



**KTH Architecture and  
the Built Environment**

**RECYCLING FILTER SUBSTRATES USED FOR  
PHOSPHORUS REMOVAL FROM WASTEWATER  
AS SOIL AMENDMENTS**

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Victor Cucarella

Stockholm, March 2009



## 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 1-6.

- I. Cucarella, V., Renman, G., 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments – a comparative study. *Journal of Environmental Quality* 38, 381-392.
- II. Cucarella, V., Zaleski, T., Mazurek, R., Renman, G., 2007. Fertilizer potential of calcium-rich substrates used for phosphorus removal from wastewater. *Polish Journal of Environmental Studies* 16 (6), 817-822.
- III. Cucarella, V., Zaleski, T., Mazurek, R., Renman, G., 2008. Effect of reactive substrates used for the removal of phosphorus from wastewater on the fertility of acid soils. *Bioresource Technology* 99, 4308-4314.
- IV. Cucarella, V., Renman, G., Renman, A., 2009. Phosphorus sorption properties of soils amended with recycled wastewater filter substrates. *Geoderma* (submitted).
- V. Cucarella, V., Mazurek, R., Zaleski, T., Kopeć, M., Renman, G., 2009. Effect of Polonite used for phosphorus removal from wastewater on soil properties and fertility of a mountain meadow. *Environmental Pollution*, doi: 10.1016/j.envpol.2009.02.007 (In Press).
- VI. Cucarella, V., Zaleski, T., Mazurek, R., Renman, G., 2009. Recycling Polonite used for on-site wastewater treatment as a soil amendment to a wheat cropping field. Manuscript.

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## ABSTRACT

This thesis studied the viability of recycling filter substrates as soil amendments after being used in on-site systems for phosphorus (P) removal from wastewater. Focus was put on the materials Filtra P and Polonite, which are commercial products used in compact filters in Sweden. A prerequisite for this choice was to review filter materials and P sorption capacity. The filter substrates (Filtra P, Polonite and wollastonite tailings) were recycled from laboratory infiltration columns as soil amendments to a neutral agricultural soil and to an acid meadow soil to study their impacts on soil properties and yield of barley and ryegrass. The amendments tended to improve the yield and showed a liming effect, significantly increasing soil pH and the availability of P. In another experiment, samples of Filtra P and Polonite were equilibrated in batch experiments with the two soils in order to study the P dynamics in the soil-substrate system. Batch equilibrations confirmed the liming potential of Filtra P and Polonite and showed that improved P availability in soils was strongly dependent on substrate P concentration, phase of sorbed P, and soil type. Finally, samples of Polonite used for household wastewater treatment were recycled as soil amendments to a mountain meadow and to an agricultural field for wheat cropping. The liming effect of Polonite was confirmed under field conditions and the results were similar to those of lime for the mountain meadow soil. However, the results were quite different for the agricultural field, where Polonite did not affect soil pH or any other chemical and physical soil properties investigated and had no impact on wheat yield and quality. The results from field experiments suggested that Polonite can be safely recycled to meadows and cropping fields at rates of 5-10 ton ha<sup>-1</sup> but long-term studies are needed to forecast the effects of accumulation.

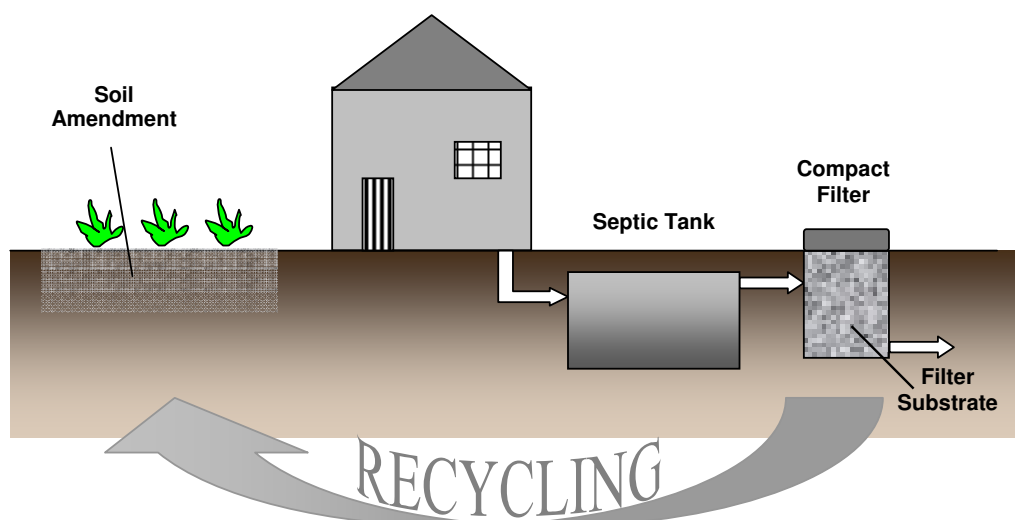
**Keywords:** Compact filter; Filtra P; Phosphorus recycling; Polonite; Soil amendment; Sorption isotherms

## 1 INTRODUCTION

Wastewater treatment in rural areas has been devoted less attention than necessary in many countries. In some countries like Sweden, wastewater discharges from private households represent an important source of phosphorus (P) pollution, affecting the quality of the surrounding water bodies (Günther, 1999). Advanced on-site treatment systems can improve notably the quality of septic tank effluents (Jantrania and Gross, 2006). Among these, compact filters have recently emerged in the market as a cost-effective option for meeting public health and quality goals in these areas. These systems require less space than most other on-site systems such as constructed wetlands or conventional soil infiltration, and can be easily operated. They incorporate reactive filter media with a high P sorption capacity. After a certain time, the filter is no longer effective and the material must be replaced. Then, it can be recycled as a soil amendment if the content of toxic compounds or ele-

ments does not restrict its use (Fig. 1). This gives one more important advantage to these treatment systems. Depending on the P concentration in the recycled substrate, it may add potential benefits as a fertilizer on soils and crops. The incorporation of other macro- and micro-nutrients may be of benefit for the fertility of soils too. Reactive filter materials for P removal are usually rich in Ca and have elevated pH values. Depending on the concentration and form of Ca compounds, and the pH drop after wastewater treatment, the recycled substrates may have a potential liming effect, which can be of particular benefit for acid soils.

A large number of filter materials with the ability to remove P from wastewater are described in literature (e.g. Johansson Westholm, 2006). Among these, Filtra P and Polonite have shown an effective performance and are used in compact filters for on-site wastewater treatment at present. However, little is known about the viability of recycling these and other substrates as soil amendments and the effects of such on soil



**Fig. 1. Diagram of compact filter technology for on-site wastewater treatment and later sustainable nutrient recycling.**

properties and plants. Therefore, the application of such amendments and the study of the risks and benefits on soils requires further investigation, especially under field conditions.

### 1.1 Objectives and scope

The main objective of this thesis was to evaluate the potential of filter substrates used for P removal in on-site wastewater treatment systems to be recycled as soil amendments. The work focused on studying the effect of the amendments on different soil properties and their ability to recycle P.

A prerequisite for this study was to review filter materials for on-site wastewater treatment and understand P sorption capacity. The substrates with high P sorption capacity may be of a greater interest when used as soil amendments.

The reactive filter materials Filtra P and Polonite were chosen for this study since they are commercial products with proven effectiveness. The key objectives for each part of the thesis were:

- Review filter materials and P sorption capacity (Paper I)
- Estimate the ability of filter substrates to recycle P (Papers II, III, IV)

- Evaluate the effects of filter substrates on soil properties in pot experiments (Papers II, III) and field experiments (Papers V, VI).

### 1.2 Limitations

This study is multidisciplinary and, therefore, deals with many situations where knowledge borders can not be overcome. The main limitations correspond to:

- The main focus was on P, and not other elements that could have been of importance.
- Nitrogen was not considered since the N retention capacity of filter materials is low (Renman et al., 2008).
- Only 3 filter materials were selected in this study and most work focused on 2 of them: Filtra P and Polonite.
- Only 2 types of soils were considered. Samples were taken from the 2 field stations where field work was later carried out.
- Only selected soil chemical (and in some cases physical) properties were studied. The plant-soil or root-soil system was not considered in this research. Only some general aspects related with above-ground biomass were studied.

## 2 BACKGROUND

Wastewater is usually hazardous to human and other living species, and must be treated prior to disposal into the environment. Large-scale centralized wastewater treatment has significantly improved water quality standards during the last two decades. However, wastewater treatment in rural areas lacks behind, in particular regarding phosphorus (P) removal (Günther, 1999).

### 2.1 Phosphorus pollution

Elevated P concentrations in surface waters are often the result of soil erosion, agricultural runoff and discharges of municipal and industrial wastewaters. Transport of P from soils to surface waters takes place in both chemical (dissolved) and physical (particulate) forms. In freshwaters, it is usually the limiting growing factor and high concentrations of P accelerates eutrophication. Agricultural runoff is the major diffuse source of P in surface waters. 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 L<sup>-1</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 L<sup>-1</sup> with a minimum reduction of 80%. In Sweden, this limit is more stringent and effluent P must remain below 0.5 mg L<sup>-1</sup>.

#### 2.1.1 Phosphorus removal and recovery

Phosphorus removal is achieved by chemical precipitation with coagulants such as aluminium salts, lime, FeCl<sub>3</sub> and FeSO<sub>4</sub> or in the biological P removal process, where phosphate ions are taken up by bacteria (Brett et al., 1997; Sincero and Sincero, 2003). In the enhanced biological phosphorus removal (EBPR) process, alternating conditions favour a particular environment for the proliferation of bacteria that accumulate phosphorus in excess of normal metabolic requirements (Bashan and Bashan, 2004). In both cases, the end product is a chemical or biological sludge to which P is tightly bound.

Phosphorus can be recovered from wastewater streams as calcium phosphate. The known DHV Crystalactor<sup>TM</sup> system recovers calcium phosphate as a pellet with a P content of up to 11% (Morse et al., 1998; Angel, 1999; Duley, 2001). Another possible pathway is magnesium ammonium phosphate (struvite), which has a potential application as a slow-release fertilizer (Johnston and Richards, 2003; Bashan and Bashan, 2004). A recent seed-induced crystallisation process has been shown to remove 80-100% P from wastewater yielding a product containing 10% P (Berg et al., 2005). Angel (1999) showed, however, that laboratory studies on a new process yielding an 18% P product, overestimated the outcome under field conditions.

The large fraction of P retained in the sewage sludge could be directly recycled to agriculture, but the risk of gradually contaminated fertile soils has resulted in increasing limitations on sludge disposal imposed by the EU (Directive 86/278/EEC), thus

**Table 1. Typical components and their concentrations in raw wastewater, septic tank and media filter effluents (from Jantrania and Gross, 2006)**

Effluent	BOD (mg L <sup>-1</sup> )	TSS (mg L <sup>-1</sup> )	NO <sub>3</sub> -N (mg L <sup>-1</sup> )	NH <sub>4</sub> -N (mg L <sup>-1</sup> )	D.O. (mg L <sup>-1</sup> )	Fecal coliform (cfu/100 mL)	P <sub>T</sub> (mg L <sup>-1</sup> )
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

posing constraints on this alternative. Landfilling and incineration are the dominant methods for sludge disposal nowadays (Duley, 2001; Stark, 2005b). In this way, the recovery of nutrients is not achieved, and, 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. Different options to recover P from sewage sludge include for example sludge fractionation (KREPRO™) and the Aqua-ReCi process with supercritical water oxidation (SCWO) (Levlin et al., 2002; Stark, 2005a). A novel technology uses phosphate-solubilizing microorganisms (PSB or PSF) to recover non-soluble phosphate compounds (Bashan and Bashan, 2004). Phosphorus can also be recovered from ash after sludge incineration (Duley, 2001; Stark et al., 2006).

Attempts for the recovery of P from wastewater, although technically possible, are often economically unfeasible (Morse et al., 1998; Driver et al., 1999; Woods et al., 1999; SEPA, 2000; Schipper et al., 2001; Stark, 2005a; Berg et al., 2007). The possibilities become even more limited in small communities and rural areas.

