms as a component of cell membranes, nucleic acids and ATP (adenosine triphosphate); and which is therefore, essential for crop plants. The increasing world population is demanding and increase in crop productivity and phosphate rock deposits are being progressively depleted for the fertilizer industry to meet this demand (Steen, 1998). The excessive application of phosphate fertilizers together with P from increasing human waste discharges has altered the natural P cycle, causing the excessive accumulation of P in waters and sediments. Conventional wastewater treatment has significantly reduced point sources of P pollution in the last two decades. On the other hand, large volumes of sludge have been deposited in landfills or incinerated, thus postponing the pollution problem and losing its potential as a nutrient (Günther, 1999). Attempts for the recovery of P from wastewater, although technically possible, are often economically unfeasible, especially in small communities and rural areas. In such places, onsite treatment facilities such as constructed wetlands and wells or infiltration beds are often used

instead of conventional sewage systems (Jantrania and Gross, 2006). Reactive materials with a high affinity for P are used as filter media for improving the quality of septic tank effluents. Such media can efficiently retain P by sorption processes on the surface of the material. The advantage of using reactive media is that, once saturated with P, they can be used as soil amendments in agriculture, thus recycling the nutrients (Fig. 1).

The amendments may be directly applied to soils if the content of toxic compounds and pathogenic bacteria does not restrict their use according to the EU directive on the use of sludge in agriculture (86/278/EEC) or other criteria. The fertilizer potential of such amendments depends on the amount and form of P in the substrates and the soil P status. In addition to direct P supply for plant uptake, the reactive substrates might have other potential benefits for soils and crops, such as increasing the pH of acid soils or improving soil structure and conditioning and thus enhancing soil fertility. A large number of reactive substrates with the ability to remove P from wastewater are described in literature (e.g. Johansson Westholm, 2006). However, little is known about their suitability as soil amendments and their effectiveness as fertilizers. Therefore, the effect of such substrates on soils and plants requires further investigation.



*Figure 1. Sustainable P cycle*

## 1.1 Objectives and scope

The objective of this thesis was to evaluate the fertilizer potential of reactive substrates used for the removal of P from wastewater. A great deal of the work focused on opoka and its commercial derivative product Polonite, since previous work has shown its efficiency and promising suitability as a fertilizer.

The first investigation studied the variation in the composition of opoka deposits and its influence on P sorption ability and sorption mechanisms and, in particular, the relationship between the content and form of Ca and the P-sorption capacity of three different deposits of opoka, wollastonite tailings and the commercially available products Polonite and Filtra P.

The second stage and main part of the work focused on estimating the fertilizer potential of three selected materials, Filtra P, Polonite and wollastonite tailings, saturated with P in infiltration columns. The materials were selected for their known ability to remove P from wastewater. They are characterized by a high content of Ca and alkaline pH values. The aim was to study the effect of the P-enriched substrates when used as soil amendments on yield and composition of barley and ryegrass, and to evaluate the effect of the amendments on soil pH, availability of P, K and Mg, hydrolytic acidity and cation exchange capacity in soils after harvest.

## 2 PHOSPHORUS IN THE ENVIRONMENT

In nature, P is released to the environment by weathering of rocks and is transported by surface runoff until it reaches water bodies and soils, thus becoming available to all living organisms. However, the increasing demand for P, mainly from agriculture, has altered the natural cycle, resulting in the progressive depletion of phosphate ores and an increase in P concentrations in waters and sediments.

### 2.1 Phosphate resources and extraction implications

Phosphorus is the eleventh most abundant element in the lithosphere. Phosphate rock deposits are found throughout the world, the largest reserves being in Morocco, USA and China. There are two types of deposits, igneous and sedimentary, widely differing in mineralogical, textural and chemical characteristics. The most prevalent phosphate minerals in these rocks are species of apatite. Igneous rock is generally low grade (low phosphate concentration) and therefore, about 80% of world phosphate is derived from sedimentary deposits (Steen, 1998). The phosphate in these rocks is built around Ca and PO<sub>4</sub> structures with varying degrees of Ca substitution by other elements such as Na, Mg and heavy metals (Pb, Cd, Cr, As). This substitution restricts the ability to extract phosphate content so that P<sub>2</sub>O<sub>5</sub> values may range from 28% in highly substituted concentrates to 42% in a good quality calcium phosphate rock (Duley, 2001). The processing methods range from simple milling and screening to extensive washing or calcinations, depending on the composition and structure of the sedimentary rocks.

The annual global production of phosphate is about 50 million tonnes of P<sub>2</sub>O<sub>5</sub> and 75% of the rock is surface mined. Phosphate ores are being progressively depleted and production costs are increasing. The current economically exploitable reserves may have a lifetime of about 100 years (Steen, 1998). In addition, Cd impurities represent a serious threat to the environment and the removal

of Cd, which is more abundant in sedimentary deposits, involves further processing costs to phosphate fertilizer prices.

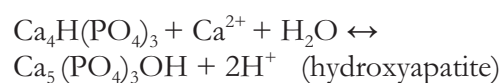
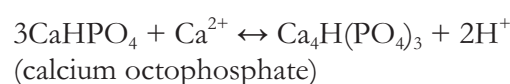
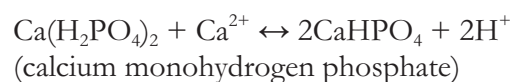
Phosphates are mostly used to produce mineral fertilizers, accounting for 80% of the ore utilisation worldwide, but are also used in detergents (12%), animal feeds (5%) and special applications (3%).

### 2.2 Phosphorus in agriculture

Phosphorus is an essential macronutrient for crop production and together with N and K is one of the main limiting factors for plant growth. However, P in soils is poorly available for plants and the application of P fertilizer is necessary in many agricultural systems in order to ensure plant productivity.

#### 2.2.1 Soil phosphorus

In neutral and calcareous soils, the relative concentration of phosphate in the soil solution depends mainly on the concentration of Ca<sup>2+</sup> ions and soil pH, which governs the formation and dissolution of calcium phosphates. The lower the Ca:P ratio of calcium phosphates, the higher the solubility in water; thus, hydroxyapatite is regarded as quite insoluble (Mengel and Kirkby, 2001).



From these equilibria it can be seen that increasing H<sup>+</sup> groups in the soil solution has a positive effect on the solubility of calcium phosphates but increasing Ca<sup>2+</sup> has the opposite effect. These calcium phosphate products may be present in different crystalline forms. However, in the upper layer of calcareous and alkaline agricultural soils, amorphous calcium phosphates generally dominate. In neutral and acid soils, phosphate adsorption is the dominant process affecting phosphate availability to plants. Phosphate ions are adsorbed on Fe and Al

**Table 1. Common soil P tests (from Valsami-Jones, 2004)**

Name	Composition
Bray 1	0.03M NH <sub>4</sub> F + 0.025M HCl
Bray 2	0.03M NH <sub>4</sub> F + 0.1M HCl
DL	0.02M Ca-lactate + 0.02M HCl
Olsen	0.5M NaHCO <sub>3</sub> - pH 8.5
Mehlich I	0.05M HCl + 0.0125M H <sub>2</sub> SO <sub>4</sub>
Mehlich II	0.015M NH <sub>4</sub> F+0.2M CH <sub>3</sub> COOH +0.25M NH <sub>4</sub> Cl+0.012M HCl
Morgan	0.54M CH <sub>3</sub> COOH + 0.7M NaC <sub>2</sub> H <sub>3</sub> O <sub>3</sub>

hydrous oxides by ligand exchange in which OH<sup>-</sup> groups are replaced by phosphate ions (Mengel and Kirkby, 2001). Phosphate adsorption is stronger the lower the OH<sup>-</sup> concentration, i.e. the lower the soil pH. Therefore, the adsorbed phosphate fraction is dominant in acid soils.

To differentiate between ‘pools’ of phosphorus in soil, a variety of soil P tests have been developed. Each test dissolves a specific P-pool using acids or alkalis as P-extractants. There is no single accepted method to determine plant-available soil P in any soil. Most methods seek to extract P that is weakly-bound to soil or P in those chemical compounds thought to predominate in different types of soil, i.e. acidic extractants for acid soils and alkaline/neutral extractants for alkaline soils. One of the first P-extractants used to estimate plant-available soil P was citric acid (1%). The most common methods used nowadays are summarized in Table 1.

The ammonium lactate (AL)-extractable P in acetic acid (Egner et al., 1960) is the standard commonly used method in Europe. Water- and CaCl<sub>2</sub>-extractable P are also used. However, these chemical extractants do not always indicate the P status satisfactorily (Hylander et al., 1996).

### 2.2.2 Plant uptake

From the point of view of plant nutrition, soil P can be considered in terms of ‘pools’ with varying accessibility to plants. Phosphorus in the soil solution is fully available to plants but the concentration of P in the

soil solution is usually quite low; in fact, more than 80% of soil P becomes immobile and unavailable for plant uptake because of adsorption, precipitation and conversion to organic form (Schachtman et al., 1998).

Plant roots take up P from the soil solution as ortho-phosphate anions, HPO<sub>4</sub><sup>2-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup> depending on the pH. The optimum pH range for the uptake of P by plants lies between 5.5-7 (Fig. 2). In addition to the low availability of soil P, the low diffusion rate of P in soil (10<sup>-12</sup> to 10<sup>-15</sup> m<sup>2</sup> s<sup>-1</sup>) creates a depleted zone around the root (Schachtman et al., 1998). During active growth, plants maintain between 0.3 and 0.5 % of P in dry matter. In cases of P deficiency, symptoms appear as a purplish colouration in the older tissues of plants due to the formation of anthocyanins (Valsami-Jones, 2004).

### 2.2.3 Crop production and P fertilizers

The application of fertilizer guarantees that soil contains sufficient readily available P to allow a crop to achieve the optimum daily uptake rate for each growing stage. Both the P status of the soil and the amount and form of P in the fertilizer influence the contribution from the soil P solution to total plant uptake (Morel and Fardeau, 1990).