## 2.2 On-site wastewater treatment

Decentralized wastewater treatment systems are a cost-effective and long-term option for meeting public health and water quality goals, particularly in rural areas (USEPA, 2002; Crites et al., 2006; Jantrania and Gross, 2006). The difference with traditional septic tanks is the level of treatment and consequently, the dependence on soil and site conditions. Advanced on-site treatment includes a variety of systems such as natural and constructed wetlands, aerobic treatment units (ATUs), waterless toilets (dry toilets), disinfection systems (UV light, chlorination/dechlorination), and media filters (Jantrania and Gross, 2006). Among the different alternatives, a great deal of work has been devoted to natural and constructed wetlands systems (Brix, 1994; Kadlec and Knight, 1996; Vymazal et al., 1998; Kløve and Mæhlum, 2000; Scholz, 2006; Vymazal, 2007). Most recently, focus is being put on

media filters for its efficiency and simplicity. Media filters are usually located after a septic tank and can improve substantially the quality of effluents (Van Buuren et al., 1999; Crites et al., 2006; Hedström, 2006; Heistad et al., 2006; Jantrania and Gross, 2006). The performance of an on-site 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. The filter media must have an appropriate particle size and consistency for the filter system to work properly. Table 1 shows typical effluent concentrations from septic tanks and media filters. The P removal efficiency depends mostly on the media filter used, although other factors may be important too. Sand and gravel filters have been used for many years, but they may remove some P for only a short period. 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 (Mann, 1996; Kløve and Mæhlum, 2000; Arias et al., 2003; Farahbakhshazad and Morrison, 2003). A large number of filter materials have been lately proposed as suitable media for P removal (Table 2).

### 2.2.1 Filter materials

Filter materials used for P removal from wastewater are characterized by a high affinity for P and appropriate hydrological properties. These materials are also called substrates and can be classified into three groups: natural materials, industrial by-products and manufactured products (Johansson Westholm, 2006). Non-reactive or inert materials such as sand and gravel have long been suggested as suitable filter media for P removal from wastewater (Mann and Bavor, 1993; Zhu et al., 1997; Arias et al., 2001; Del Bubba et al., 2003). Reactive materials are referred to as adsorbents or sorbents and specifically interact with targeted chemical species (e.g. phosphate ions).

Calcium-rich natural materials are of interest due to the strong interaction of P with some Ca compounds. Among these, opoka, a

**Table 2. Filter materials with reported ability to remove P from solutions or wastewater**

<i>Filter material</i>	<i>Origin/ Properties/ Composition</i>	<i>References</i>
<i>Natural</i>		
Bauxite	Al and Fe oxides	Drizo et al., 1999; Antuldogan and Tumen, 2003
Gravel	Gravel	Mann and Bavor, 1993; Mann 1997
Limestone	Calcium carbonate	Drizo et al., 1999; Johansson 1999; Zhou and Li, 2001
Opoka	Sedimentary rock rich in calcium carbonate and silica	Cucarella, 2000; Brogowski and Renman, 2004; Cucarella et al., 2007; Renman, 2008
Sand	Sand	Brix et al., 2001; Arias et al., 2001; Del Bubba et al., 2003; Dunne et al., 2008
Serpentine	Mg-rich silicate mineral	Drizo et al., 2006
Shale	Limestone-derived	Drizo et al., 1999
Shell sand	Carbonic material mainly produced by shells, snails, and coral alga	Roseth, 2000; Sovik and Klove, 2005; Adam et al., 2007a
Tobermorite	Calcium silicate mineral	Berg et al., 2005,2006
Volcanic ash	Volcanic ash	Ping and Michaelson, 1986
Wollastonite	Calcium silicate mineral	Brooks et al., 2000; Gustafsson et al., 2008
Zeolite	Aluminum-silicate	Sakadevan and Bavor, 1998; Drizo et al., 1999
<i>By-products</i>		
BFS	Blast furnace slag (from steel making industry)	Yamada et al., 1986; Mann and Bavor, 1993; Sakadevan and Bavor, 1998; Johansson and Gustafsson, 2000; Agyei et al., 2002; Orguz, 2004; Renman et al., 2004; Kostura et al., 2005; Hylander et al., 2006; Shilton et al., 2006; Korkusuz et al., 2007; Gustafsson et al., 2008; Renman, 2008
EAF	Electric arc furnace slag (steel making)	Drizo et al., 2002; 2006
Fe and Ca DWTR	Drinking water treatment residuals (DWTR)	Ippolito et al., 2003; Dayton and Basta, 2005; Dunne et al., 2008
Fly ash	Fly ash (from coal combustion processes)	Cheung et al., 1994; Urgulu and Salman, 1998; Drizo et al., 1999; Cheung and Venkitachalam, 2000; Grubb et al., 2000; Agyei et al., 2002; Li et al., 2006; Chen et al., 2007
Iron oxide tailings	Iron mining	Zeng et al., 2004
Ochre	Iron mining	Heal et al., 2003; 2005; Dobbie et al., 2009
Oil-shale ash	Thermal power plants (solid fuel)	Kaasik et al., 2007
Red mud	Bauxite residue	Summers et al., 1993, 1996; Cheung et al., 1994; Lopez et al., 1998; Li et al., 2006; Huang et al., 2008
<i>Manufactured/ Commercial</i>		
Absol	LWA with cement and Al	Renman, pers. com.
Fe-Al-quartz	Fe and Al oxides coated quartz particles	Arias et al., 2006
Fe-sand and brick	Fe-coated sand and brick (0.3-0.5% Fe)	Boujelben et al., 2007
Filtra P	Lime, Fe compounds and gypsum	Hedström, 2006; Gustafsson et al., 2008
Filtralite P	LECA enriched in Ca	Zhu et al., 1997; Adam et al., 2006; 2007ab; Heistad et al., 2006
Half-burned dolomite	Ca-Mg carbonate thermally treated	Roques et al., 1991
LECA	Light expanded clay aggregates	Johansson, 1997; Zhu et al., 1997; Drizo et al., 1999
Phoslock™	P binding clay	Robb et al., 2003
Polonite	Thermally treated opoka	Cucarella, 2000; Brogowski and Renman, 2004; Renman et al., 2004; Renman, 2008; Gustafsson et al., 2008
Reactive mixtures	Silica, limestone, and Fe and Al oxides	Baker et al., 1998
UTELITE	Light weight aggregate (LWA)	Zhu et al., 1997



sedimentary deposit with a high content of calcium carbonate and silica, has shown promising results when heated to more than 900°C (Brogowski and Renman, 2004; Cucarella et al., 2007). Some other Ca-rich natural materials investigated include limestone (Drizo et al., 1999; Johansson, 1999), shale (Drizo et al., 1997; 1999), shell sands (Ádám et al., 2007ab; Søvik and Kløve, 2005) and wollastonite (Brooks et al., 2000). Among those with Al and Fe as dominant constituents are for example aluminium-silicate based zeolites (Sakadevan and Bavor, 1998; Drizo et al., 1999), Al and Fe oxides based bauxite (Drizo et al., 1999) or Fe-rich sands (Kvarnström et al., 2004). Although many of the materials investigated are of natural origin, the greatest interest has been devoted to industrial by-products such as slag materials and fly ash (Yamada et al., 1986; Mann and Bavor, 1993; Sakadevan and Bavor, 1998; Drizo et al., 1999; Johansson, 1999; Drizo et al., 2002; Orguz, 2004; Kostura et al., 2005; Xu et al., 2006). Slags are by-products of steel making works and can vary widely in form and composition depending on the manufacture process. They usually contain elevated concentrations of CaO and relatively high concentrations of Al and Mg oxides. Electric arc furnace (EAF) steel slag is rich in both Ca and Fe (Drizo et al., 2002). Fly ash is the by-product of the coal combustion process and the composition of fly ash can vary strongly depending on the process conditions. Among the samples of fly ash investigated, there is a wide range of pH values and chemical composition. Other by-products of relevance are mine drainage derived ochre (Heal et al., 2003, 2005; Dobbie et al., 2009) and bauxite residue red mud (Summers et al., 1993; López et al., 1998; Li et al., 2006; Huang et al., 2008). The group of lightweight aggregates (LWA) has also been widely studied by many authors (Zhu et al., 1997; Drizo et al., 1999; Johansson, 1999; Ádám et al., 2006, 2007ab) and the most popular in this group are LECA and Filtralite. The latter is the product of processing LECA to improve its P sorption capacity.

The increasing demand for efficient materials for P removal from wastewater has led to the appearance of new derivatives and the manufacture of novel products. Some of the most effective are the commercial products Polonite (Bioptech AB, Sweden) (derived from opoka) and Filtra P (Nordkalk, Finland) (Renman et al., 2004; Cucarella et al., 2007; Hylander et al., 2006; Gustafsson et al., 2008). Both of these have relatively high pH values and a high content of CaO.

### **2.2.2 Phosphorus sorption capacity**

The ability of a material to remove P from wastewater depends on its physical and chemical properties. The shape, particle size and porosity of the grains or aggregates define their specific surface area, and, generally, the smaller the particle size the larger the surface area to undergo P sorption (Nair et al., 1984; Mann, 1996; Zhu et al., 1997). The chemical composition together with the pH determines the affinity or reactivity and the strength of the interaction. The P removal efficiency of a material is closely related to the content of Al, Ca and Fe, as well as the pH (Grubb et al., 2000; Johansson and Gustafsson, 2000; Arias et al., 2001; Khadhraoui et al., 2002; Arias et al., 2006), and the abundance of these elements times the surface area defines the number of sorption sites. Thus, the sorption capacity depends on both the number and affinity of sorption sites.

The term sorption was described by McBride (1994) as a continuous process that ranges from adsorption to precipitation reactions. This term is very convenient when the chemical processes governing the interaction are not fully known, as is the case for the reaction of phosphate ions with the different reactive materials studied and used for P removal from wastewater. In surface chemistry, adsorption can be defined as the net accumulation of matter at the solid-water interface (Stumm and Morgan, 1996). Ion exchange involves non-specific electrostatic forces that render the phosphate ion readily exchangeable, i.e. other anions can displace the phosphate ion (Brady and Weil, 1996). Precipitation is closely related to the pH of the substrate and cannot occur until the

solubility product of a particular phase is exceeded, i.e. some degree of super saturation is required (McBride, 1994).

The P sorption capacity can be estimated in batch experiments, which consist of placing a fixed amount of the material with a mass  $M$  (g) in a beaker or Erlenmeyer flask containing a volume  $V$  (L<sup>-1</sup>) of a prepared P solution at one of a range of increasing concentrations. The samples are shaken in a rotator at speed  $v$  (rpm) for a time  $t$  (h) at temperature  $T$  (°C). The difference between the initial and final P concentrations in solution at equilibrium (assumed to be reached at time  $t$ ),  $C_0$  and  $C_{eq}$  respectively, is assumed to be sorbed to the material. The concentration of P is determined by colorimetric methods (e.g. Murphy and Riley, 1962). The amount of P sorbed to the material ( $S$ ) is expressed in unit mass P (mg or g) per unit mass of the material (kg) and is calculated as:

$$S = \frac{(C_0 - C_{eq}) \cdot V}{M} \quad (1)$$

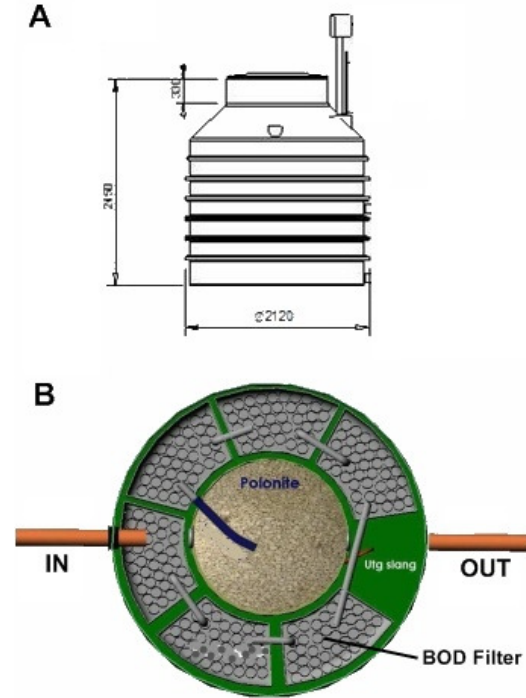
However, the P sorption capacity is relative because it is estimated under different conditions. The data strongly depend on the experimental procedure itself and the most important parameters influencing the results are the form and amount of the material, the material:solution ratio, the nature, pH and initial concentration of the P solution, the contact time, agitation and temperature (Barrow, 1978; Nair et al., 1984; McKay, 1996). The presence of competing anions, if any, may also influence the results.

The P sorption capacity can also be estimated in column experiments, which usually obtain estimates that better represent the performance of the filter material in real conditions (Drizo et al., 2002). However, column tests are time-consuming and normally defined for a particular filter system with set conditions, i.e. contact time, influent P concentration, etc.

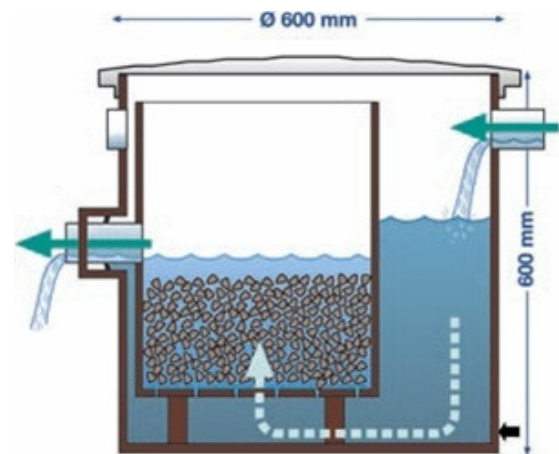
### 2.2.3 Compact filters

A compact solution for media filters requires filter materials with a high P sorption capacity. That is the case of the commercial systems BioP® (Biotech AB, Sweden) that

incorporates Polonite, and Nordkalk Filtra P filter (Nordkalk, Finland). Although these two systems are based on the same principle, they operate differently. The Biotech BioP® includes a BOD pre-treatment package before the effluent flows through the Polonite filter downwards with unsaturated con-



**Fig. 2. Compact filter BioP® (Biotech AB, Sweden). A: Dimensions of the container; B: Diagram of the interior of the container showing BOD filters and Polonite® media.**



**Fig. 3. Compact filter Nordkalk, Finland, filled with the reactive filter material Filtra P (500K).**

ditions (Fig. 2). The Filtra P filter works upwards under saturation conditions (Fig. 3). Another compact system used in the Scandinavian countries is that using the light weight aggregate Filtralite P (Heistad et al., 2006). This filter system requires a rather larger space (3.4 m<sup>3</sup> biofilter and 6 m<sup>3</sup> media filter) than that required for Polonite and Filtra P filters (which remains below 1 m<sup>3</sup>). In all systems, the filter has a lifetime that depends on the volume of wastewater treated and the amount of the material used. For Polonite, a packed 500 kg filter may last for about 2 years for a single house with 3-5 people (Renman, 2008). After that time, the media has to be replaced and the filter substrate may be recycled as a soil amendment.

### 2.3 Recycling filter substrates

Just like the sludge from conventional wastewater treatment works, the media used in on-site 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 (Renman et al., 2009). Land and agricultural application of sewage sludge has often been regarded as a feasible alternative (Lassen et al., 1984; Sloan and Basta, 1995; Singh and Agrawal, 2008). Depending on the nature of the sludge, it may contribute positively to the fertility of the soil (particularly regarding OM, P, N), but, at the same time, its application may be strongly limited (heavy metals or other toxic compounds). The application of industrial by-products to soils have also been widely studied. In many cases, the application of such amendments has improved soil structure, condition and/or even fertility, in particular increasing the pH of acid soils (Demeyer et al., 2001; Matsi and Keramidas, 1999; Mittra et al., 2004; Kühn et al., 2006). In addition, those by-products with known ability to retain P have shown a potential fertilizer potential. This has been reported for bauxite residue (red mud) (Snars et al., 2004ab; Eastham et al., 2006) and for P-saturated ochre, which 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). The by-product blast furnace slag (BFS) saturated with P has also shown positive results in pot experiments (Hylander and Simán, 2001; Hylander et al., 2006). In contrast with large-scale wastewater treatment, household derived wastewater from normal human activities usually has low concentrations of hazardous components and therefore, the recycled substrates from on-site treatment systems may not be a threat to the receiving environment. A number of pot experiments have recently been conducted in order to study the plant availability of P from different substrates design for on-site wastewater treatment. In most cases, the P-saturated substrates improved the yield compared with no P addition. Among the substrates studied, Polonite has been found to improve the yield of barley (Hylander et al., 2006). In another study, Filtralite P improved the yield of ryegrass and it was shown to be an effective liming agent (Nyholm et al., 2005). Studies on Ferich sands and LECA have shown that P sorbed to these substrates is as available as a water-soluble P compound to ryegrass plants (Kvarnström et al., 2004). The potential for P recycling depends on both substrate and soil P status.

#### 2.3.1 Substrate P

The solubility of P in the substrate varies depending on its composition and form but it should be in a form capable of dissolving or desorbing, and preferably being released to the soil P solution, thus becoming available to plants. 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. Both the amount and form of P in the substrate and the soil P status influence the contribution from the soil solution to

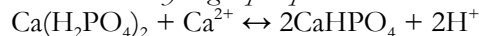


total plant uptake (Morel and Fardeau, 1990).

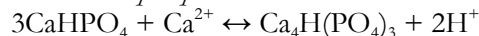
### 2.3.2 Soil P

In neutral and calcareous soils, the relative concentration of phosphate in the soil solution depends mainly on the concentration of  $\text{Ca}^{2+}$  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 compared with other calcium phosphates as it can be deduced from these chemical equilibria (Mengel and Kirkby, 2001):

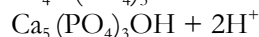
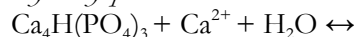
*Calcium monohydrogen phosphate*



*Calcium octophosphate*

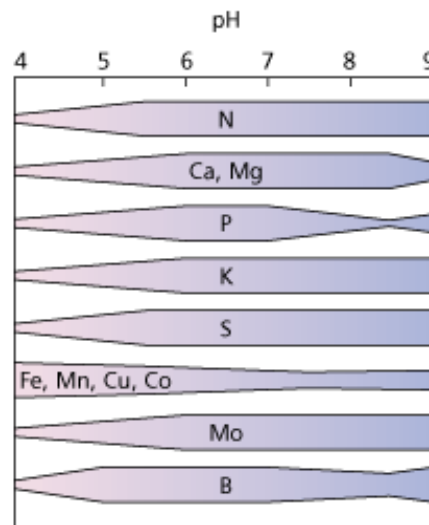


*Hydroxyapatite*



From these equilibria it can be seen that increasing  $\text{H}^+$  groups in the soil solution has a positive effect on the solubility of calcium phosphates but increasing  $\text{Ca}^{2+}$  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 (Brady and Weil, 1996). In neutral and acid soils, phosphate adsorption is the dominant process affecting phosphate availability to plants. Phosphate ions are adsorbed on Fe and Al hydrous oxides by ligand exchange in which  $\text{OH}^-$  groups are replaced by phosphate ions (Hartikainen and Simojoki, 1997; Mengel and Kirkby, 2001). Phosphate adsorption is stronger the lower the  $\text{OH}^-$  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 water, neutral salt solutions, acids or alkalis as P-extractants. There is no single accepted method to determine



**Fig 4. Schematic overview of the bioavailability of P and other elements in soil as a function of pH (the wider the more bioavailable).**

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. The ammonium lactate (AL)-extractable P in acetic acid (Egner et al., 1960) is the standard commonly used method in Europe. Water- and  $\text{CaCl}_2$ -extractable P are also used. However, these chemical extractants do not always indicate the P status satisfactorily (Hylander et al., 1996).

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 (Holford, 1997; Schachtman et al., 1998). Plant roots take up P from the soil solution as ortho-phosphate anions,  $\text{HPO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$  depending on the pH. The optimum pH range for the uptake of P by plants lies between 6 and 7 (Fig. 4). In addition to the low availability of soil P, the low diffusion rate of P in soil ( $10^{-12}$  to  $10^{-15} \text{ m}^2 \text{ s}^{-1}$ ) 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).

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. The principal P fertilizers in use today are triple superphosphate (TSP) 47%  $P_2O_5$ , diammonium phosphate (DAP) 18% N, 46%  $P_2O_5$ , and monoammonium phosphate (MAP) 12% N, 52%  $P_2O_5$  (Isherwood, 2000; Valsami-Jones, 2004). Other sources of P inputs to agriculture include organic manures (2.0-2.5 %P), biosolids (sewage sludge), and recovered phosphates from wastewater streams (Kirkham, 1982; Lassen et al., 1984; Sharpley and Withers, 1994; Hall, 1995; Morse et al., 1998; Johnston and Richards, 2003; Siddique and Robinson, 2003; Bashan and Bashan, 2004; McDowell and Sharpley, 2004; Krogstad et al., 2005). However, in areas with intensive agriculture, this becomes a major potential source of diffuse losses of P to surface waters (Sharpley et al., 1994; Sharpley 1995; Sharpley et al., 2001; McDowell and Sharpley, 2001; McDowell et al., 2001; Withers et al., 2001; Smith et al., 2007). It is known that intensive use of fertilizers and manures has lead to the accumulation of P in many European soils during the last decades (Barberis et al., 1996; Djodjic et al., 2005). The proper management of P-enriched soils and the reduction of P fertilization are important measures to be taken in order to prevent P losses to surface waters. Enhancing water infiltration by improving soil structure has also been proposed as a mitigation measure (Ulén and Jakobsson, 2005). 'Mining' soil P by growing deep-rooting crops without any additional P fertilization is another possible strategy for P-enriched soils to decrease the risk of P leaching (Koopmans et al., 2004). The application of industrial by-products with the ability to retain P has been recently regarded as a viable mitigation measure (Summers et al., 1993, 1996; McDowell et al., 2008).

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. As for P, the plant availability of some of these elements is strongly dependent on soil pH (Fig. 4). On the other hand, factors such as soil structure or water supply can limit yields irrespective of the amount of nutrients applied.

### ***2.3.3 Benefits of P recycling***

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%) (Isherwood, 2000; Duley, 2001). The annual global production of phosphate is about 50 million tonnes of  $P_2O_5$  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.

In countries like Sweden, due to increased food imports (rising to 39% of P imported in 2000), it is estimated that 50-55 tonnes of P could be recycled (mostly from large but also small scale wastewater treatment) if P recycling strategies were developed (Schmid Neset et al., 2008). In this respect, the Swedish EPA has proposed a target of at least 60% P recycling from wastewater by 2015 (SEPA, 2000). Some other EU countries such Germany and the Netherlands have already announced national objectives on P recovery from sewage (Stark, 2005a). Recycling P, particularly in agriculture, is necessary for sustainable development. On-site wastewater systems using reactive filter media may contribute to recycle P in rural areas and small communities, thus helping to preserve this finite and non-renewable resource.

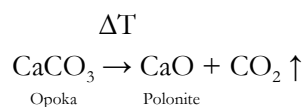
### 3 MATERIALS AND METHODS

#### 3.1 Filter materials

The materials used in this study were 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 compact filter systems.

##### 3.1.1 Polonite

Polonite (Polonite®) is a commercial product used for on-site wastewater treatment in Sweden and it is produced from 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) and mainly consists of silica and calcium carbonate but also contains significant amounts of aluminium and iron oxides (Brogowski and Renman, 2004; Cucarella et al., 2007). The processing of opoka consists of thermal treatment at high temperatures for an adequate 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 contact time. The powder fraction of Polonite showed a P-sorption capacity of 60–80 g P kg<sup>-1</sup> in batch tests with an estimated maximum capacity of approximately 117 g P kg<sup>-1</sup> (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. 5A) is manufactured by the Swedish company Biotech AB 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.). Polonite used in Papers II, III and IV was supplied by Biotech AB, Sweden. Polonite-ww samples correspond to Polonite used for about two years in a filter well for household wastewater treatment in Uppsala, Sweden (Fig. 6) and were used for batch equilibrations (paper IV) and as soil amendment in the two field experiments (Papers V and VI). Prior to use, Polonite-ww was crushed and sieved to a fraction <2 mm in order to have a homogeneous distribution and enhance the release of P and other elements to the soil solution. Polonite-col samples (Paper IV) were obtained from the surface layer (0–5 cm) of a column leaching experiment using an N+P solution (Gustafsson et al., 2008).

##### 3.1.2 Natural wollastonite

Natural wollastonite is a calcium metasilicate compound (CaSiO<sub>3</sub>) with reported P sorption ability (Brooks et al., 2000). This material was chosen for its mineralogical similarity to Polonite. Wollastonite tailings (Fig. 5B) produced by Tricorona AB (Banmossen, Heby, Sweden) with a particle size of 1–3 mm and containing 27.3% of pure wollastonite were used in this study (Papers II and III).

##### 3.1.3 Filtra P

Filtra P (Fig. 5C) 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.





**Fig. 5. Filter materials: (A) Polonite, (B) wollastonite tailings, (C) Filtra P.**

Filtra P samples (Papers II, III and IV) were obtained from Nordkalk, Finland, and Filtra P-col (Paper IV) was taken from the same column experiment as Polonite-col (Gustafsson et al., 2008).