The principal P fertilizers in use today are triple superphosphate (TSP) 47% P<sub>2</sub>O<sub>5</sub>, diammonium phosphate (DAP) 18% N, 46% P<sub>2</sub>O<sub>5</sub>, and monoammonium phosphate (MAP) 12% N, 52% P<sub>2</sub>O<sub>5</sub>. Other sources of P inputs to agriculture include organic manures such as farmyard manure and slurry, biosolids (sewage sludge), and recovered phosphates from wastewater streams. Manures contain around 2.0-2.5 % P on a dry matter basis. Applied instead of inorganic fertilizers, manures may reduce P losses (Smith et al., 2007). However, manures contain more P relative to N and the application of manures has resulted in P enrichment of soils on farms with animal production. In areas with high animal densities, this becomes a major potential source of diffuse losses of P to surface waters (Sharpley et al., 1994). ‘Mining’ soil P by growing deep-rooting crops without any additional P fertilization has been proposed as a possible

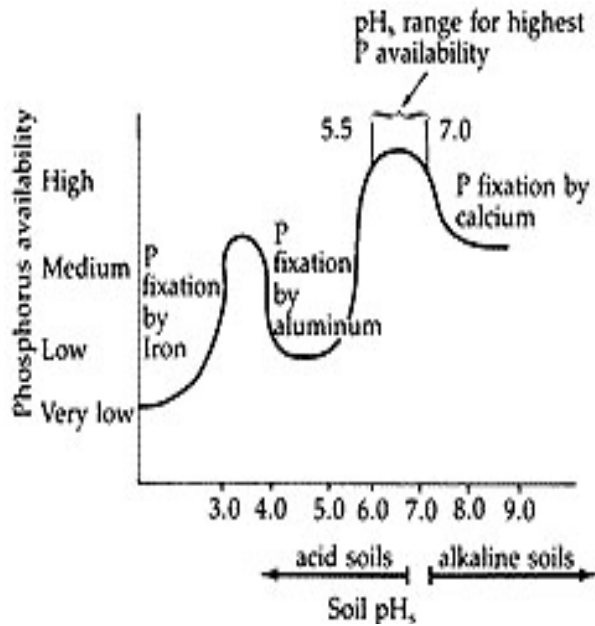


Figure 2. Phosphorus availability in relation to soil pH

strategy for P-enriched soils to decrease the risk of P leaching (Koopmans et al., 2004).

In addition to P, N and K, other important plant macronutrients include Ca, Mg and S. Other elements such as B, Cl, Cu, Fe, Mn, Mo, and Zn are needed in small or trace amounts. Factors such as soil structure or water supply can limit yields irrespective of the amount of nutrients applied.

### 2.3 Phosphorus pollution

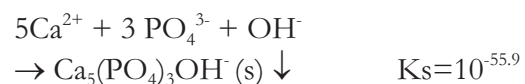
Elevated phosphorus concentrations in surface waters can sometimes be of natural origin (bedrock), but are often the result of soil erosion, agricultural runoff and discharges of municipal and industrial wastewaters. Agricultural runoff is the major diffuse source of P in surface waters. Transport of P from soils to surface waters takes place in both chemical (dissolved) and physical (particulate) forms. In freshwaters P is usually the limiting growing factor and high concentrations of P accelerates eutrophication.

On the other hand, point sources of P account for more than half of the phosphates discharged in Europe (Farmer, 2001). Phosphorus in municipal wastewater originates mainly from human sources (accounting for about 2 g P person<sup>-1</sup> day<sup>-1</sup>), but also from detergents, food waste, food additives and

other products. Typical P concentrations in municipal wastewater range from 6-12 mg P·dm<sup>-3</sup>. According to the EU directive on urban wastewater treatment (91/271/EEC), the total P effluent concentrations must be reduced to 1-2 mg·dm<sup>-3</sup> with a minimum reduction of 80%.

### 2.4 Phosphorus removal and recovery

The principle of phosphorus removal is based in the transfer of soluble phosphorus to the solid phase, with a subsequent separation process. There are several alternatives for removing P from wastewater. Chemical precipitation of phosphates is carried out by the addition of coagulants such as alum, lime, FeCl<sub>3</sub> and FeSO<sub>4</sub>. The final products are Al, Ca or Fe phosphates precipitated in the chemical sludge (Brett et al., 1997). Precipitation with Ca salts can also be used but has a high dependence on pH variations. The final product in this case is hydroxyapatite. The choice of chemical depends mainly on the pH of the effluent, cost of chemicals and the nature of the secondary biological processes. These are the main reactions involved in the precipitation of phosphate and the solubility constants of the phosphate compounds (Sincero and Sincero, 2003):



In the biological P removal process, phosphate ions are taken up by bacteria. The mechanism is based on the importance of phosphorus as an essential nutrient for microorganisms because of its role in the storage and transfer of energy (Brett et al., 1997). Conventional activated sludge only uses enough phosphorus to satisfy their basic metabolism requirements, resulting in typical removal rates of 20-40 %. However, in a treatment plant designed to remove phosphorus, a particular environment is created for the proliferation of bacteria that accumulate phosphorus in excess of normal

metabolic requirements. An example is the enhanced biological phosphorus removal (EBPR) process in which, alternating conditions from initially carbon-rich strictly anaerobic incubation using polyphosphates as a source of energy are followed by a carbon-poor aerobic environment that enhances the uptake of a larger amount of orthophosphate by bacteria (Bashan and Bashan, 2004). In both cases, the end product is a chemical or biological sludge to which P is tightly bound.

From both chemical precipitation and biological removal processes, P can be recovered either from the supernatant or from the sludge by different technologies.

#### **2.4.1 Phosphorus recovery from wastewater streams**

Phosphorus can be recovered from wastewater streams as calcium phosphate, which can be directly utilized in the phosphate industry. A good example is the DHV Crystalactor™ system in the Geetmerambacht enhanced biological treatment (the Netherlands), which recovers calcium phosphate as a pellet formed around a silica sand seed particle, with a P content of up to 11% (Duley, 2001). Another possible pathway is magnesium ammonium phosphate (struvite), which forms spontaneously in wastewater with high concentrations of soluble phosphorus and ammonium, low concentrations of suspended solids and pH above 7.5 (Bashan and Bashan, 2004). Struvite has a potential application as a slow-release fertilizer for direct application in agriculture. The use of struvite as source of P for plants in a pot experiment was found to produce similar effects on the yield of ryegrass to monocalcium phosphate (MCP) (Johnston and Richards, 2003). A recent innovative seed-induced crystallisation process has been shown to efficiently remove P from wastewater (80-100% P removal) yielding a product containing 10% P (w/w) that could be recycled by the phosphate industry or even used directly as a fertilizer (Berg et al., 2005). The economic viability of these processes depends significantly on the P content in the recovered product. Laboratory scale tests

may show promising results, but different factors affect the processes in larger pilot plants. This was demonstrated by Angel (1999) for a new process in which a product containing 18% P in the laboratory was found to contain far below that amount in field conditions. In both laboratory and field experiments the removal of P was satisfactory (>98% and >95% respectively).

#### **2.4.2 Phosphorus recovery from sludge**

With the full implementation of the Urban Wastewater Directive, sludge volumes will subsequently increase. This sewage sludge could be recycled directly to agriculture. However, increasing limitations on sludge disposal imposed by the EU (Directive 86/278/EEC) are imposing constraints on this alternative. This is because wastewater treatment plants inevitably receive not only household but also industrial waste, some of which may contain toxic and/or persistent non-biodegradable compounds, pathogens, hormones and other undesirable substances.

Land application, landfilling and incineration are the dominant methods for sludge disposal nowadays and the costs of the last two options are important (Stark, 2005b). In addition to elevated costs, these major routes of waste disposal are not acceptable in a sustainable society, where the recovery of nutrients must be achieved. In addition, dumping biodegradable waste must be reduced according to the Landfill of Waste Directive (99/31/EC), so landfilling of sludge will be limited. Some EU countries such as Sweden, Germany and the Netherlands, have already announced national objectives on P recovery from sewage. The Swedish EPA has proposed a target of at least 60% P recycling from wastewater by 2015 (SEPA, 2000).

There are different options to recover P from sewage sludge, either as a chemical precipitate or concentrated in biomass. One of the most well-known methods of sludge fractionation is KREPRO™, which treats the digested sludge with acid hydrolysis at high temperatures producing iron phosphate. However, the fertilizer potential of iron phosphate is unclear (Stark, 2005a).

Another method is the Aqua-Reci process with supercritical water oxidation (SCWO), which decomposes organic matter contaminants, followed by chemical processes to recover components including iron or calcium phosphates in the residual ash. A novel technology using phosphate-solubilizing microorganisms (PSB or PSF) together with non-soluble phosphate compounds such as iron phosphate may become a feasible alternative to recover the nutritive value (Bashan and Bashan, 2004).

If the use of sludge in agriculture is not possible, the sludge is dewatered and incinerated. Phosphorus can be then recovered from the ash by hydrochloric acid digestion as phosphoric acid. Ash usually contains high concentrations of Zn and Cu, which limit its use as a fertilizer.

Sewage sludge typically contains between 1-5% P and reliable technologies may allow 50-80% recovery of sewage phosphates. The implementation of P recovery, although technically feasible, involves elevated investment costs, which gives uncertainty to the economic feasibility. For instance, the estimated investment cost for the KREPRO™ system in 1999 was 7.3 million EUR and for the supercritical water oxidation process (SCWO) 8.5 million EUR (Stark, 2005a).

Furthermore, it is probable that P recovery from conventional wastewater treatment systems in rural areas cannot be economically justified.

### 3 ONSITE WASTEWATER TREATMENT SYSTEMS

In some countries, water discharges from private households represent an important source of P pollution, and it is estimated that these discharges are of the same magnitude as the total discharges from all municipal sewage treatment plants. Decentralized wastewater treatment systems are a cost-effective and long-term option for meeting public health and water quality goals, particularly in rural areas (Jantrania and Gross, 2006). The difference with traditional septic tanks is the level of treatment and consequently, the dependence on soil and site conditions. In order to meet the targets on nutrient removal from wastewater imposed by the EU, the quality of septic tank effluents must be improved. Advanced onsite treatment is a feasible option to meet the target and may consist of different systems grouped as follows:

- Media filters
- Natural systems (wetlands, greenhouse)
- Aerobic treatment units (ATUs)
- Waterless toilets (dry toilets)
- Disinfection systems (UV light, chlorination/dechlorination)

Among the different alternatives, focus is being put on media filters for its efficiency and simplicity. Media filters are pre-packaged units usually located after a septic tank that can improve substantially the qual-

**Table 2. Typical components and their concentrations in raw wastewater, septic tank and media filter effluents (from Jantrania and Gross, 2006)**

Effluent	BOD (mg/l)	TSS (mg/l)	NO <sub>3</sub> -N (mg/l)	NH <sub>4</sub> -N (mg/l)	D.O. (mg/l)	Fecal coliform (cfu/100ml)	P <sub>T</sub> (mg/l)
Sewage	155-286	155-330	< 1	4-13	-	10 <sup>6</sup> -10 <sup>8</sup>	6-12
Septic tank	130-250	30-130	0-2	25-60	< 2	10 <sup>5</sup> -10 <sup>7</sup>	4-20
Media filter	5-25	5-30	15-30	0-4	3-5	10 <sup>2</sup> -10 <sup>4</sup>	(*)

\* It strongly depends on the media filter used

ity of effluents (Hedström, 2006; Jantrania and Gross, 2006).