### 3.2 Soils

Two different types of soils were used together with the material amendments in the pot experiments and batch equilibrations (Papers II, III and IV).

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 and consists of 54% sand, 39% silt and 7% clay (FAO-ISRIC-ISSS, 1998). 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 and consists of 60% sand, 38% silt and 2% clay (sandy loam) (FAO-ISRIC-ISSS, 1998). The physical and chemical properties of the soils are presented in Table 3. The field experiments were located in the same place where soils 1 and 2 were acquired (Łazy and Czarny Potok respectively). However, some soil properties were slightly different. The experimental field station where soil 2 was acquired is a mountain meadow surrounded by forest. Some soil properties were found to be markedly affected by the proximity to forest trees. Soil 2 was taken from the edge region in order to allow better transport accessibility. Differently, the field experiment took place in a sub-area centrally located within the meadow. Soil pH and the concentration of Ca and Mg were visibly higher in the central region. The second experimental field (Łazy) was previously exposed to intensive agriculture practices, which notably increased the concentration of nutrients in the soil.

### 3.3 Methods

#### 3.3.1 Review and synthesis (Paper I)

A number of studies using batch experiments to estimate the P sorption capacity of filter materials have been reviewed (Mann and Bavor, 1993; Cheung et al., 1994; Zhu et al., 1997; Sakadevan and Bavor, 1998; Drizo et al., 1999; Johansson, 1999; Zhou and Li, 2001; Drizo et al., 2002; Kostura et al., 2005; Li et al., 2006; Xu et al., 2006; Ádám et al., 2007a; Boujelben et al., 2008). The studies were selected for their relevance to the sub-



**Fig. 6. Filter well in Vikstaby, Uppsala, from where Polonite-ww samples were taken (Photos by Gunno Renman).**

**Table 3. Physical-chemical properties of Soil 1 and Soil 2**

Parameter	Soil 1	Soil 2
BD (Mg m <sup>-3</sup> )	-	1.12
TP (vol.%)	-	57
WFC (vol.%)	-	36
pH <sub>H2O</sub>	6.88	4.22
C/N	10.4	13.4
Ca (g kg <sup>-1</sup> )	0.86	0.10
Mg (g kg <sup>-1</sup> )	1.64	2.06
Fe (g kg <sup>-1</sup> )	16.0	12.7
Al (g kg <sup>-1</sup> )	-	67.1
P (mg kg <sup>-1</sup> )	664	569
Mn (mg kg <sup>-1</sup> )	246	115
Zn (mg kg <sup>-1</sup> )	52.9	47.6
Cu (mg kg <sup>-1</sup> )	12.3	5.47
Pb (mg kg <sup>-1</sup> )	15.5	20.3
Cd (mg kg <sup>-1</sup> )	0.16	0.19
AL-P (mg kg <sup>-1</sup> )	7.51	4.32
AL-K (mg kg <sup>-1</sup> )	61.3	26.9

ject and repercussions on later research (citation index). The selected studies cover a large variation in filter materials.

The estimated P sorption capacity was contrasted with physical and chemical properties of the materials (particle size, pH, chemical composition) and with the batch experiment governing parameters (material:solution ratio, P concentration range, agitation, etc.).

### 3.3.2 Pot experiments (Papers II and III)

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 substrates (Filtira P, Polonite and wollastonite tailings) in quantities based on previous research (Hylander et al., 2006). No P was added to the control treatment. The substrates were previously saturated by placing 200 g of each material in infiltration columns made from 1-litre plastic graduated cylinders with perforated bases (Paper II). The materials were used in their original fractions (see section 4.1). The columns

were gravity fed (unsaturated flow) with a 25 mg P L<sup>-1</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 substrates were equilibrated in a 100 mg P L<sup>-1</sup> solution for 2 days in order to ensure a homogeneous P content in the substrates. Prior to use, they were dried at 105 °C, 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 (a certain amount was milled in a mortar for chemical analysis).

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 (approximately 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 (day 50) for ryegrass and on 18 July (day 64) 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 for total element concentration analysis. Soil samples from each pot were dried at 55°C and milled for analysis.

### 3.3.3 P-dissolution studies (Paper IV)

The soils were milled and sieved with a 1 mm mesh, while the substrates were crushed and sieved below 2 mm. This is a reasonable particle size regarding the practical applications of this type of substrates. Soil and substrate samples were mixed vigorously with 100 mL distilled water in a 1:10 (w:v) soil:solution ratio and a 1:20 substrate:solution ratio, in an end-over-end rotator for 96 hours. The larger ratio used for substrates was intended to compensate for particle size differences. In parallel to

these equilibrations, soils amended with increasing doses (2.5, 5, and 10% dry weight) of each of the substrates (pristine Polonite, pristine Filtra P, Polonite-ww, Polonite-col, Filtra P-col), calcite ( $\text{CaCO}_3$ ) and slaked lime ( $\text{Ca(OH)}_2$ ), were also mixed vigorously with 100 mL distilled water in an end-over-end rotator for 96 hours. After that time, the pH was measured and the solution was decanted, filtered and stored in a refrigerator for later P determination. The solid phase residues were dried at 55 °C and reused for the study on P sorption.

The dried solid phase residues of untreated soils and soils amended with filter substrates and calcite were divided into 2 g sub-samples, transferred to 40 mL of artificial P solutions ( $\text{KH}_2\text{PO}_4$ ) containing different P concentrations (5, 10, 15, 20 and 25  $\text{mg P L}^{-1}$ ) and shaken for 24 h at room temperature (21°C) (e.g. Nair et al., 1984). The samples were then allowed to settle and an aliquot from the solution was filtered and saved for P determination. The difference between the initial plus background P and final P concentration at equilibrium was assumed to be sorbed by the soil or soil-amendment mixture. Background P ( $C_{\text{bkg}}$ ) was assumed to equal the equilibrium P concentration in the solution from the solubility study (previous step). Phosphorus sorption by soil,  $S$  ( $\text{mg kg}^{-1}$ ), was calculated according to equation 2.

$$S = \frac{(C_{\text{bkg}} + C_0 - C_{\text{eq}}) \cdot V}{M} \quad (2)$$

where  $M$  is mass of soil (kg),  $V$  is the volume of the solution (L),  $C_{\text{bkg}}$  is the background P concentration ( $\text{mg L}^{-1}$ ),  $C_0$  is the initial P concentration ( $\text{mg L}^{-1}$ ) and  $C_{\text{eq}}$  is the equilibrium P concentration ( $\text{mg L}^{-1}$ ). The sorption data were fitted to the Langmuir equation (3) and the Freundlich equation (4) and the isotherm parameters were obtained by iterative non-linear regression according to Bolster (2007).

$$S = S_{\text{max}} \cdot \frac{K_L \cdot C_{\text{eq}}}{1 + K_L \cdot C_{\text{eq}}} \quad (3)$$

where  $K_L$  ( $\text{L kg}^{-1}$ ) is related to the energy of adsorption and  $S_{\text{max}}$  ( $\text{mg kg}^{-1}$ ) reflects the maximum adsorption capacity.

$$S = K_F \cdot C_{\text{eq}}^{b_F} \quad (4)$$

where  $K_F$  ( $\text{L kg}^{-1}$ ) expresses the adsorption capacity (the larger value the higher the capacity) and  $b_F$ , which ranges from 0 to 1, is the heterogeneity factor.

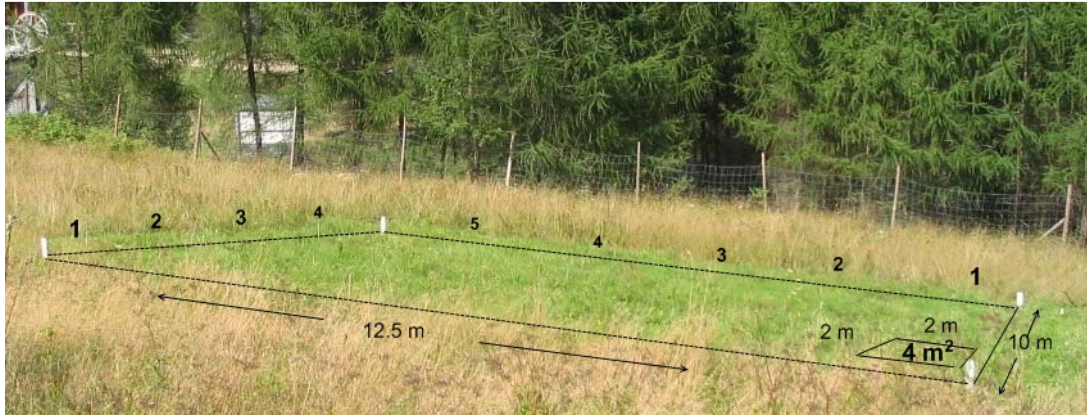
### 3.3.4 Field experiments (Papers V and VI)

In the first experiment the field station was located in Czarny Potok, a southern region of Poland within the Carpathian Mountains (20°54'E, 49°24'N, altitude 720 m asl). The soil from this mountain meadow is equivalent to soil 2 but with slightly higher pH ( $\text{pH}_{\text{H}_2\text{O}}$  of 5.2) and available P, K and Mg of 16.5, 117.6 and 99.1  $\text{mg kg}^{-1}$  respectively. The water field capacity of this soil is 0.30-0.35 (v/v) (Zaleski and Kopeć, 1999). The average yearly precipitation in this mountain region over the 30 years preceding the experiment was 821 mm and the average annual temperature 5.8°C, while the average precipitation and temperature over the April-September period were 543 mm and 11.7°C respectively (Kopeć, 2000). An area of approximately 125  $\text{m}^2$  (10m×12.5m) was divided into twenty plots of 4  $\text{m}^2$  each (2m×2m) with 50 cm spacings (Fig. 7). The natural meadow consisted of an established grass cover (*Gladiolo-Agrostietum*) and neither weeding nor herbicides were applied. Each plot received fertilization according to five different treatments on 8 May 2007 (day 0):

- 1: N
- 2: NPK
- 3: NK+Polonite-ww
- 4: Polonite-ww
- 5: Lime (CaO)

Nitrogen (N) was added as  $\text{NH}_4\text{NO}_3$  containing 34% N to reach a level of 50  $\text{kg N ha}^{-1}$  (0.04  $\text{kg NH}_4\text{NO}_3$  per plot). Potassium (K) was applied as KCl with 60%  $\text{K}_2\text{O}$  to reach 60  $\text{kg K ha}^{-1}$  (0.02  $\text{kg KCl}$  per plot). Phosphorus (P) was added as triple superphosphate (0.04  $\text{kg per plot}$ ) containing 40%  $\text{P}_2\text{O}_5$  or as P bound to Polonite-ww (5.3  $\text{kg Polonite-ww per plot}$ ), in both cases to reach a dose of 20  $\text{kg P ha}^{-1}$ . This ratio,  $\text{N}_{50}\text{P}_{20}\text{K}_{60}$ , has been used in previous research carried out in this mountain meadow during the past 30 years (Kopeć, 2000). Lime contain-



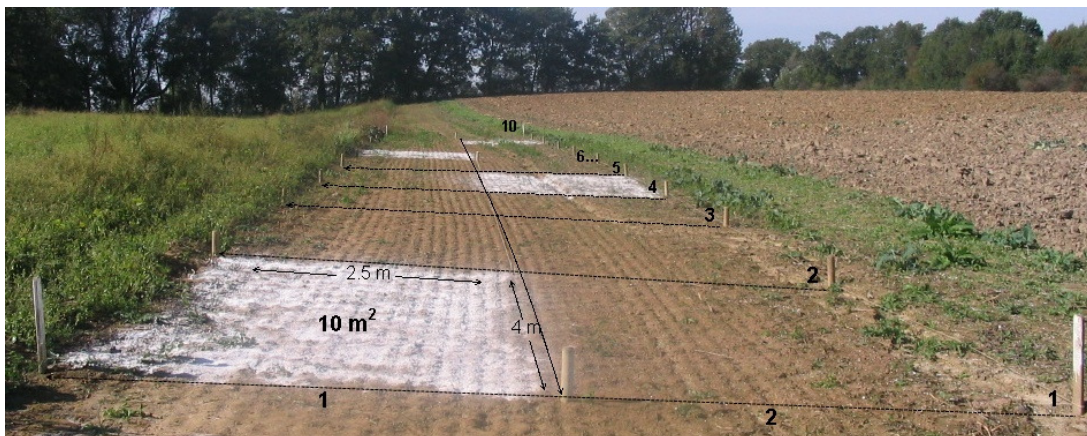


**Fig. 7. Field experiment 1 (Czarny Potok): Dimensions of the field with 20 plots (distributed in 4 rows and 5 columns) for the 5 different treatments in 4 replicates.**

ing 32% CaO was added to reach the same level of Ca in Polonite-ww amendments. Each treatment was performed in four replicates. Fertilizer compounds, Polonite-ww and lime were directly applied and equally distributed on the soil surface by hand. This experimental design aimed at comparing different treatment alternatives for the management of the meadow and contrasting the effects of applying Polonite-ww (with and without NK fertilization) with known fertilization practices and conventional liming. The meadow plants (mainly grass) were harvested on 6 July (day 59) and 14 September (day 70) 2007. The plants were cut manually from a sub-area of  $1.45 \text{ m} \times 2 \text{ m}$  at approximately 1 cm above the soil surface, dried at  $55^\circ\text{C}$ , weighed, chopped and milled. Initial soil samples (day 0) and soil samples

taken after the second harvest (day 70) were collected manually from the top horizon. The experiment continued during 2008 and 2009 without application of Polonite-ww but receiving N fertilization as per May 2007.