The performance of an onsite wastewater system using media filters depends on different factors such as incoming wastewater properties, pre-treatment step, size and arrangement of the system, hydraulic loading, contact time, temperature, etc. Table 2 shows typical effluent concentrations from media filters. The P removal efficiency depends mostly on the media filter used, although it can be affected by other factors too. Sand and gravel filters have been used for many years, but clean sand may remove some P for only a short period of time. A material with a strong affinity for P is necessary to remove it efficiently. Natural systems such as constructed wetlands may also incorporate such media to improve the performance of the system. A large number of reactive materials have been lately proposed as suitable filter media for P removal.

### 3.1 Reactive filter media

Reactive media may consist of a porous material with a high affinity for P. Such media are often called P-sorbents or reactive substrates. A large variety of reactive substrates with the ability to adsorb P are described in the literature (Mann and Bavor, 1993; Zhu et al., 1997; Baker et al., 1998; Sakadevan and Bavor, 1998; Drizo et al., 1999; Brooks et al., 2000; Drizo et al., 2002; Brogowski and Renman, 2004; Johansson Westholm, 2006; Ádám et al., 2007). The studied substrates can be classified in three groups including natural materials, industrial

by-products and manufactured commercial products. Table 3 gathers some of the reactive filter media reported in literature.

The substrate must have an appropriate size and consistency for the filter system to work properly. The P removal efficiency of a reactive substrate depends on its structure, particle size, porosity, pH, and amount of reactive groups or sorption sites. Substrates are usually rich in Ca, Fe or Al compounds, which favour the interaction with P. The mechanisms of P retention involve sorption processes at the surface of the material.

#### 3.1.1 Phosphorus sorption capacity

The term sorption was described by McBride (1994) as a continuous process that ranges from adsorption to precipitation reactions. Adsorption can be defined as the net accumulation of matter at the interface between a solid phase and an aqueous solution phase and it can take place via different mechanisms. In the case of P adsorption, ligand exchange is the predominant mechanism. The binding forces involved in the ligand exchange are covalent bonding, ionic bonding, or a combination of the two. Phosphate ions form inner-sphere complexes on the solid surface (Fig. 3). These forces are much stronger than those involved in anion exchange, and the phosphate anion is therefore said to be specifically adsorbed. In contrast to non-specifically adsorbed ions, specifically adsorbed ions are not considered readily exchangeable.

Ion exchange involves non-specific electro-

*Table 3. Different types of reactive filter media for phosphorus removal*

<i>Natural materials</i>	<i>Industrial by-products</i>	<i>Commercial products</i>
- Bauxite	- Blast furnace slag (BFS)	- Filtralite <sup>®</sup> P (from LECA)
- Fe-rich sands	- Electric arc furnace slag (EAF)	- Light expanded clay aggregates (LECA)
- Limestone	- Fly ash	- Nordkalk Filtra P
- Opoka	- Red mud (Bauxite residue)	- Polonite <sup>®</sup> (from opoka)
- Shale	- Ochre	- UTELITE <sup>™</sup> (from LWA)
- Shell sands	- Steel furnace slag	
- Wollastonite		
- Zeolites		



static forces that render the phosphate ion readily exchangeable, i.e. other anions can displace the phosphate ion. This is important, since this exchange is an important means of providing readily available nutrient anions to higher plants (Brady and Weil, 1996). Precipitation, or the formation of moderately soluble phosphate minerals, is closely related to the pH of the substrate. Precipitation of a solid phase cannot occur until the solubility product of that phase has been exceeded, i.e. some degree of super saturation is required. Depending on the degree of saturation, non-crystalline to highly crystalline solids are formed (McBride, 1994). Precipitation mechanisms are in general much slower than adsorption reactions.

The P sorption capacity of a substrate can be determined in batch and column experiments and is expressed as the amount of P sorbed per unit (usually mass) of substrate. The P sorption capacity of a substrate can range from a few hundred milligrams up to several grams of P per kg of substrate. However, this depends appreciably on the particle size of the material as well as the procedure used to estimate the capacity. Some industrial by-products and manufactured products have shown a high to very high P sorption capacity, for example some types of fly ash (Xu et al., 2006; Li et al., 2006), different slag materials such as BFS (Sakadevan and Bavor, 1998; Johansson and Gustafsson, 2000) and EAF (Drizo et al., 2002, 2006), recovered ochre (Heal et al., 2005), products derived from light weight aggregates such as UTELITE™ (Zhu et al., 1997), LECA (Johansson, 1997; Drizo et al., 1999) and Filtralite® P (Ádám et al., 2007), the opoka rock derivative Polonite® (Brogowski and Renman, 2004; Renman et al., 2004) and the commercial product Filtra P (Gustafsson et al., 2007).

Not only the sorption capacity but also the percentage of P removal is relevant when choosing an appropriate substrate. In some cases, P removal efficiencies from wastewater can be as high as 95%. This is true for Polonite (Renman et al., 2004) and Filtra P (Gustafsson et al., 2007).

### 3.1.2 Recycling of reactive media

Just like the sludge from conventional wastewater treatment works, the media used in onsite filter systems may be recycled directly to agriculture if the content of toxic compounds and pathogenic bacteria does not restrict their use according to the EU Directive 86/278/EEC. Household derived wastewater from normal human activities usually has no hazardous components and therefore, the saturated media from onsite treatment systems may not be a threat to the receiving environment.

Land and agricultural application of waste products has always been regarded as a possible solution for the disposal of different industry-derived sub-products. In many cases, the application of such amendments has improved soil structure, conditioning and/or even fertility. In the particular case of acid soils, different amendments have

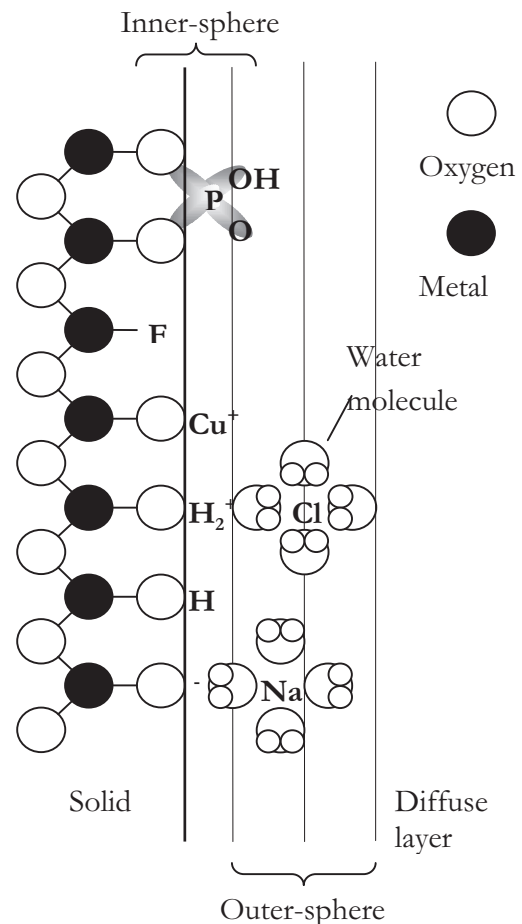


Figure 3. Phosphate complexation at the surface of a substrate (from Schnoor, 1996)

shown good results in increasing soil pH. Some of these include alkaline biosolids (Sloan and Basta, 1995), wood ash (Demeyer et al., 2001), fly ash, a by-product of the coal combustion process (Matsi and Keramidas, 1999; Mittra et al., 2004), and the steel works by-product blast furnace slag (Kühn et al., 2006). It is known that cattle manures can also increase the pH of acid soils and, additionally, recycle P, N and other nutrients to soils (Whalen et al., 2000). However, as mentioned before, the excessive application of manures leads to the accumulation of P in soils, with the subsequent risk of P leaching to surface waters. Some of reactive materials have been proposed as appropriate soil amendments to retain P thus reducing P leaching (Summers et al., 1993; Cheung et al., 1994). Bauxite residue (red mud), an alkaline by-product from the alumina industry, has been shown to reduce P leaching from P-enriched sandy soils (Summers et al., 1996) and to improve P uptake by plants (Snars et al., 2004). The efficiency of bauxite residue as nutrient source for plants has recently been studied (Eastham et al., 2006). These are some of the examples of beneficial outcomes from waste disposal. In some cases, the increase in soil pH results in in-

creasing P availability, thus improving soil fertility and crop yield.

In the case of P-saturated media, their fertilizer potential in agriculture has to be tested. Alternatively, such products may be recovered by the fertilizer industry depending on their composition. The solubility of P in the substrate varies depending on its composition and form but it should be in a form capable of desorbing and being released to the soil P solution, thus becoming available to plants. Both the soil P status and the amount and form of P in the substrate influence the contribution from the soil solution to total plant uptake (Morel and Fardeau, 1990).

A number of pot experiments have recently been conducted in order to study the plant availability of P from different substrates used for onsite wastewater treatment. In most cases, the P-saturated substrates improved the yield compared with no P addition. Among the substrates studied, blast furnace slag and Polonite have been shown to efficiently improve the yield of barley (Hylander et al., 2006). Studies on Fe-rich sands and LECA have shown that P sorbed to these substrates is as available to ryegrass

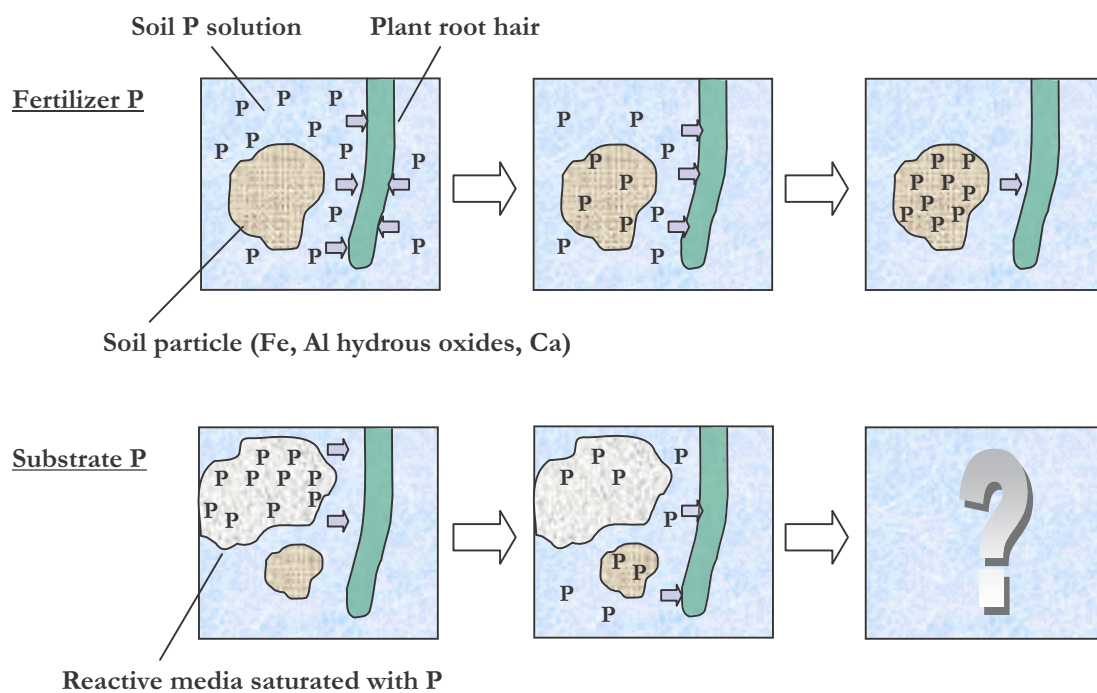


Figure 4. Schematic representation of phosphorus fertilizing conditions

as a water-soluble P compound (Kvarnström et al., 2004). Phosphorus-saturated ochre, a by-product from iron mining, has been shown to function as a slow-release fertilizer being as effective as conventional P fertilizer for grass and barley crops (Heal et al., 2003; Dobbie et al., 2005).