In the second experiment, the field station was situated in Łazy, about 40 km east of Krakow, Poland ( $20^\circ30'\text{E}$ ;  $49^\circ58'\text{N}$ ; altitude 320 m), with soil properties similar to those of soil 1 but exposed to intensive agricultural practices (elevated accumulation of nutrients). An area of approximately  $200 \text{ m}^2$  ( $40 \text{ m} \times 5 \text{ m}$ ) was divided into twenty plots of  $10 \text{ m}^2$  each ( $4 \text{ m} \times 2.5 \text{ m}$ ) with 50 cm spacing (Fig. 8). This area was uncultivated during the year preceding the experiment, but it was intensively used for cropping during the past years, which has increased notably the concentration of nutrients in the soil, par-



**Fig. 8. Field experiment 2 (Łazy). Distribution and dimensions of 20 plots (distributed in 10 rows and 2 columns) for 5 different treatments in 4 replicates (white plots received lime).**

ticularly the concentration of P. The regular application of lime has been used to maintain a pH between 6-7 on the top-soil, while the pH is lower in deeper horizons. Each treatment received nitrogen ( $30 \text{ kg N ha}^{-1}$ ) as  $\text{NH}_4\text{NO}_3$  containing 34% N and potassium ( $140 \text{ kg K ha}^{-1}$ ) as KCl with 60%  $\text{K}_2\text{O}$  on 1 October 2007. In addition, each plot received a different treatment:

- 1: Control
- 2: TSP
- 3: TSP+Lime
- 4: Polonite-ww1 (dose 1)
- 5: Polonite-ww2 (dose 2)

Phosphorus was added as triple superphosphate (TSP) containing 46%  $\text{P}_2\text{O}_5$  to reach a rate of  $90 \text{ kg P ha}^{-1}$ . This is the common dose that has been used in this field for intensive wheat cropping. Regularly, lime has also been added, and therefore, treatment 3 incorporated liming containing 32% CaO. Polonite-ww has been added in two doses based on previous experiences (this thesis work). Doses 1 and 2 were equivalent to 6 kg and 8 kg per plot ( $10 \text{ m}^2$ ) respectively. All was added on the surface and then mixed into the upper soil layer (0-20 cm) by ploughing.

Winter wheat (*Triticum aestivum*, L., variety Mikula) was sown on 11 October 2007 at a rate of  $200 \text{ kg ha}^{-1}$ . Pesticides and growing regulators were spread over the field on April and May 2008. The average temperature in this field during the experimental time-span (1 Oct 2007-8 Aug 2008) was  $8.8^\circ\text{C}$  and the total precipitation 463.2 mm. These data was obtained at the field research station in Łazy, Poland, which belongs to the Jagiellonian University.

The harvest took place on 8 August 2008. The wheat plants were cut manually from a sub area of  $0.5 \text{ m}^2$  at approximately five centimeter above the soil surface, dried and weighed. For each sample of wheat plant, the stems were counted manually; the spikes were chopped, weighed and subsequently crushed to separate the grain. The weight of one hundred grains in three replicates was used to calculate the mass of a thousand grains. In parallel, a number of five shoots

were separated from each sample, the shoots and spikes measured and weighed, grains separated, counted, weighed and milled for protein content determination. The protein content was estimated by using a conversion factor of 5.7 from total Kjeldahl N concentration in dry grains (Jones, 1926). Soil samples were taken from the top soil (0-10 cm) in eight different locations from each plot using sampling cylinders. The samples were dried at  $55^\circ\text{C}$  and milled for chemical analysis.

### 3.3.5 Sample analysis

In the solubility studies (Paper IV), soluble P in the extracts was determined as orthophosphate P following the standard ammonium molybdate method (Murphy and Riley, 1962) by means of Flow Injection Analysis (FIA) with an Aquatec-Tecator autoanalyser.

In the pot and field experiments (Papers II, III, V and VI) filter substrates and soil samples were analyzed for total element concentration by means of atomic spectrometry using an ICP-AES JY 238 Ultrace after digestion with nitric and perchloric acids by heating ( $90\text{-}165^\circ\text{C}$ ) for 3-4 days and subsequent filtration (Strowska et al., 1991). The pH was measured in a 1:2.5 (w/v) material:water or soil:water and KCl 0.1M solution suspensions (Klute, 1996). Available forms were measured as ammonium lactate (AL)-extractable P and K in acetic acid (Egner et al., 1960), and as  $\text{CaCl}_2$ -extractable Mg according to the Schachtschabel method (Litynski et al., 1976). The hydrolytic acidity (Hh) in soil was determined according to the Kappen method using  $1 \text{ mol L}^{-1}$   $\text{CH}_3\text{COONa}$  solution (Klute, 1996). The Hh is also termed as exchangeable acidity, and in most soils it is composed of (i) exchangeable  $\text{H}^+$ , (ii) exchangeable Al as either  $\text{Al}^{3+}$  or partially neutralized Al-OH compounds such as  $\text{AlOH}^{2+}$  or  $\text{Al}(\text{OH})_2^+$  and (iii) weak organic acids (Carter and Gregorich, 2008). The base cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) concentration was determined by atomic spectrometry using an AAS Solar M6 System after extraction with a  $0.5 \text{ mol L}^{-1}$   $\text{CH}_3\text{COONH}_4$  or  $\text{NH}_4\text{Cl}$  solution. Total exchangeable base (TEB) cations concentration, cation exchange capacity (CEC) and



base saturation (BS) percentage were then calculated as follows:

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

$$CEC = Hh + TEB \quad (6)$$

$$BS(\%) = \frac{TEB}{CEC} \times 100 \quad (7)$$

Total element concentrations in plants were determined by atomic spectrometry using an ICP-AES JY 238 Ultrace after digestion with a mixture of concentrated nitric and perchloric acids at 200 °C for 4 hours under reflux conditions.

Physical properties including bulk density (BD), water field capacity (WFC) and water conductivity coefficient (Ks) were determined in soil samples with undisturbed structure collected in 100 cm<sup>3</sup> cylinders (Klute, 1996). WFC corresponded to a water potential of -9.81 kPa (pF=2.0) and was assessed using a porous plate inside a pressure chamber. The coefficient Ks was estimated according to the Wit method. Solid phase density (SPD) was determined by the pycnometer method. Total porosity (TP) was calculated as per equation 8:

$$TP = \frac{SPD - BD}{SPD} \quad (8)$$

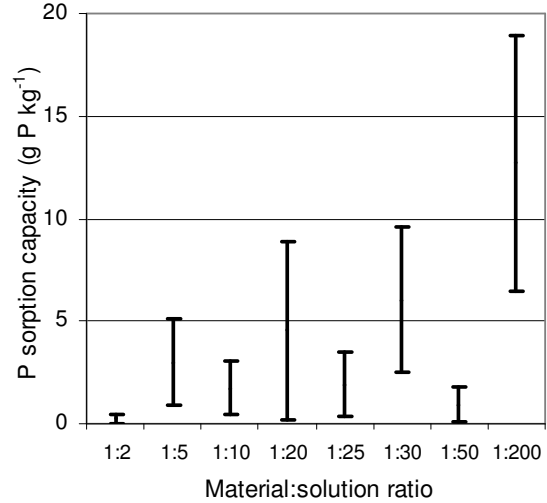
### 3.3.6 Statistical analysis

The results in Papers II, III, V and VI are expressed as the mean of three (pots) or four (plots) samples and the standard error (SE) indicates the variation between replicates: n=3 (pots) and n=4 (plots). The results were analyzed statistically using one-way analysis of variance (ANOVA) by Tukey's test at p<0.05 with STATISTICA 6.1 and SPSS 15.0/16.0.

## 4 RESULTS AND DISCUSSION

### 4.1 Review and synthesis (Paper I)

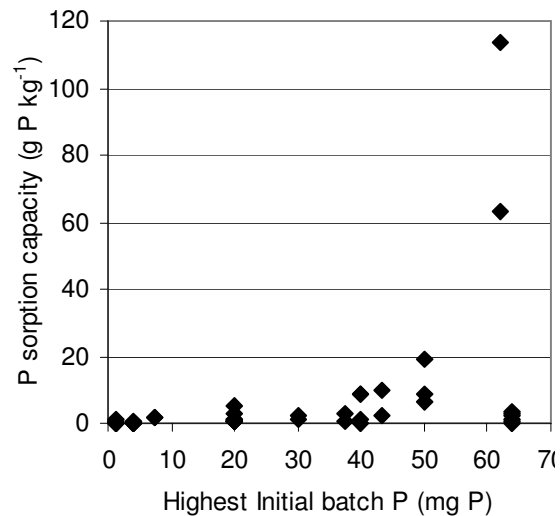
The filter materials investigated in a number of selected studies vary considerably in origin, particle size, chemical composition and pH (Paper I). There is a visible relationship between the estimated P sorption capacity of the materials investigated and their particle size and pH. There is a stronger correlation between P sorption and some of the batch parameters, i.e. material:solution ratio and



**Fig. 9. Phosphorus sorption capacity range at different material:solution ratios used in batch experiments in the selected studies (highest P sorption values excluded).**

initial P concentration (Figs. 9 and 10), suggesting that batch parameters have great repercussions for the results.

The present comparison shows that batch experimental parameters are arbitrarily established and vary significantly among studies. Large discrepancies exist in the form and



**Fig. 10. Relationship between the P sorption capacity of the materials investigated and the amount of initial P at the highest concentration in batch solution in the selected studies.**

**Table 4. Classification of the filter materials investigated according to the P sorption capacity and particle size**

<i>P sorption</i>	<i>P sorption capacity</i> (g P kg <sup>-1</sup> )	<i>Filter materials</i>	
		<i>Fine (&lt;1 mm)</i>	<i>Coarse (&gt;1 mm)</i>
Very low	<0.1	Soils	Gravels
Low	0.1-0.5	Sand; Soils	LECA; Limestone; Opoka
Moderate	0.5-1	Bentonite; Ca-rich soils; Fly ash <sup>a</sup> ; Spodosol	Bauxite; BFS <sup>a</sup> ; Zeolite <sup>a</sup>
High	1-10	BFS <sup>a</sup> ; Fly ash <sup>a</sup> ; Fe-coated sand and brick	BFS <sup>a</sup> ; EAF; Filtra P; Filtralite P; Polonite; Shell sand; UTELITE
Very high	>10	BFS <sup>a</sup> ; Fly ash <sup>a</sup> ; Polonite; Red mud	-

<sup>a</sup> depending on chemical composition

amount of the material used, material:solution ratio, P concentration range and extent of agitation. These differences render it impossible to compare the capacity of the materials and question the validity of the results. A set of recommendations for batch experiment procedure is presented in Paper I.

Filter materials can be classified according to their P sorption capacity into five groups (Table 4). The classification further subdivides the materials into two categories according to their particle size. The classification system is a helpful tool for material screening and may be used to categorize new filter materials.

## 4.2 Pot experiments (Paper II and III)

The three materials Filtra P, Polonite and wollastonite tailings were used as soil amendments in a pot experiment. The materials were previously saturated in infiltration columns with artificial P solutions. The P sorption capacity of the three materials investigated varied markedly under the given experimental conditions (Table 5). The total P concentration in the recycled substrates after the column experiment (when the effluent concentration was similar to the influent at the feeding flow rate) is referred to as the P saturation potential in Paper II. The saturation potential of Polonite (nearly 2 g P kg<sup>-1</sup>) was considerably higher than that of Filtra P and wollastonite in this experiment. The effect of the amendments on soil properties and plant yield are discussed in

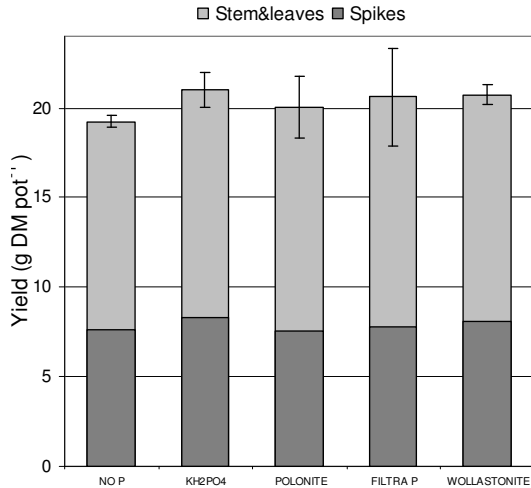
Papers II and III and summarized here in the following sections.

### 4.2.1 Effects on yield

The average yield of barley grown under five different treatments is shown in Fig. 11. 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 (KH<sub>2</sub>PO<sub>4</sub>) and P from saturated substrates compared with the control treatment (No P). In other studies, Polonite

**Table 5. Physical-chemical properties of P-saturated amendment materials used in the pot experiments**

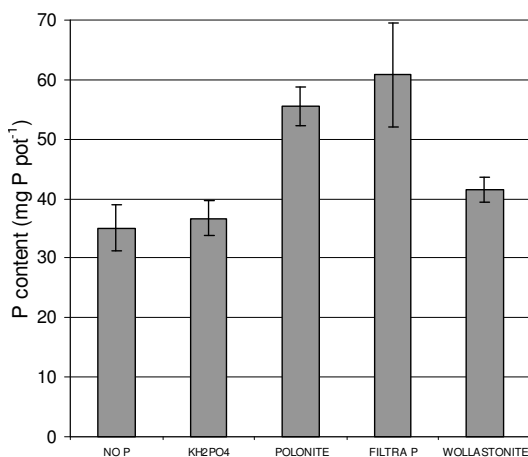
<i>Parameter</i>	<i>Polonite</i>	<i>Filtra P</i>	<i>Wollastonite</i>
Particle size (mm)	2-5.6	2-10	1-3
Bulk density (Mg m <sup>-3</sup> )	0.7	1	1.4
pH H <sub>2</sub> O	9.9	11.5	9.0
Ca (g kg <sup>-1</sup> )	230±1.5	343±0.7	162±4.2
Mg (g kg <sup>-1</sup> )	5.0±0.1	5.6±0.1	1.8±0.1
Fe (g kg <sup>-1</sup> )	11.2±0.1	44.4±0.4	7.6±0.7
P (mg kg <sup>-1</sup> )	1862±53.4	714±116	254±12.7
Mn (mg kg <sup>-1</sup> )	49.9±0.3	196±1.2	395±15.1
Zn (mg kg <sup>-1</sup> )	53.2±0.3	92.8±1.1	21.3±0.1
Cu (mg kg <sup>-1</sup> )	4.4±0.1	6.0±0.2	3.1±0.1
Pb (mg kg <sup>-1</sup> )	0.6±0.2	7.0±0.3	1.0±0.1
Cd (mg kg <sup>-1</sup> )	< 0.5	< 0.5	< 0.5
AL-P (mg kg <sup>-1</sup> )	49.9±0.3	5.62±0.38	13.93±0.61
AL-K (mg kg <sup>-1</sup> )	62.1±0.02	23.5±0.6	4.5±0.01



**Fig. 11.** Average yield of barley grown under five different treatments on soil 1 and dry matter distribution (bars indicating SE for total yield).

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 of ryegrass did not show significant differences between treatments, but there was a tendency for higher yield with substrate treatment compared with both control (No P) and potassium phosphate treatments (KH<sub>2</sub>PO<sub>4</sub>) (Paper III). In previous work, P sorbed to different sub-



**Fig. 12.** Average total P content in ryegrass grown under five different treatments on soil 2 (bars indicating SE).

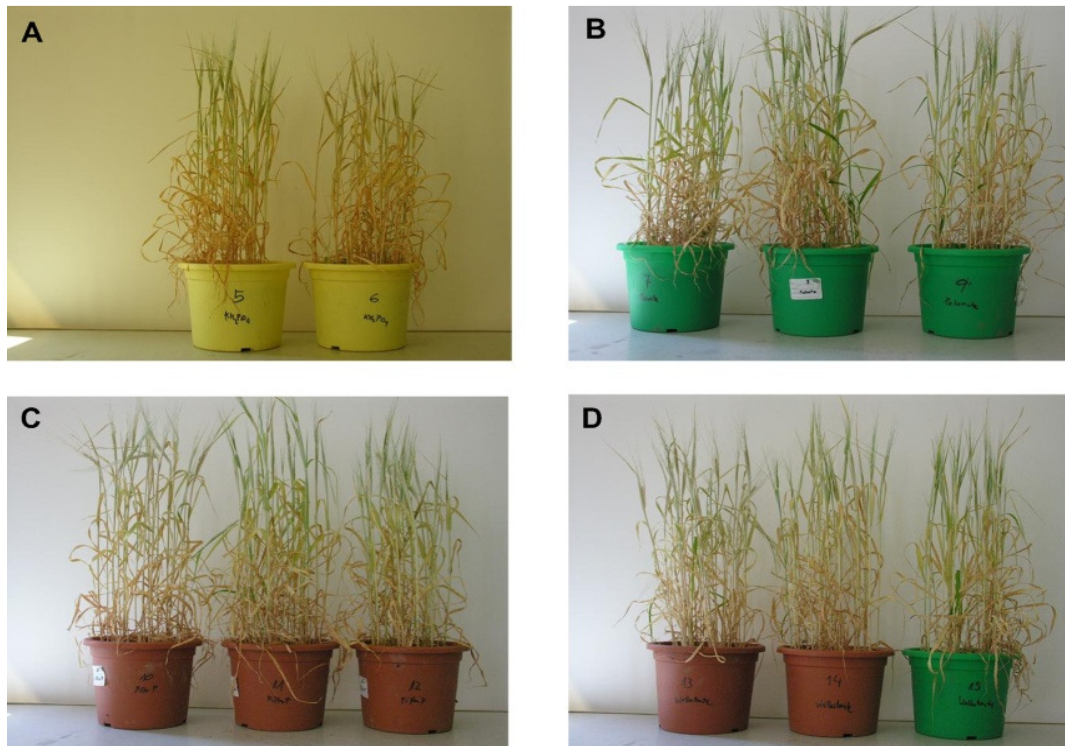
strates including Fe-rich sands and LECA (light expanded clay aggregates) was as available as a water-soluble P compound to ryegrass plants (Kvarnström et al., 2004). For both barley and ryegrass, the yield/amendment ratio was in agreement with the initial P content in the substrates giving a comparative 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 (Paper II). It can be concluded that the substrates did not affect the composition of barley spikes. As for ryegrass, the concentrations of P (Fig. 12) and Ca were significantly higher in ryegrass grown with Filtra P and Polonite 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. The grown barley and ryegrass plants right before harvesting are shown in Figures 13 and 14.

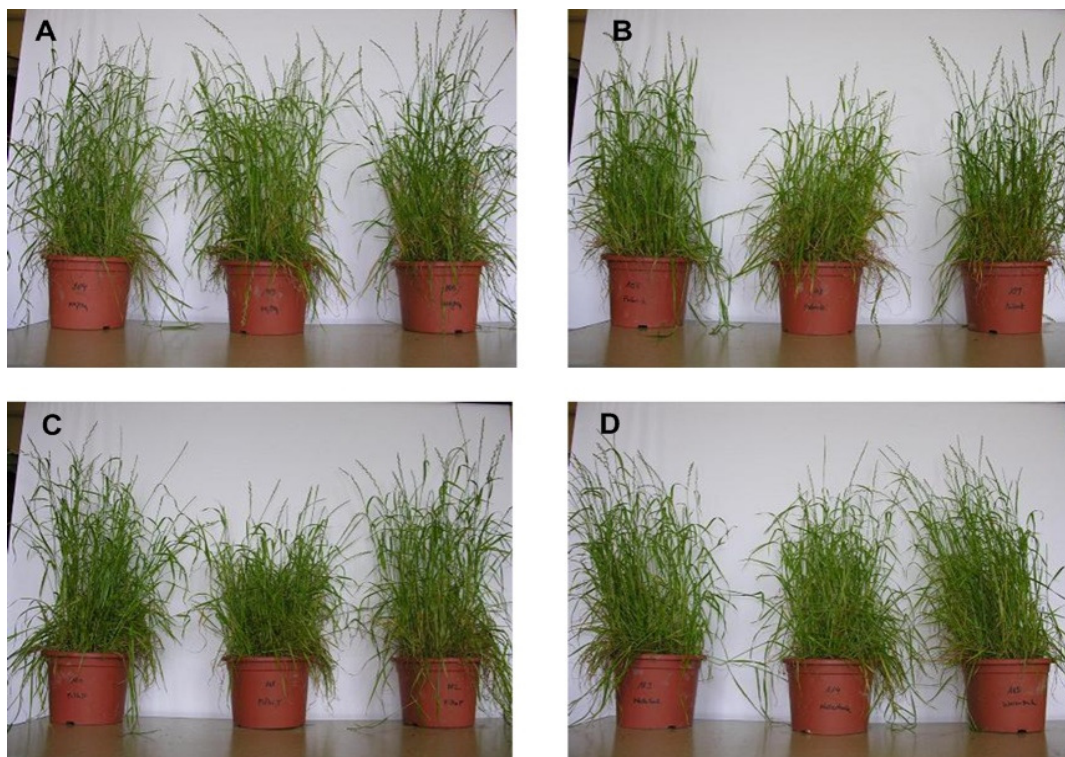
#### 4.2.2 Effects on soil pH and P availability

The pH of soil 1 (neutral) was unaffected during the experiment for the control and potassium phosphate treatments but it significantly increased with substrate treatment since all substrates had relatively high pH values (Table 6). 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 7). 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





**Fig. 13.** Pot experiment with barley plants grown on an agricultural soil under five different treatments (control treatment not shown). A:  $\text{KH}_2\text{PO}_4$ ; B: Polonite; C: Filtra P; D: Wollastonite.



**Fig. 14.** Pot experiment with ryegrass plants grown on an acid soil under five different treatments (control treatment not shown). A:  $\text{KH}_2\text{PO}_4$ ; B: Polonite; C: Filtra P; D: Wollastonite.

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 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 (Matsi and Keramidas, 1999; Snars et al., 2004). In the present study, the increase in soil P availability was probably 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.