It has been shown that P bound to Ca compounds is more plant-available than P bound to Al and Fe for some substrates (Hylander and Simán, 2001). Therefore, calcium derivatives might be more attractive from the point of view of nutrient recycling effectiveness. In addition, such substrates usually have high pH values, which efficiently reduce the bacteria content in wastewater (Renman et al., 2004) and may increase soil pH when used as soil amendments.

Only a fraction of fertilizer P is taken up immediately by crops, while the remainder becomes adsorbed and, possibly after further reactions, absorbed to soil particles (Fig. 4). The speed at which this sorption and other reactions occur depends on the type and size of the soil particles and the presence of other elements such as Al, Fe, Ca, soil acidity and organic matter. Phosphorus in many of the substrates is not as soluble as in most mineral fertilizers and therefore, more investigation about their value as a source of P for crop production is necessary.

## 4 MATERIALS AND METHODS

### 4.1 Materials

The materials used in this study were opoka, Polonite, wollastonite tailings and Filtra P. They were chosen for their suitability as filter media for the removal of P from wastewater. Polonite and Filtra P are commercially available products used in Scandinavia for the removal of P in onsite wastewater treatment systems.

#### 4.1.1 Opoka

The bedrock opoka is a calcium rich sedimentary deposit from the late Cretaceous period called Mastrych, formed from the remains of minute marine organisms (diatoms). Deposits are mainly found in Poland,

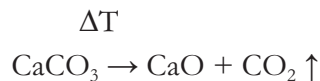
but also in Ukraine, Lithuania and Russia. Opoka mainly consists of  $\text{SiO}_2$  and  $\text{CaCO}_3$  but also contains significant amounts of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (Brogowski and Renman, 2004). There is great variation in opoka deposits in terms of the silica and carbonate content, which ranges from 37.5 to 52.1 % silica and 34.5-50.4% calcium carbonate. Thus, opoka can be classified as light-weight (more  $\text{SiO}_2$ ) and heavy-weight opoka (more  $\text{CaCO}_3$ ). Polish literature gives a wider range of silica content from 17.06 to 51.88 % (Bolewski and Turnau-Morawska, 1963). This type of rock can also be classified as geza when the silica dominates.

The ability of opoka to remove P from wastewater is well-known. The process occurs mainly through Ca-P interactions (Johansson and Gustafsson, 2000). Opoka has a moderate to low P sorption capacity; while some studies have also shown a poor P-availability for plant uptake from P-saturated opoka (Hylander and Simán, 2001).

Natural opoka was acquired from three different quarries located in the region of Miechów, about 60 km north of Krakow, Poland. The Strzezów quarry contains large deposits of opoka, which are mainly used for construction purposes (Fig. 5), while at the Cisie (Antolka) quarry, a confined layer of less than one metre depth is present (Fig. 6). The Widnica quarry is abandoned but opoka can be acquired at surface level. The materials were crushed and sieved to appropriate fractions. A particle size of 2-5.6 mm was used in the column infiltration experiment.

#### 4.1.2 Polonite

Polonite (Polonite<sup>®</sup>) is the product of opoka processing, which consists of thermal treatment at high temperatures for an appropriate period of time. By heating the material, most of the calcium carbonate is transformed into calcium oxide, which has a higher solubility product than calcium carbonate and is therefore more reactive in aqueous solutions. The material is then sieved to the appropriate fraction to be used in filter systems.



The P sorption capacity of Polonite is considerably higher than that of opoka. Its P-sorption efficiency depends strongly on particle size and retention time. The powder fraction of Polonite showed a P-sorption capacity of 60-80 mg P g<sup>-1</sup> in batch tests with an estimated maximum capacity of 117.65 mg P g<sup>-1</sup> according to the Langmuir isotherm (Cucarella Cabañas, 2000). Other studies have reported a P sorption capacity of up to 119 g P·kg<sup>-1</sup> (Brogowski and Renman, 2004). Polonite used in an appropriate size fraction (2-5.6 mm) for infiltration of sewage showed over 98% P removal and nearly 99.5% bacteria removal (Renman et al., 2004). Some studies have shown promising results of Polonite saturated with P as a fertilizer (Hylander et al., 2006).

Polonite (Fig. 7A) is manufactured by the Swedish company NCC from raw opoka bedrock extracted in Poland. Polonite used in this study had a particle size of 2-5.6 mm, which is the most appropriate fraction for large-scale production (Renman, pers. com.).

#### 4.1.3 Natural wollastonite

Natural wollastonite is a calcium metasilicate compound with reported P-sorption ability (Brooks et al., 2000). This material was chosen for its mineralogical similarity to Polonite. Wollastonite tailings (Fig. 7B) produced in 1-3 mm particle size containing 27.3% of pure wollastonite were used in this study.

#### 4.1.4 Filtra P

Filtra P (Fig. 7C) is a commercial product developed by the Finnish company Nordkalk. It consists of lime, iron compounds and gypsum, forming spherical aggregates with a diameter between 2-13 mm. It is characterized by high pH values and Ca content, which favours the interaction with phosphates. Filtra P has a high P-removal efficiency, but no studies about its fertilizer potential were found in the literature.

#### 4.1.5 Soils

Two different types of soils were used together with the material amendments in the pot cultivation experiments.

Soil 1 was acquired in Łazy, situated 40 km south of Krakow, Poland (20°30' E; 49°58'N; altitude 320 m asl). It was taken from the A horizon (0-25 cm) of a cultivated field, classified as a Haplic Luvisol (FAO-ISRIC-SICS, 1998), and consists of 12% sand, 56% silt and 32% clay, with a pH<sub>H<sub>2</sub>O/KCl</sub> of 6.88/6.42, C/N 7.8, and AL-extractable P and K of 7.5 and 61 µg g<sup>-1</sup> dry soil respectively.

Soil 2 was acquired in Czarny Potok, a region of southern Poland within the Carpathian mountains (20°54'E, 49°24'N, altitude 720 m asl). It was taken from the A horizon (0-20 cm) of a mountainous meadow classified as a Dystric Cambisol (FAO-ISRIC-SICS, 1998) and consists of 40% sand, 37% silt and 23% clay, with a pH<sub>H<sub>2</sub>O/KCl</sub> of 4.22/3.66, and AL-extractable P and K of 4.3 and 27 µg g<sup>-1</sup> dry soil respectively.

## 4.2 Methods

### 4.2.1 Chemical analysis

The materials and soil samples were crushed and milled in a mortar. Triplicate 2 g samples were used for analysis after extraction with nitric and perchloric acids by heating for 3-4 days followed by filtration. The element content was determined by atomic absorption and emission spectrophotometry using an AAS Ssolar M6 and ICP-AES JY 238 Ultrace.

Natural opoka (Opk) and opoka heated to 900 °C for 1 hour (900Opk) were analysed for P, Al, Fe, Ca, Mg, Na, K, Mn, Cu, Zn, Co and Cd. The silica content was calculated from the remaining weight of the filter after incineration at a temperature of 900 °C. The CaCO<sub>3</sub> content was analysed using the Scheibler method. The pH was measured in a 1M KCl:water (1:2.5) solution.

Polonite®, Filtra P and wollastonite tailings, saturated with P and soil samples were analysed for total P, Al, Fe, Ca, Mg, Mn, Cu, Zn, Pb and Cd. The pH was then measured in a 1:2.5 (w/v) material:water and KCl 1M solution suspension.



*Figure 5. Deposits of opoka in the quarry of Strzezów*



*Figure 6. Deposits of opoka in the quarry of Cisie*



**Figure 7. Reactive filter media: Polonite (A), wollastonite tailings (B), Filtra P (C)**

#### 4.2.2 Phosphorus sorption capacity

The P sorption capacity of the materials (sorbents) was estimated in batch and column experiments. In the batch experiments 0.1 g of powdered material was placed in 50 ml flasks with an artificial P solution ( $\text{KH}_2\text{PO}_4$ ) containing increasing concentrations of P (0, 10, 25, 50, 100, 200, 300, 500  $\text{mg P}\cdot\text{dm}^{-3}$ ) and then mixed in a rotator at 60 rpm for one hour at room temperature (21 °C). The materials were milled to powdered fractions in order to keep a comparable particle size. The effluent pH was then measured and the samples were centrifuged at 6000 rpm and filtered through a 0.45  $\mu\text{m}$  membrane filter for P determination. The P was analysed using the standard ammonium molybdate method (Murphy and Riley, 1962) in a Beckman DU 600 spectrophotometer. The difference between the initial ( $C_i$ ) and final ( $C_f$ ) P concentrations at equilibrium was assumed to be sorbed to the material.