#### 4.2.3 Effects on soil sorption 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 (Tables 6 and 7). 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

**Table 6. Soil pH, available forms and sorption properties (average  $\pm$  SE) of Soil 1 for the five different treatments of the pot experiment (Paper II)**

Parameter	NO P	$\text{KH}_2\text{PO}_4$	POLONITE	FILTRA P	WOLLASTONITE
$\text{pH}_{(\text{H}_2\text{O})}$	6.77	6.83	7.34	7.24	7.18
AL-P ( $\text{mg kg}^{-1}$ )	11.7 $\pm$ 0.3	12.7 $\pm$ 0.5	13.9 $\pm$ 0.1	13.7 $\pm$ 0.3	12.9 $\pm$ 0.4
AL-K ( $\text{mg kg}^{-1}$ )	24.1 $\pm$ 1.5	24.4 $\pm$ 0.9	24.1 $\pm$ 0.9	21.2 $\pm$ 0.8	22.6 $\pm$ 0.5
Hh ( $\text{cmol}(+) \text{kg}^{-1}$ )	1.1 $\pm$ 0.1	1.2 $\pm$ 0.1	0.7 $\pm$ 0.03	0.6 $\pm$ 0.03	0.7 $\pm$ 0.03
$[\text{Ca}^{2+}]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	15.9 $\pm$ 0.5	16.4 $\pm$ 0.4	20.7 $\pm$ 0.5	29.5 $\pm$ 1.2	20.4 $\pm$ 0.3
$[\text{Mg}^{2+}]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	1.3 $\pm$ 0.1	1.3 $\pm$ 0.02	1.1 $\pm$ 0.01	1.3 $\pm$ 0.04	1.3 $\pm$ 0.01
$[\text{K}^+]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	0.5 $\pm$ 0.1	0.4 $\pm$ 0.02	0.4 $\pm$ 0.01	0.3 $\pm$ 0.01	0.4 $\pm$ 0.01
$[\text{Na}^+]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	0.6 $\pm$ 0.1	0.5 $\pm$ 0.1	0.3 $\pm$ 0.1	0.7 $\pm$ 0.1	1.3 $\pm$ 0.1
TEB ( $\text{cmol}(+) \text{kg}^{-1}$ )	18.3	18.6	22.5	31.7	23.3
CEC ( $\text{cmol}(+) \text{kg}^{-1}$ )	19.3	19.8	23.2	32.3	24.0
BS (%)	94.5	93.9	97.1	98.1	97.0

**Table 7. Soil pH, available forms and sorption properties (average  $\pm$  SE) of Soil 2 for the five different treatments of the pot experiment (Paper III)**

Parameter	NO P	$\text{KH}_2\text{PO}_4$	POLONITE	FILTRA P	WOLLASTONITE
$\text{pH}_{(\text{H}_2\text{O})}$	4.60	4.51	5.12	5.52	5.02
AL-P ( $\text{mg kg}^{-1}$ )	5.7 $\pm$ 0.1	6.1 $\pm$ 0.2	6.5 $\pm$ 0.1	6.3 $\pm$ 0.1	6.3 $\pm$ 0.4
AL-K ( $\text{mg kg}^{-1}$ )	15.3 $\pm$ 0.3	16.4 $\pm$ 0.3	15.7 $\pm$ 0.1	14.6 $\pm$ 0.8	15.5 $\pm$ 0.6
Hh ( $\text{cmol}(+) \text{kg}^{-1}$ )	8.3 $\pm$ 0.1	9.9 $\pm$ 0.1	6.9 $\pm$ 0.3	3.5 $\pm$ 0.2	6.4 $\pm$ 0.2
$[\text{Ca}^{2+}]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	1.5 $\pm$ 0.03	1.4 $\pm$ 0.03	5.7 $\pm$ 0.3	11.0 $\pm$ 0.6	4.9 $\pm$ 0.2
$[\text{Mg}^{2+}]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	0.6 $\pm$ 0.01	0.6 $\pm$ 0.01	0.6 $\pm$ 0.02	0.6 $\pm$ 0.02	0.6 $\pm$ 0.03
$[\text{K}^+]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	0.3 $\pm$ 0.01	0.3 $\pm$ 0.01	0.3 $\pm$ 0.01	0.3 $\pm$ 0.01	0.3 $\pm$ 0.01
$[\text{Na}^+]$ ( $\text{cmol}(+) \text{kg}^{-1}$ )	1.2 $\pm$ 0.1	0.9 $\pm$ 0.1	0.5 $\pm$ 0.1	0.4 $\pm$ 0.1	0.9 $\pm$ 0.4
TEB ( $\text{cmol}(+) \text{kg}^{-1}$ )	3.6	3.2	7.0	12.2	6.7
CEC ( $\text{cmol}(+) \text{kg}^{-1}$ )	11.9	13.1	13.9	15.8	13.0
BS (%)	30.1	24.2	50.4	77.6	51.2

complex. This was observed in soil 1, where the concentration of  $K^+$  and  $Na^+$  ions in the sorption complex decreased with substrate treatment. The reduction in Hh as a result of substrate treatment involves a decrease in  $Al^{3+}$  ions in the sorption complex, which reduces Al availability for plants. This was observed as a slight decrease in Al concentrations in barley (spikes) grown in soil 1 amended with substrate treatment (Paper II) 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 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  $Ca^{2+}$  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.

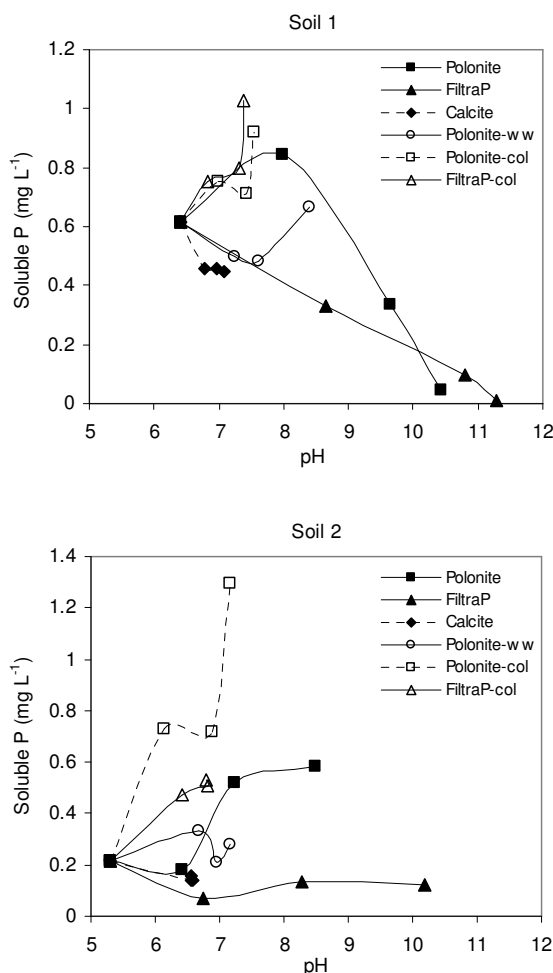
#### 4.3 P-dissolution studies (Paper IV)

The pH and soluble P of filter substrates and untreated soils determined in a 1:20 (w:v) substrate:solution ratio and a 1:10 (w:v) soil:solution ratio are shown in Table 8. Natural occurring P in the pristine materials (Filtra P and Polonite) is rather insoluble. The solubility of P in the recycled substrates (Polonite-ww, Polonite-col and Filtra P-col) is in agreement with their total P content.

**Table 8. Total and soluble P, and pH in the pristine and recycled filter substrates and in the two soils**

Substrate / Soil	Total P ( $mg\ kg^{-1}$ )	Soluble P ( $mg\ kg^{-1}$ )	pH
Polonite	340 <sup>a</sup>	1.5	11.2
Filtra P	1440 <sup>a</sup>	0.2	12.5
Polonite-ww	1496	7.4	9.1
Polonite-col	7390 <sup>a</sup>	45.2	8.8
Filtra P-col	19400 <sup>a</sup>	54.9	8.4
Soil 1	664	6.2	6.4
Soil 2	569	2.2	5.3

<sup>a</sup> data from Gustafsson et al., 2008



**Fig. 15. Relationship between soil pH and soluble P in Soils 1 and 2 amended with increasing levels of different materials.**

Soil P solubility of soil 2 is considerably lower than that of soil 1.

The two soils were amended with increasing levels (2.5, 5, and 10% dry weight) of pristine or recycled substrates, calcite ( $CaCO_3$ ) and slaked lime ( $Ca(OH)_2$ ). All the amendments increased soil pH. The recycled substrates had a liming effect comparable to that of calcite, but far below that of lime, whereas the liming effect of the pristine materials may be comparable to that of slaked lime.

The P solubility was considerably different for the two types of soils investigated and for each of the substrates used as amendments. Polonite-col and Filtra P-col increased P solubility in soil 1, while Polonite-ww did not (Fig. 15), although all three



substrates had a similar liming effect. This was probably because the substrates recycled from the column experiment (Polonite-col and Filtra P-col) had a considerably higher concentration of P than Polonite-ww (Table 8). This suggests that the observed differences were the result of P released from the column-derived substrates. This effect was even more apparent in soil 2 and particularly for Polonite-col, which markedly increased the P concentration in solution (Fig. 15), while recycled Filtra P with nearly 2% P did not increase P solubility as much as Polonite (0.7% P), possibly due to less soluble Fe-associated P phases in the former. In both soils, two interdependent phenomena were responsible for this outcome. Increasing soil pH tends to reduce P adsorption onto Fe and Al (hydr)oxides, while the incorporation of  $\text{Ca}^{2+}$  ions favors Ca-P precipitation reactions at relatively higher pH values (Barrow, 1984; McDowell et al., 2003). The first phenomenon is important in soil 2, while the second may be more relevant in soil 1.

Soil P sorption was characterised by interpreting sorption isotherms (Barrow, 1978; Sposito, 1989; Holford et al., 1990; McGechan and Lewis, 2002). However, the results might be taken with caution since it is known that pH variations due to P addition in the isotherm procedure may alter equilib-

rium conditions (Barrow, 1979, 1984). The linearization of Langmuir and Freundlich equations has been found to render erroneous results in many cases (Bolster and Hornberger, 2007). Therefore, non-linear regression was used to fit the data (Bolster, 2007, 2008). The recycled Polonite samples (Polonite-ww and Polonite-col) did not alter soil P sorption properties, while Filtra P-col amendments tended to increase P sorption in the same way that calcite did. This was confirmed for the acid soil using data from non-linear regression analysis of Langmuir and Freundlich equations (Paper IV).

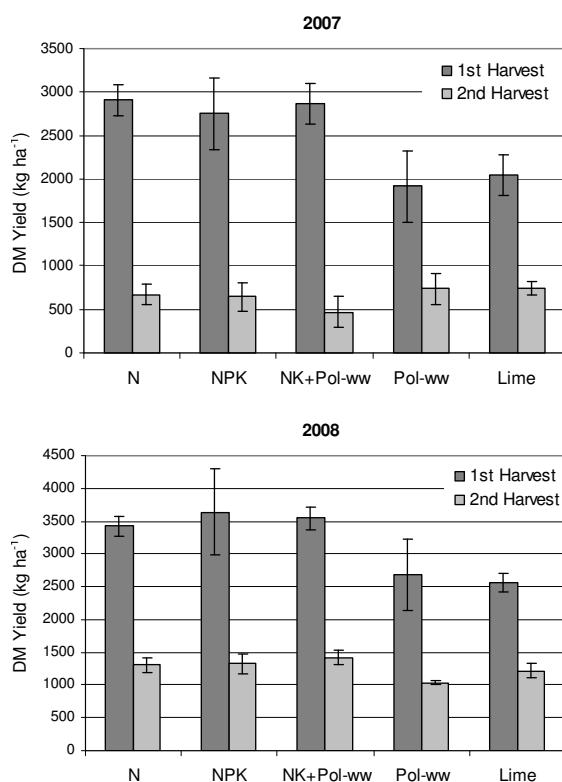
#### 4.4 Field experiments (Papers V, VI)

The two field experiments were performed in the area where soils 1 and 2 were acquired. In both experiments, the goal was to study the viability (risks and benefits) of disposing of the wastewater filter substrate Polonite-ww as a soil amendment. However, the amendment was thought to fulfil P requirements in field experiment 1 (mountain meadow) while its application was not meant to cover P fertilization for wheat on the agricultural field (field experiment 2), since this field was enriched in soil P after intense fertilization practices prior to the experiment. The same substrate (Polonite-ww) was used as amendment in the two experiments.