Phosphorus sorption isotherms were plotted using the amount of P sorbed to the material ( $C_s$ ,  $\text{mg}\cdot\text{g}^{-1}$ ), at different influent P concentrations ( $C_i$ ,  $\text{mg}\cdot\text{dm}^{-3}$ ). The isotherm may be curved reaching a 'plateau' at which higher P concentrations do not increase the sorption and this is assumed to be the maximum P-sorption capacity ( $C_s^{\text{max}}$ ). The experimental data were fitted to Langmuir and Freundlich isotherms according to equations 1 and 3 respectively. Sorption parameters were calculated by plotting graphically the inverse and logarithm, for Langmuir and Freundlich respectively, of the sorbed portion ( $C_s$ ) against the inverse and logarithm of the

initial concentration ( $C_i$ ) at equilibrium (eq. 2,4). This gave a straight line and the Langmuir and Freundlich constants were obtained from the y-axis intercept and the slope (McKay, 1996).

$$C_s = K_L \cdot C_i / 1 + a_L \cdot C_i \quad (1)$$

$$1/C_s = 1/C_i \cdot 1 / K_L + a_L / K_L \quad (2)$$

where  $K_L$  ( $\text{dm}^3\cdot\text{g}^{-1}$ ) reflects the adsorptivity and  $a_L$  ( $\text{dm}^3\cdot\text{mg}^{-1}$ ) is related to the energy of adsorption.  $K_L/a_L$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is obtained from the y-axis intercept and reflects the maximum adsorption capacity.

$$C_s = a_F \cdot C_i^{b_F} \quad (3)$$

$$\log C_s = b_F \cdot \log C_i + \log a_F \quad (4)$$

where  $a_F$  ( $\text{dm}^3\cdot\text{g}^{-1}$ ) expresses the adsorbent capacity (the larger the value the higher the



**Figure 8. Column experiment set-up**

capacity) and  $b_F$ , which ranges from 0 to 1, is the heterogeneity factor.

The column experiments were conducted placing 200 g of each material in columns made from 1-litre plastic graduated cylinders with perforated bases (Fig. 8). The materials were used in their original fractions (see section 4.1). The columns were gravity fed (unsaturated flow) with a 25 mg P·dm<sup>-3</sup> solution as KH<sub>2</sub>PO<sub>4</sub> until saturation was reached, i.e. the influent and effluent P concentrations did not differ significantly. The effluent pH was measured and the samples were centrifuged at 6000 rpm and then filtered through a 0.45 µm membrane filter for P determination according to the standard ammonium molybdate method (Murphy and Riley, 1962) in a Beckman DU 600 spectrophotometer.

The amount of P sorbed to the materials after saturation was determined by atomic emission spectrophotometry using an ICP-AES JY 238 Ultrace after extraction with nitric and perchloric acids by heating for 3-4 days followed by filtration.

#### 4.2.3 Pot cultivation experiments

Polonite®, Filtra P and wollastonite saturated with P in the column experiment were equilibrated in a 100 mg P·dm<sup>-3</sup> solution for 2 days in order to ensure a homogeneous P-content in the substrates. After that, the materials were dried at 105 °C and milled for analysis according to section 4.2.1.

Plastic pots (5-litre) were filled with 4.0 kg wet soil (30-35 vol.%) and received 1.5 g K<sub>2</sub>SO<sub>4</sub>, 0.5 g MgSO<sub>4</sub> and 1.0 g NH<sub>4</sub>NO<sub>3</sub> as basic fertilization, incorporated and mixed in the middle-upper soil layer (5-10 cm). Phosphorus was added as KH<sub>2</sub>PO<sub>4</sub> or as P-sorbed to the materials in quantities based on previous research (Hylander et al., 2006). The materials were previously crushed and sieved to a fraction of 0.5-1 mm in order to keep a comparable size and enhance P release to the soil solution. No P was added to the control treatment.

Spring barley (*Hordeum vulgare* cv. Poldek) was sown in soil 1 and perennial ryegrass (*Lolium multiflorum* cv. Mowester) in soil 2 on 16 May 2006 at a rate of 20 seeds (approx-

mately 0.9 g) per pot and 0.6 g per pot, respectively. The pots were randomly distributed in a greenhouse situated in Krakow (19°51'54,43"N; 50°00'41,30"E), Poland, with an insolation of 343 hours (ryegrass) and 440 hours (barley) during the experiment. The plants were watered every one or two days to maintain an average soil moisture of 30-35 vol.%. The pots were rearranged every one or two weeks. The average air temperature during the experiment in the greenhouse was 15-20°C. Harvesting took place on 4 July 2006 (50 days) for ryegrass and on 18 July (64 days) for barley. The plants were cut manually at approximately 1 cm above the soil surface, dried at 55°C and weighed. Next, leaves and stem from ryegrass and spikes from barley were cut and milled and the total P, Al, Fe, Ca, Mg, Cu, Mn, Cd, Pb and Zn concentrations were determined by atomic spectrometry using an ICP-AES JY 238 Ultrace after extraction with a mixture of nitric and perchloric acids at 200°C under recirculation conditions.

After harvesting, soil samples from each pot were analysed for AL-extractable P, K and Mg in acetic acid (Egner et al., 1960). The pH was measured in a 1:2.5 (w/v) soil:water and soil:KCl 1M solution suspension. The hydrolytic acidity (Hh) in soil after harvesting was determined according to the Kappen method using 1 mol·dm<sup>-3</sup> CH<sub>3</sub>COONa solution. The base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup>) were determined by atomic spectrometry using an AAS Ssolar M6 System after extraction with a 0.5 mol·dm<sup>-3</sup> NH<sub>4</sub>Cl solution. Total exchangeable bases (TEB), cation exchange capacity (CEC) and percentage base saturation (BS) were then calculated as follows:

$$\text{TEB} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{K}^{+}] + [\text{Na}^{+}] \quad (5)$$

$$\text{CEC} = \text{Hh} + \text{TEB} \quad (6)$$

$$\text{BS} (\%) = (\text{TEB} / \text{CEC}) \cdot 100 \quad (7)$$

All the results were analysed statistically for a sample size of n=3 (yield), n=6 (element concentration in plant and AL-extractable P, K, Mg in soil) and n=9 (Hh and base cations in soil) and a significance level of p<0.05

was used to compute the confidence level. Values lying outside the established confidence interval (based on the  $p < 0.05$  confidence level) for a given population mean were considered significantly different.

## 5 RESULTS AND DISCUSSION

### 5.1 Reactive media composition

The chemical composition of the studied materials is shown in Table 4. According to the content of silica and calcium carbonate, opoka can be classified as light-weight (more  $\text{SiO}_2$ ) and heavy-weight (more  $\text{CaCO}_3$ ) opoka. The variability in composition of three different opoka deposits is presented in Paper I. Opoka from Strzeżów (Opk1) can be classified as light opoka and the other two samples, Opk2 from Cisie (Antolka) and Opk3 from Widnica, with higher carbonate content, can be classified as heavy opoka. There was a noticeably higher content of Al and Fe oxides in light opoka (Opk1). The rest of the components appeared in similar proportions for all three sources of opoka. The pH was slightly higher in heavy opoka as a consequence of the higher Ca content.

Most of the  $\text{CaCO}_3$  and other possible Ca forms in opoka convert to CaO after heating to 900 °C. This has been already reported and it is the basis for a strong Ca-P interaction due to the higher reactivity of CaO (Johansson and Gustafsson, 2000; Brogowski and Renman, 2004). The reason for the increasing amounts of Si and Ca in 900Opk samples is simply the result of a 7-16% weight lost due to decomposition of carbonate to  $\text{CO}_2$  (the higher the  $\text{CaCO}_3$ , the higher the weight loss) increasing the relative amount of other compounds per unit mass of the material. The pH values increase drastically after heating, which also favours the Ca-P reaction.

The composition of Polonite was comparable with that of 900Opk1, indicating that it had been produced from light opoka. However, it had noticeably higher amounts of Mg and Fe. The content of Ca in Filtra P lay between that of light and heavy burned opoka. It contained substantial amounts of

Fe and relatively higher amounts of Pb compared with the other materials. Wollastonite contained less Ca, its concentration being comparable with that of light opoka. It had visibly higher amounts of Mn than the rest of the materials. Discussion about the composition of soils is beyond the scope of this section and is taken into consideration when discussing the pot experiments using the filter materials as soil amendments.

### 5.2 Phosphorus sorption capacity

#### 5.2.1 Batch experiments

The batch experiments showed a high P-sorption capacity for powder fractions of all three types of opoka heated to 900 °C (900Opk1, 900Opk2 and 900Opk3), Polonite and Filtra P. The natural form of opoka was not tested in this study since it has already been reported to have a low P sorption capacity (Johansson and Gustafsson, 2000). The observed P sorption capacity was higher for the samples of burned heavy opoka, 900Opk2 and 900Opk3, compared with the other materials. This was expected from its higher Ca content, although, light opoka has a higher porosity that could favour P movement through cavities and make more sorption places available in the long term. Heavy opoka has a more compact structure due to its higher content of  $\text{CaCO}_3$  and this may have some implications when using the material in filter systems (see section 5.2.2). The amount of P sorbed to the materials from the highest influent P concentration ( $C_s^{\text{max}}$ ) represents the maximum sorption capacity (Table 5). The Langmuir and Freundlich isotherms fitted well to the experimental data (Fig. 9, 10). The Langmuir isotherm appeared to model the sorption by burned heavy opoka (900Opk2 and 900Opk3) and Filtra P more accurately, while the Freundlich isotherm fitted better for burned light opoka (900Opk1) and Polonite. In previous studies, the Freundlich equation seemed to work better than Langmuir for slags, zeolites (Sakadevan and Bavor, 1998), limestone and calcareous soils (Zhou and Li, 2001).



Table 4. Element concentration and pH in the studied materials and soils

	units	Soil 1 (Lazy)	Soil 2 (Czarny)	Opk1 (Strzeżów)	Opk2 (Cisie)	Opk3 (Widnica)	900Opk1 (Strzeżów)	900Opk2 (Cisie)	900Opk3 (Widnica)	Polonite	Filtra P	Wollastonite
SiO <sub>2</sub>	g·kg <sup>-1</sup>	n.a.	n.a.	494.87	326.17	330.69	664.63	480.92	449.37	n.a.	n.a.	n.a.
Ca	g·kg <sup>-1</sup>	0.86	0.10	171.34	326.20	311.58	220.79	424.70	419.75	230.44	343.22	162.41
Mg	g·kg <sup>-1</sup>	1.64	2.06	2.56	2.75	2.83	2.02	2.87	3.11	5.01	5.61	1.76
Fe	g·kg <sup>-1</sup>	15.99	12.65	10.07	6.38	6.87	6.72	5.71	5.76	11.15	44.42	7.55
Al	g·kg <sup>-1</sup>	n.a.	n.a.	8.96	5.85	7.32	6.41	5.55	7.11	27.0*	11.1*	54.6*
Na	g·kg <sup>-1</sup>	n.a.	n.a.	0.19	0.22	0.22	0.13	0.20	0.21	1.46*	1.46*	12.30*
K	g·kg <sup>-1</sup>	n.a.	n.a.	1.32	0.84	0.99	0.49	0.43	0.46	9.45*	4.89*	26.6*
P	g·kg <sup>-1</sup>	0.66	0.57	0.42	0.29	0.34	0.39	0.29	0.32	n.a.	n.a.	n.a.
Mn	mg·kg <sup>-1</sup>	246.43	114.48	41.43	51.92	42.33	36.87	65.82	43.41	49.90	195.65	394.87
Zn	mg·kg <sup>-1</sup>	52.86	47.55	19.87	18.14	19.58	15.19	16.00	15.74	53.18	92.84	21.34
Cu	mg·kg <sup>-1</sup>	12.26	5.47	5.31	4.76	6.16	2.32	2.78	3.41	4.41	5.98	3.12
Co	mg·kg <sup>-1</sup>	n.a.	n.a.	1.29	0.95	1.11	1.43	1.44	0.91	n.a.	n.a.	n.a.
Pb	mg·kg <sup>-1</sup>	15.49	20.27	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.64	7.01	0.97
Cd	mg·kg <sup>-1</sup>	0.16	0.19	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
pH H <sub>2</sub> O		6.88	4.22	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	12.0	12.5	9.4
pH KCl		6.42	3.66	7.48	7.64	7.55	12.39	12.46	12.41	n.a.	n.a.	n.a.

n.a.= not analyzed; \*from Gustafsson et al. (2007)

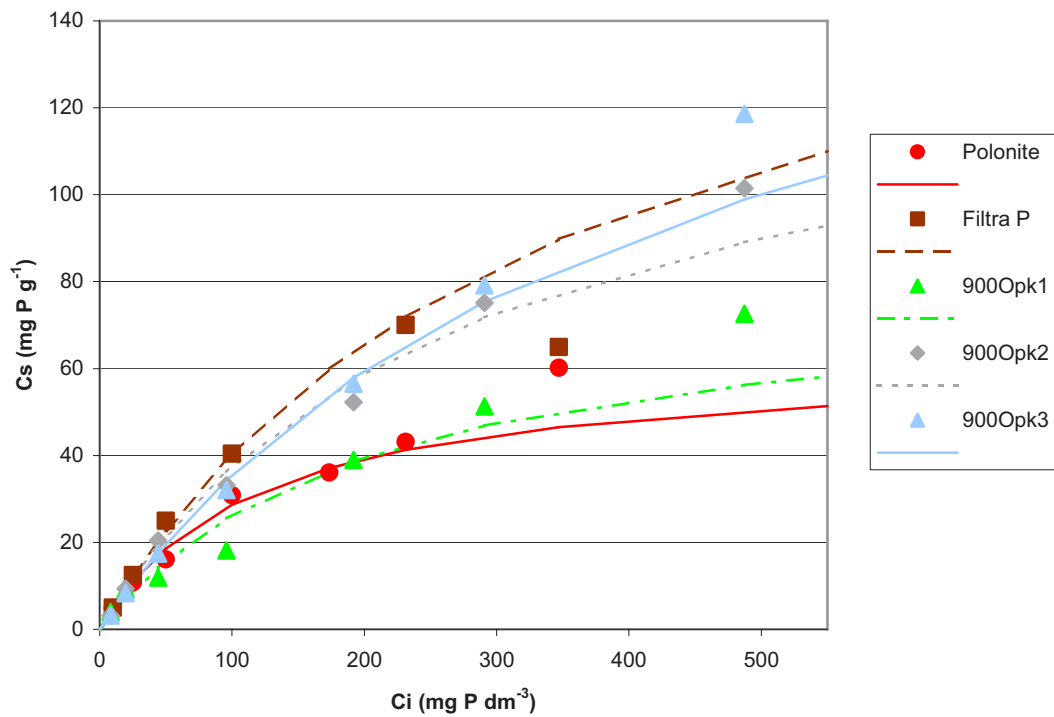


Figure 9. P-sorption isotherms for different substrates (lines indicating Langmuir isotherms)

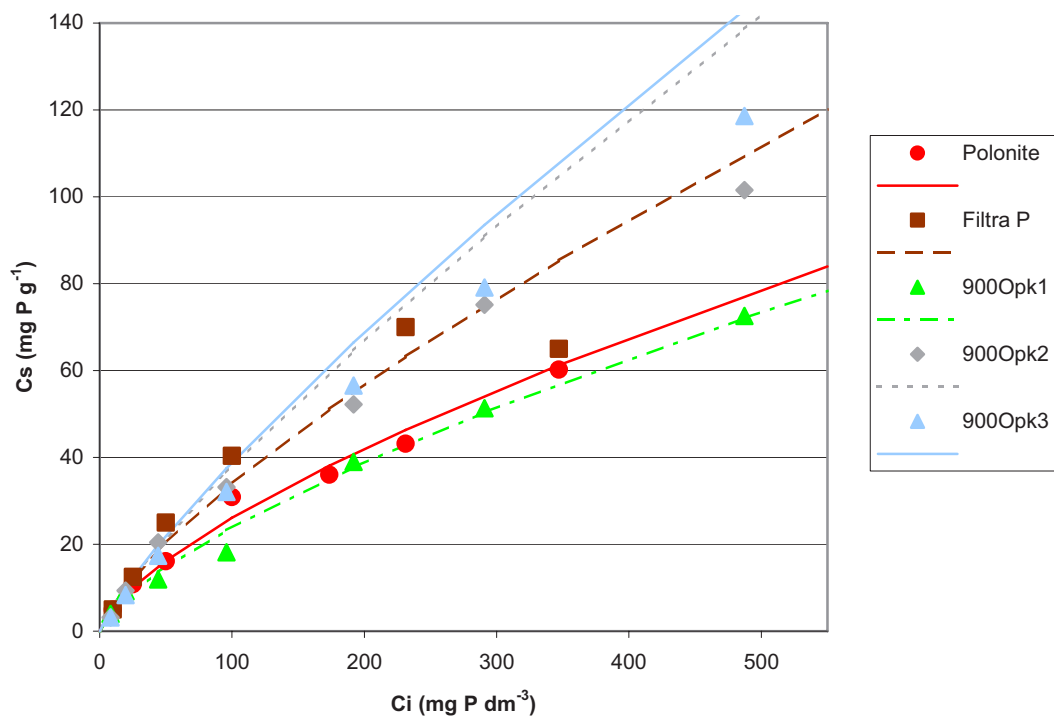


Figure 10. P-sorption isotherms for different substrates (lines indicating Freundlich isotherms)

**Table 5. Observed maximum P-sorbed ( $C_s^{max}$ ) and calculated sorption parameters from Langmuir and Freundlich equations**

	Observed	Langmuir			Freundlich		
	$C_s^{max}$ (mg·g <sup>-1</sup> )	R <sup>2</sup>	$K_L$ (dm <sup>3</sup> ·g <sup>-1</sup> )	$K_L/a_L$ (mg·g <sup>-1</sup> )	R <sup>2</sup>	$a_F$ (dm <sup>3</sup> ·g <sup>-1</sup> )	$b_F$
Polonite	60	0.9980	0.5294	62.3319	0.9947	1.1072	0.6860
Filtra P	70	0.9990	0.5190	179.1495	0.9745	1.1157	0.7416
900Opk1	72	0.9777	0.3909	79.3651	0.9836	0.9768	0.6950
900Opk2	100	0.9973	0.5126	136.9863	0.9833	0.8714	0.8192
900Opk3	120	0.9991	0.4405	181.8182	0.9994	0.8794	0.8227

The sorption parameters calculated are shown in Table 5. The maximum P sorption capacity according to the Langmuir model was lower for burned light opoka (900Opk1) and Polonite and higher for burned heavy opoka (900Opk2 and 900Opk3) and Filtra P. The Langmuir maxima correlated well with the observed maxima ( $C_s^{max}$ ) for burned light opoka and Polonite, since these materials showed a better fit to the Langmuir model. The Freundlich  $a_F$  values give a measure of the relative P adsorption capacity. In this study, the values were not directly related to the adsorption maxima from the Langmuir equation. This has been previously observed by Sakadevan and Bavor (1998), when using other reactive substrates and it was attributed to the precipitation of P in addition to P adsorption. Thus, adsorption mechanisms dominate in burned light opoka and Polonite, while precipitation may contribute considerably to the P sorption process in burned heavy opoka and Filtra P. The relationship between the Ca content and P-sorption capacity is also discussed in paper I. The estimated P-sorption capacity showed a

linear correlation with the CaO concentration in the materials. It is not known exactly what Ca-P compounds were formed. Previous work has shown that slag materials and opoka may form hydroxyapatite when a certain supersaturation is reached (Johansson and Gustafsson, 2000). Depending on the Ca:P ratio, pure CaCO<sub>3</sub> can form four main different species (House, 1999). The P sorbed may be more or less available depending on the strength of the interaction and type of compound formed. It is known that hydroxyapatite is a strong component, in which form P is not available to plants. Recent studies have shown that the Ca-P phase formed in Polonite and Filtra P is amorphous in nature and that only a proportion of the phosphorus may have crystallized to slightly less soluble phases (Gustafsson et al., 2007).

It is important to remember that this research was performed with artificial P solutions and the results may differ when using wastewater due to the presence of other substances that may interfere the accessibil-

**Table 6. Physical properties, pH value and P-content in soils and in the saturated reactive substrates**

	Soil 1 (Lazy)	Soil 2 (Czarny)	Polonite	Filtra P	Wollastonite
Particle size (mm)	-	-	2-5.6	2-13	1-3
Bulk density (g·cm <sup>-3</sup> )	-	-	0.7	1.0	1.4
pH <sub>H2O</sub> / pH <sub>KCl</sub>	6.88/6.42	4.22/3.66	9.88 / 9.90	11.49 / 11.36	9.02 / 8.76
P ± SE (µg·g <sup>-1</sup> )	663.73±7.85	569.13±11.28	1862.15±53.58	713.64±115.99	253.96±12.73
AL-extractable P ± SE (µg·g <sup>-1</sup> )	7.51 ± 0.15	4.32 ± 0.06	49.88 ± 0.31	5.62 ± 0.38	13.93 ± 0.61
AL-extractable K ± SE (µg·g <sup>-1</sup> )	61.33 ± 0.24	26.91 ± 0.35	62.13 ± 0.02	23.48 ± 0.58	4.49 ± 0.01

ity of P to the sorption sites.

These results are not applicable when using other fractions of the materials and they should be viewed with caution. Coarser fractions have higher hydraulic conductivity and are therefore more suitable for infiltration systems, but they have smaller surface area and their expected sorption capacity will be lower than that estimated with powdered material.