**Table 9. Soil pH, available forms and sorption properties (average  $\pm$  SE) at the initial stage, first (2007) and second (2008) year of field experiment 1 (mountain meadow in Czarny Potok)**

Treatment	pH	Avail-P <i>mg kg<sup>-1</sup></i>	Avail-K	Hb	$[\text{Ca}^{2+}]$	$[\text{K}^+]$	TEB	CEC	BS %
					<i>cmol(+) kg<sup>-1</sup></i>				
Initial	5.20	33.0 $\pm$ 6.0	235 $\pm$ 19.5	9.1 $\pm$ 0.3	2.2 $\pm$ 0.3	0.44 $\pm$ 0.03	3.7 $\pm$ 0.4	12.7 $\pm$ 0.3	28.7 $\pm$ 2.6
2007									
N	5.31	26.0 $\pm$ 3.3	144 $\pm$ 16.5	9.9 $\pm$ 0.6	1.7 $\pm$ 0.2	0.27 $\pm$ 0.03	2.8 $\pm$ 0.2	12.8 $\pm$ 0.5	22.5 $\pm$ 2.3
NK	5.34	29.7 $\pm$ 10.4	173 $\pm$ 20.8	9.5 $\pm$ 0.5	1.9 $\pm$ 0.1	0.33 $\pm$ 0.04	3.4 $\pm$ 0.3	12.9 $\pm$ 0.3	26.4 $\pm$ 2.8
NK+Pol-ww	5.79	36.9 $\pm$ 8.0	188 $\pm$ 17.3	6.7 $\pm$ 0.6	3.9 $\pm$ 0.3	0.35 $\pm$ 0.03	5.5 $\pm$ 0.5	12.2 $\pm$ 0.3	45.1 $\pm$ 4.3
Pol-ww	5.80	28.1 $\pm$ 8.2	151 $\pm$ 10.7	7.2 $\pm$ 0.6	3.6 $\pm$ 0.4	0.29 $\pm$ 0.02	5.2 $\pm$ 0.4	12.4 $\pm$ 0.3	42.0 $\pm$ 3.8
Lime	6.14	20.3 $\pm$ 1.7	226 $\pm$ 18.0	5.3 $\pm$ 0.9	4.6 $\pm$ 0.7	0.43 $\pm$ 0.04	6.1 $\pm$ 0.6	11.5 $\pm$ 0.3	54.0 $\pm$ 7.0
2008									
N	4.98	29.5 $\pm$ 4.7	82.3 $\pm$ 4.3	11.2 $\pm$ 0.5	2.0 $\pm$ 0.3	0.18 $\pm$ 0.01	3.3 $\pm$ 0.3	14.5 $\pm$ 0.2	22.7 $\pm$ 2.5
NK	4.98	41.2 $\pm$ 12.4	99.1 $\pm$ 5.1	11.3 $\pm$ 0.4	2.1 $\pm$ 0.3	0.22 $\pm$ 0.01	3.6 $\pm$ 0.4	14.9 $\pm$ 0.3	24.2 $\pm$ 2.5
NK+Pol-ww	5.57	42.1 $\pm$ 10.0	84.1 $\pm$ 3.7	7.7 $\pm$ 0.6	4.7 $\pm$ 0.6	0.19 $\pm$ 0.01	6.1 $\pm$ 0.6	13.8 $\pm$ 0.4	44.1 $\pm$ 3.8
Pol-ww	5.72	39.8 $\pm$ 8.1	84.1 $\pm$ 5.8	7.3 $\pm$ 0.9	4.9 $\pm$ 0.8	0.18 $\pm$ 0.01	6.5 $\pm$ 0.9	13.8 $\pm$ 0.4	46.9 $\pm$ 6.2
Lime	5.93	22.4 $\pm$ 3.1	77.1 $\pm$ 3.7	6.1 $\pm$ 1.0	6.7 $\pm$ 1.4	0.19 $\pm$ 0.01	8.0 $\pm$ 1.4	14.1 $\pm$ 0.5	56.1 $\pm$ 8.5

\*Pol-ww is the abbreviation of Polonite-ww (Polonite used for onsite wastewater treatment)



**Fig. 16.** Average dry matter (DM) yield of meadow plants in 2007 and 2008 for the five different treatments of field experiment 1 (bars indicating SE). Pol-ww stands for Polonite used for onsite wastewater treatment (Polonite-ww).

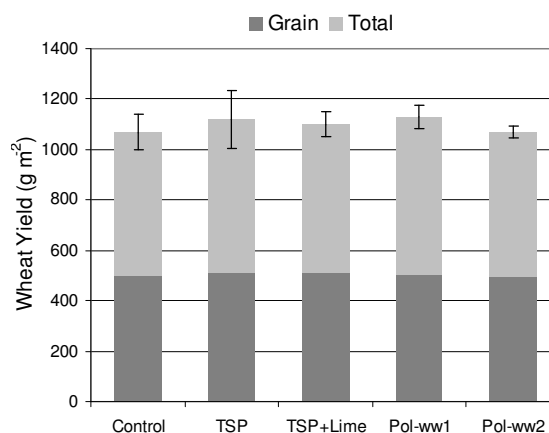
Polonite-ww was recycled from a filter well for household wastewater treatment (Renman, 2008). In the first field experiment (mountain meadow soil), the amendment showed a liming potential, while in the second (agricultural soil for wheat cropping) had no significant effects on soil properties or wheat yield, thus suggesting that the substrate could be safely recycled.

#### 4.4.1 Effects on a mountain meadow soil

Polonite-ww with and without NK fertilization was added to a mountain meadow soil. The amendments significantly increased total soil Ca and the concentration of exchangeable  $\text{Ca}^{2+}$  ions in the sorption complex during the first season alone (2007). The application of Polonite-ww also increased soil pH and decreased the hydrolytic acidity (Table 9). The CEC of soil examined in this study was relatively low due to its low

clay and humus content. Soil CEC after harvest was similar for all treatments because the increase in TEB was compensated by the decrease in Hh. These results disagree with the findings of Paper III in which Polonite significantly increased CEC (Table 7). The P availability tended to increase with mineral P fertilization and Polonite-ww. This was probably the result of a combination between direct substrate P supply and liming effect. The yield of meadow plants was unaffected by mineral P fertilizer and Polonite-ww for treatments with N fertilization (Fig. 16). The yield was lower when Polonite-ww was added alone, which showed that the substrate should be used together with N fertilization to ensure optimum productivity. In both cases (with and without N), Polonite-ww tended to decrease the uptake of metals by plants. All these results (season 2007) are further discussed in Paper V.

Similar results were observed in 2008 regarding soil properties (Table 9) and yield (Fig. 16). However, whereas the concentration of exchangeable  $\text{Ca}^{2+}$  ions increased,  $\text{K}^{+}$  concentration tended to decrease. This fact was confirmed from the lower available K concentrations in the soil, which may have been due to K leaching and/or significant plant uptake (Mengel and Kirkby, 2001). These and the coming 2009 results will be gathered



**Fig. 17.** Wheat total and grain yield for the five different treatments (average values and SE for total yield mean). Pol-ww (2 doses) stands for Polonite used for onsite wastewater treatment (Polonite-ww).



**Table 10. Soil chemical and physical selected properties and wheat grain mass and protein content for the five different treatments in the field experiment 2 (winter wheat cropping on agricultural soil in Łazy).**

Treatment	Wheat quality		pH	Soil chemical properties			Soil physical properties	
	Grain mass (g 10 <sup>3</sup> grains)	Protein in grains (%)		Avail-P (mg kg <sup>-1</sup> )	CEC (cmol+ kg <sup>-1</sup> )	BS (%)	TP (% v/v)	K <sub>s</sub> (cm d <sup>-1</sup> )
Control	51.1±0.2	13.3±0.5	6.59	91.9±5.9	9.3±0.3	67.5±2.2	0.62±0.03	2.97±0.35
TSP	49.3±0.8	15.0±0.5	6.69	111±18.1	9.2±0.4	65.9±3.8	0.58±0.03	2.21±0.28
TSP+Lime	50.5±0.7	14.2±0.5	6.62	98.0±7.5	9.9±0.5	70.7±0.7	0.60±0.03	4.44±1.58
Pol-ww1	49.7±0.7	13.4±0.6	6.67	111±13.4	9.5±0.3	67.3±1.6	0.60±0.02	3.24±0.56
Pol-ww2	50.3±0.9	14.5±0.3	6.54	87.9±4.3	9.7±0.2	68.6±3.6	0.59±0.03	2.85±0.78

together in a future publication.

#### 4.4.2 Effects on an agricultural field

In the second field experiment, Polonite-ww showed no significant effects on yield and quality of winter wheat, and on soil chemical and physical properties. The mean dry matter (DM) yield of winter wheat (total and grain yield) grown in an agricultural field under the five different treatments is shown in Figure 17. Since the treatments mainly differed in P application, the results suggest that soil P was sufficient for crop demand, which may have been due to intensive fertilization practices in this agricultural soil during the past years. Some parameters determining yield quality (grain mass and protein content in grains) are shown in Table 10 and most are presented in paper VI for the five different treatments. Similarly to DM yield, the size and mass of shoots, spikes and grain and the protein content in grains and shoots did not show any significant differences between treatments. Furthermore, mineral P fertilization (TSP with or without liming) had no effect on these properties either.

The availability of P in soil tended to increase with TSP and Polonite-ww1 treatments compared with the control, but the difference was not significant (Table 10). Since the yield was similar for all treatments, and the concentration of available P in soil was not significantly different either, the mass balance suggests that most P applied as TSP (90 kg P ha<sup>-1</sup>) was probably washed out by surface run-off or subsurface leaching. The large pool of soluble P though, may

have an impact on the surrounding water bodies when not needed (McDowell et al., 2001; Sharpley et al., 2001).

The amendments did not alter the soil bulk density, total porosity and water infiltration, although a tendency for higher conductivity (K<sub>d</sub>) values was observed with Ca-containing treatments, especially compared with mineral (TSP) fertilization. The negative effect of mineral fertilization on soil infiltration has been found to become a relevant issue affecting run-off P pollution (Ulén and Jakobsson, 2005).

Polonite-ww could be safely disposed of at rates of 6-8 ton per hectare for one year (equivalent to the dosage used in this study). By simple extrapolation, it can be argued that Polonite-ww may be disposed of at rates of approximately 1 ton ha<sup>-1</sup> year<sup>-1</sup> for about 10 years. Thus, for a small community of 100 inhabitants served by Polonite filters, the amount produced (about 12.5 ton Polonite-ww per year) could be safely recycled to a surface of about 12.5 ha. The potential for P recycling, however, would be low. This could represent about 0.5-1 kg P ha<sup>-1</sup> per year only, although this value could increase to 10 kg P ha<sup>-1</sup> per year if higher rates are applied.

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

The filter substrates did not contain large amounts of hazardous compounds except for the content of Pb in Filtra P (Paper II). When used with real wastewater, the content of metals in the substrates may increase

since they can efficiently adsorb metals (Kietlińska and Renman, 2005). This was observed for some metals in Polonite derived from household wastewater treatment (Polonite-ww). However, the concentration was far below the limits imposed by legislation (Renman et al., 2009). The plant availability of metals decreased with Polonite-ww amendments (Paper V). In particular, it was observed a decrease in Mn, which could become limiting in poor soils. The filter substrates have a low P content compared with mineral fertilizers and probably can not be used alone. This will depend on the soil P status and P requirements. For example, meadow plants require less P, which could be fully supplied by substrate P and increased soil P availability due to the liming effect of the substrate.

The high content of Si in Polonite and wollastonite might improve soil structure as well. Furthermore, Si is known to favour P mobilization (Koski-Vahala et al., 2001). Wollastonite contains substantial amounts of Mn compared with other substrates. This can be of benefit for plants, but due to its lower pH and P sorption capacity, wollastonite may not be of benefit to soils. 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, pers. com.) may limit its use in agriculture. Polonite appears to be the most appropriate substrate for several reasons. It has a moderate to high P saturation potential of nearly  $2 \text{ g kg}^{-1}$  and up to  $7 \text{ g kg}^{-1}$  in laboratory studies when used with a particle size of 2-5.6 mm (Gustafsson et al., 2008). In addition, it has a liming effect similar or greater than calcite limestone and to some extent, comparable to lime, on acid soils (Papers III, IV, and V). The application rate of approximately  $12 \text{ ton ha}^{-1}$  showed a liming effect on a mountain meadow soil for at least 2 years under field conditions. Polonite can also be safely recycled as a soil amendment in cropping systems at rates of 6-8 ton per hectare for at least one year (Paper VI). However, these short-term studies can not forecast the effects in the long run.

## 5 CONCLUSIONS

There is a large number of filter materials for P removal from wastewater described in literature, but there is not a similar procedure to estimate their P sorption capacity. This work gives a set of recommendations for batch experiment procedure and presents a classification system according to the P sorption capacity and particle size.

The substrates Filtra P and Polonite recycled from laboratory infiltration columns tended to increase the yield of barley and ryegrass when used as soil amendments in a pot experiment. The amendments showed a potential liming effect, especially on acid soils.

Phosphorus dissolution studies showed that the ability of recycled substrates to improve P availability in soils was strongly dependent on substrate pH, P concentration and phase of sorbed P, and on soil pH and the phases controlling P solubility in soils.

Field experiments confirmed the liming potential of Polonite on acid soils, and suggested that the substrate can be safely recycled to meadows and also to cropping fields at rates of  $5\text{-}10 \text{ ton ha}^{-1}$ , depending on both substrate and soil properties such as pH and P content.

## 6 FUTURE RESEARCH

Future work shall focus on the design of filter systems to maximize the capacity of the sorbents and on improving the P sorption capacity of filter materials. Thus, the potential for P recycling would be greater.

Further studies that evaluate the effect of recycled filter substrates on soils and crops are needed. These studies shall consider other filter materials of interest, different types of soils and cropping systems. In particular, long-term studies are encouraged.

New directions may look towards the appropriate handling of soil P with adequate substrate dosage. Another interesting idea is that of combining P sorbents with filter materials capable to accumulate nitrogen, thus using recycled substrates that could provide full fertilization in agriculture.

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