### 5.2.2 Column experiments

The column studies were used to estimate the P saturation potential of the materials in a filter system. The columns containing burned heavy opoka (900Opk2 and 900Opk3) clogged shortly after the beginning of the experiment, showing poor suitability for infiltration when used in a fraction between 2-5.6 mm. Differences between light and heavy opoka regarding porosity and content of Ca may be critical for the success of a system. Heavy opoka has a lower porosity and more compact structure, which often leads to clogging of the system. The burned light opoka (900Opk1), despite performing better, reached saturation quickly at the incoming flow rate. Polonite, Filtra P and wollastonite tailings performed well during the whole experiment. Polonite and especially Filtra P effluents were markedly turbid, while wollastonite effluents were very clear. The materials were assumed to be saturated when the effluent concentration was similar to the influent at the feeding flow rate. The content of P and pH in the materials after saturation is shown in Table 6 and these results are discussed in paper II.

The saturation potential of Polonite (nearly  $2 \text{ mgP}\cdot\text{g}^{-1}$ ) was considerably higher than that of Filtra P and wollastonite. Previous work using Polonite for wastewater treatment showed a saturation potential of about  $1.3 \text{ mg P}\cdot\text{g}^{-1}$ , suggesting that the material was not fully saturated (Hylander et al., 2006). Recently, a filter system with alternating flow has shown that Polonite has a much higher P saturation potential (Gustafsson et al., 2007). The lower P content in Filtra P suggests that P precipitated by either Ca or Fe may have leaked out of the column as a

larger compound, which could not pass through the  $0.45 \mu\text{m}$  filter for  $\text{P-PO}_4$  determination. Supporting this explanation is the fact that Filtra P disintegrated in water with time, giving a yellow colour to the effluent. The P sorption capacity of wollastonite was much lower and saturation was reached quicker. Previous research has shown that wollastonite can remove over 80% of P from wastewater with hydraulic residence times of more than 40 h (Brooks et al., 2000), which is much longer than the residence time used in this experiment.

### 5.3 Fertilizer potential of the materials

The three materials Polonite, Filtra P and wollastonite were used as soil amendments in a pot experiment. The fertilizer potential on barley and ryegrass yield is discussed in Paper II and III respectively. The effect of the amendments on the properties of acid soils is broadly described in Paper III.

#### 5.3.1 Effect on yield and composition of barley and ryegrass

The average yield of barley and element composition in barley spikes grown under five different treatments is shown in Table 7. There was no significant difference between treatments in terms of dry matter (DM) production but there was a tendency for higher yield when P was applied in a water-soluble form ( $\text{KH}_2\text{PO}_4$ ) and P from saturated substrates compared with the control treatment (No P). In other studies, Polonite saturated with P from wastewater streams has been shown to improve the yield of barley when added to a P-depleted soil (Hylander et al., 2006).

The average yield and element composition of ryegrass grown under five different treatments is shown in Table 8. There was no significant difference between treatments but there was a tendency for higher yield of ryegrass with substrate treatment compared with both control (No P) and potassium phosphate treatments ( $\text{KH}_2\text{PO}_4$ ). All plants showed healthy growth during the experiment and no changes in physiology due to substrate treatment were observed (Fig. 11). In previous work, P sorbed to different

substrates including Fe-rich sands and LECA (light expanded clay aggregates) was as available to ryegrass as a water-soluble P compound (Kvarnström et al., 2004). For both barley and ryegrass, the yield/amendment ratio was in agreement with the initial P content in the substrates giving a comparative idea of substrate effectiveness and decreasing in the order Polonite > Filtra P > wollastonite. The increase in yield with substrate treatment compared with the control may be due to direct P

supply for plant uptake, but there is no evidence of P release from the substrates in this study. The substrates may also enhance soil P availability, as discussed in the next section. The element concentration in barley spikes revealed no significant difference between treatments (Table 7).

It can be concluded that the substrates did not affect the composition of barley spikes. As for ryegrass (Table 8), the concentrations of P and Ca were significantly higher in ryegrass grown with substrate treatment

**Table 7. Amendment rate, yield and composition (spikes) of barley and pH, AL-extractable P, K and Mg, hydrolytic acidity (Hh), base cations concentration, TEB, CEC and BS in soil 1**

	units	NO P	KH <sub>2</sub> PO <sub>4</sub>	POLONITE	FILTRA P	WOLLASTONITE
Amendment	g·pot <sup>-1</sup>	-	0.12	22	24	32
BARLEY						
Fresh weight	g·pot <sup>-1</sup>	33.3 ± 0.51	34.43 ± 1.43	33.36 ± 2.17	33.10 ± 2.89	33.30 ± 0.98
Yield	gDM·pot <sup>-1</sup>	19.23 ± 0.33	21.00 ± 0.98	20.03 ± 1.70	20.60 ± 2.72	20.73 ± 0.54
Spike mass	gDM·pot <sup>-1</sup>	7.60 ± 0.32	8.26 ± 1.08	7.53 ± 1.09	7.76 ± 1.17	8.06 ± 0.69
Yield ratio			-	0.91	0.85	0.64
P	g·kg <sup>-1</sup>	4.59 ± 0.17	4.09 ± 0.12	4.16 ± 0.17	4.83 ± 0.11	4.48 ± 0.15
Ca	mg·kg <sup>-1</sup>	112.12 ± 10.49	147.43 ± 10.08	129.96 ± 8.698	117.22 ± 7.573	146.73 ± 14.96
Mg	mg·kg <sup>-1</sup>	792.79 ± 48.69	782.24 ± 50.83	736.85 ± 33.43	867.67 ± 32.19	706.78 ± 31.52
Fe	mg·kg <sup>-1</sup>	99.77 ± 3.80	94.55 ± 9.122	90.86 ± 3.79	94.89 ± 1.72	76.69 ± 3.50
Al ± SE	mg·kg <sup>-1</sup>	59.75 ± 1.62	57.58 ± 1.31	51.24 ± 3.53	50.69 ± 3.05	45.93 ± 1.33
Mn	mg·kg <sup>-1</sup>	21.35 ± 2.18	31.86 ± 4.02	21.66 ± 0.82	17.63 ± 1.67	23.21 ± 3.05
Zn	mg·kg <sup>-1</sup>	49.02 ± 1.40	47.50 ± 1.85	43.48 ± 1.53	45.10 ± 1.65	42.32 ± 1.10
Cu	mg·kg <sup>-1</sup>	8.64 ± 0.95	8.84 ± 1.55	8.94 ± 1.68	10.0 ± 1.69	9.86 ± 2.07
Pb	mg·kg <sup>-1</sup>	5.22 ± 0.50	7.83 ± 0.58	8.61 ± 1.31	5.82 ± 0.51	10.25 ± 1.49
Cd	mg·kg <sup>-1</sup>	0.48 ± 0.08	0.40 ± 0.06	0.39 ± 0.03	0.49 ± 0.04	0.32 ± 0.07
SOIL 1						
pH <sub>H2O</sub>		6.77	6.83	7.34	7.24	7.18
pH <sub>KCl</sub>		6.50	6.38	7.04	7.17	6.79
AL-P	mg·kg <sup>-1</sup>	11.71 ± 0.26	12.72 ± 0.49	13.88 ± 0.10	13.65 ± 0.32	12.89 ± 0.40
Al-K ± SE	mg·kg <sup>-1</sup>	24.11 ± 1.49	24.35 ± 0.94	24.13 ± 0.93	21.15 ± 0.75	22.60 ± 0.48
AL-Mg	mg·kg <sup>-1</sup>	657.19 ± 4.48	634.72 ± 16.14	656.94 ± 24.58	709.03 ± 13.24	651.00 ± 40.16
Hh	cmol·kg <sup>-1</sup>	1.07 ± 0.05	1.20 ± 0.06	0.67 ± 0.03	0.60 ± 0.03	0.72 ± 0.03
Ca <sup>2+</sup>	cmol·kg <sup>-1</sup>	15.86 ± 0.52	16.38 ± 0.38	20.67 ± 0.48	29.45 ± 1.16	20.40 ± 0.33
Mg <sup>2+</sup> ± SE	cmol·kg <sup>-1</sup>	1.32 ± 0.05	1.27 ± 0.02	1.14 ± 0.01	1.26 ± 0.04	1.25 ± 0.01
K <sup>+</sup>	cmol·kg <sup>-1</sup>	0.53 ± 0.06	0.40 ± 0.02	0.38 ± 0.01	0.34 ± 0.01	0.38 ± 0.01
Na <sup>+</sup>	cmol·kg <sup>-1</sup>	0.57 ± 0.11	0.50 ± 0.08	0.34 ± 0.06	0.65 ± 0.07	1.27 ± 0.13
TEB	cmol·kg <sup>-1</sup>	18.28	18.55	22.53	31.70	23.29
CEC	cmol·kg <sup>-1</sup>	19.34	19.75	23.20	32.29	24.01
BS%		94.49	93.92	97.13	98.14	97.02

**Table 8. Amendment rate, yield and composition of ryegrass and pH, AL-extractable P, K and Mg, hydrolytic acidity (Hh), base cations concentration, TEB, CEC and BS in soil 2**

	units	NO P	KH <sub>2</sub> PO <sub>4</sub>	POLONITE	FILTRA P	WOLLASTONITE
Amendment	g·pot <sup>-1</sup>	-	0.12	22	24	26
RYEGRASS						
Fresh weight	g·pot <sup>-1</sup>	81.83 ± 0.60	83.63 ± 2.15	88.13 ± 3.66	93.63 ± 4.44	88.66 ± 2.01
Yield	gDM·pot <sup>-1</sup>	16.93 ± 0.17	16.86 ± 0.41	17.36 ± 0.49	17.56 ± 0.49	17.00 ± 0.15
Yield ratio			-	0.79	0.73	0.65
P	g·kg <sup>-1</sup>	2.07 ± 0.14	2.17 ± 0.08	3.20 ± 0.07	3.46 ± 0.26	2.44 ± 0.08
Ca	mg·kg <sup>-1</sup>	624.55 ± 56.87	608.34 ± 48.36	1891.11 ± 236.13	4060.60 ± 536.68	2699.42 ± 166.35
Mg	mg·kg <sup>-1</sup>	1570.14 ± 77.26	1386.11 ± 42.39	1925.32 ± 97.35	1738.27 ± 67.11	1823.69 ± 87.69
Fe	mg·kg <sup>-1</sup>	398.37 ± 39.32	197.33 ± 7.89	200.33 ± 2.44	192.10 ± 18.45	170.43 ± 6.65
Al ± SE	mg·kg <sup>-1</sup>	97.07 ± 0.79	86.44 ± 1.82	78.19 ± 2.37	64.52 ± 2.67	85.14 ± 1.91
Mn	mg·kg <sup>-1</sup>	420.13 ± 18.08	374.70 ± 29.10	227.08 ± 20.54	148.12 ± 9.08	242.41 ± 20.64
Zn	mg·kg <sup>-1</sup>	83.79 ± 1.14	73.45 ± 1.64	59.17 ± 0.82	50.40 ± 2.42	66.46 ± 1.25
Cu	mg·kg <sup>-1</sup>	24.66 ± 5.40	21.17 ± 4.79	19.64 ± 4.15	15.70 ± 3.33	17.31 ± 3.13
Pb	mg·kg <sup>-1</sup>	6.39 ± 0.70	24.31 ± 10.82	23.43 ± 4.06	32.87 ± 16.19	48.34 ± 2.02
Cd	mg·kg <sup>-1</sup>	2.97 ± 1.43	0.74 ± 0.03	0.79 ± 0.04	1.00 ± 0.07	3.05 ± 1.79
SOIL 2						
pH <sub>H2O</sub>		4.60	4.51	5.12	5.52	5.02
pH <sub>KCl</sub>		3.72	3.68	4.28	5.15	4.06
AL-P	mg·kg <sup>-1</sup>	5.72 ± 0.10	6.06 ± 0.24	6.48 ± 0.10	6.32 ± 0.12	6.27 ± 0.38
Al-K ± SE	mg·kg <sup>-1</sup>	15.32 ± 0.26	16.38 ± 0.30	15.74 ± 0.11	14.62 ± 0.81	15.51 ± 0.58
AL-Mg	mg·kg <sup>-1</sup>	1257.91 ± 70.60	1313.30 ± 20.74	1128.07 ± 19.26	1143.16 ± 46.60	1117.53 ± 66.45
Hh	cmol·kg <sup>-1</sup>	8.28 ± 0.05	9.90 ± 0.12	6.90 ± 0.26	3.53 ± 0.20	6.35 ± 0.22
Ca <sup>2+</sup>	cmol·kg <sup>-1</sup>	1.51 ± 0.03	1.37 ± 0.03	5.71 ± 0.30	10.97 ± 0.56	4.87 ± 0.24
Mg <sup>2+</sup> ± SE	cmol·kg <sup>-1</sup>	0.58 ± 0.01	0.56 ± 0.01	0.58 ± 0.02	0.62 ± 0.02	0.58 ± 0.03
K <sup>+</sup>	cmol·kg <sup>-1</sup>	0.29 ± 0.00	0.29 ± 0.00	0.27 ± 0.01	0.27 ± 0.01	0.28 ± 0.01
Na <sup>+</sup>	cmol·kg <sup>-1</sup>	1.18 ± 0.08	0.94 ± 0.10	0.45 ± 0.10	0.37 ± 0.11	0.93 ± 0.42
TEB	cmol·kg <sup>-1</sup>	3.57	3.16	7.00	12.23	6.67
CEC	cmol·kg <sup>-1</sup>	11.85	13.06	13.90	15.76	13.02
BS%		30.10	24.20	50.37	77.58	51.21

compared with both control and potassium phosphate treatments. There was a slight increase in the concentration of Mg in ryegrass grown with substrate treatment and a slight decrease in Fe and Al compared with the control treatment. The relationship between substrate amendment and ryegrass composition depends strongly on soil properties. This is further discussed in Paper III.

### 5.3.2 Effect on soil pH and soil P availability

The pH of soil 1 (neutral) was unaffected during the experiment for the control and potassium phosphate treatments but it slightly increased with substrate treatment

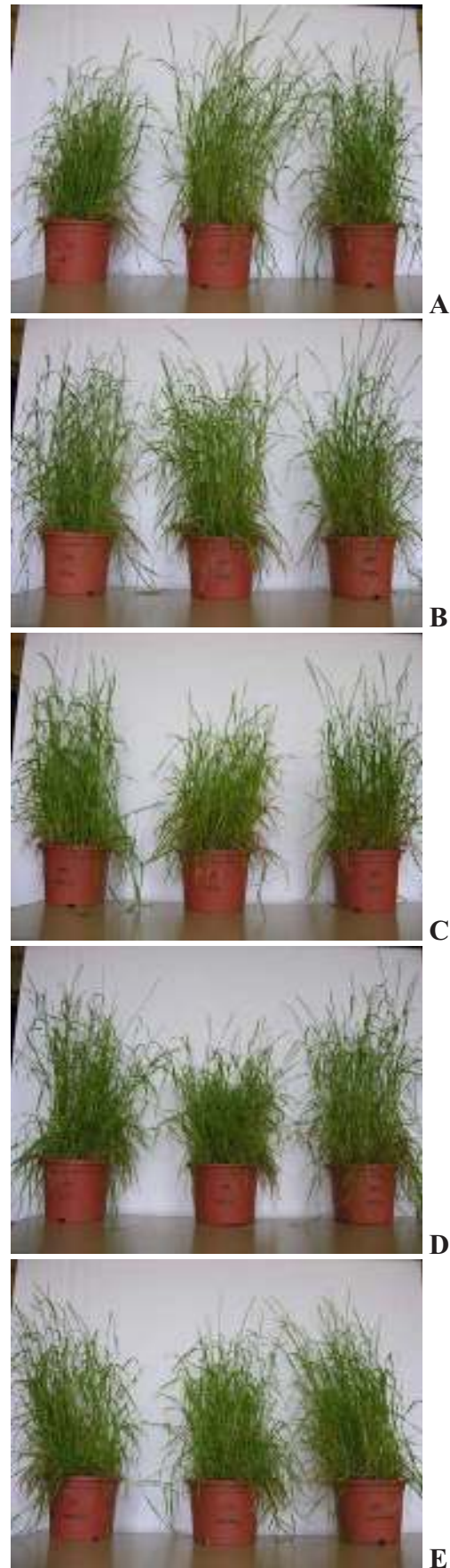
since all substrates had relatively high pH values (Table 7). In the case of soil 2 (acid), the pH increased during the experiment for all treatments and the increase was higher with substrate treatment (table 8). In both cases, there was an increase in AL-extractable P during the experiment for all treatments and the increase was higher with substrate treatment. The AL-extractable P from both soils correlated well with the initial P content in the substrates and it was highest in soil treated with Polonite. This suggests that P in the substrates was able to desorb and dissolve in the soil solution. On

the other hand, soil P availability may increase as a result of a soil pH increase, which favours the dissolution of P bound to Fe and Al oxides in soil particles. Several studies have shown that alkaline substrates can increase the pH of acid soils and, subsequently, soil P availability (Sloan and Basta, 1995; Matsi and Keramidas, 1999; Snars et al., 2004). In the present study, the increase in soil P availability was the result of a combination of increased soil pH and direct P release from the reactive substrates.

There was a decrease in AL-extractable K in both soil 1 and 2 for all treatments, which may indicate insufficient K fertilization in the experiment. However, there was no significant difference between treatments regarding AL-extractable K and Mg.

### 5.3.3 Effect on other soil properties

The application of the reactive substrates to both soil 1 and 2 decreased the hydrolytic acidity (Hh) and increased the cation exchange capacity (CEC) compared with both control and potassium phosphate treatments. The increase in soil CEC is mainly the result of increasing amounts of  $\text{Ca}^{2+}$  ions in the sorption complex derived from the high Ca content in the substrates applied. This can be particularly beneficial for acid soils, although it can reduce the concentration of other ions in the sorption complex. This was observed in soil 1, where the concentration of  $\text{K}^+$  and  $\text{Na}^+$  ions in the sorption complex decreased with substrate treatment. The reduction in Hh as a result of substrate treatment involves a decrease in  $\text{Al}^{3+}$  ions in the sorption complex, which reduces Al availability for plants. This can be observed as a slight decrease in Al concentrations in barley grown in soil 1 amended with substrate treatment (Table 7) despite the noticeable content of Al in the substrates. In the case of acid soils (soil 2), the substrates can be particularly beneficial since they can reduce the risk of Al toxicity, which



**Figure 11.** Pot experiment showing ryegrass yield for five different treatments, **A:** No P, **B:**  $\text{KH}_2\text{PO}_4$ , **C:** Polonite, **D:** FiltralP, **E:** Wollastonite

is one of the primary limitations for agriculture on acid soils (Kochian et al., 2004). Filtra P amendments greatly increased the percentage base saturation and significantly decreased the hydrolytic acidity by introducing large amounts of  $\text{Ca}^{2+}$  ions into the sorption complex. This is probably due to the high solubility of Ca compounds in Filtra P. The implications of such amendments are further considered in Paper III.

#### 5.4 Suitability of the substrates as soil amendments

The materials did not contain large amounts of hazardous compounds except for the content of Pb in Filtra P (Table 4). When using the materials with real wastewater, the content of metals may increase since they can efficiently adsorb metals too (Kietlińska et al., 2004). However, if the materials are used for domestic wastewater treatment only, their levels of metals may be kept low. Thus, the saturated materials may fulfil the requirements of the EU directive on the use of sewage sludge in agriculture (86/278/EEC).

The reactive media saturated with P may be a reliable source of P for plants and can influence nutrient availability in soils. The substrates can also increase soil pH and act as soil conditioners. The high content of Si in Polonite and wollastonite might improve soil structure as well. Wollastonite is a natural product and contains substantial amounts of Mn (Table 4) compared with other substrates. This can be of benefit for plants, but due to its lower P sorption capacity, wollastonite may not be a reliable source of P in the long term. Filtra P was able to increase the amount of soluble P and especially Ca in the soil solution. However, the elevated content of Pb and also Hg (Renman, personal communication) may limit its use in agriculture. Polonite appears to be the most appropriate substrate for several reasons. It has a high P saturation potential, which can ensure P supply for plant uptake during a reasonable period of time. In addition, it can

provide considerable amounts of other macro- and micronutrients and since it is derived from a natural bedrock (opoka), it does not contain hazardous levels of heavy metals.

## 6 CONCLUSIONS

This work shows that reactive filter media saturated with P can be used as fertilizer substrates in agriculture. The P content in the substrates depends on their P sorption capacity, which depends mainly on the amount and form of Ca compounds in the material. The results show that the sorption capacity increases linearly with the CaO concentration in the material. The mechanisms of P sorption differ as a consequence of varying Ca:P ratio. The suitability of the materials as filter media depends on the structure, chemical composition and particle size.

Polonite, Filtra P and wollastonite tailings saturated with P showed a tendency for higher dry matter yield of barley and ryegrass in pot experiments. According to the yield/amendment ratio, Polonite was the most effective fertilizer substrate. All three amendments increased soil pH, availability of P and cation exchange capacity. The increase was more obvious in the acid soil (soil 2). Filtra P amendments produced the highest increase in soil pH and cation exchange capacity, causing significant changes in soil properties probably due to its alkaline pH and high content of soluble Ca. On the other hand, Polonite produced the highest increase in P availability in both soils due to its higher content of P.

The results suggest that the substrates can act as a source of P for plants and improve nutrient availability in soils, while also increasing soil pH and acting as soil conditioners. Among the substrates studied here, Polonite can be regarded as the most suitable material for the purpose of P recycling from wastewater to agriculture.



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