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Iron coated sand/glauconite filters for phosphorous removal from artificially drained agricultural fields

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List of abbreviations and acronyms

EC: European Commission

EPA: Environment Protection Agency

MAP: Manure Action Plan

PSD: Phosphorous Saturation Degree

WFD: Water Framework Directive

pH: Hydrogen Potential

Ksat: Saturated Hydraulic conductivity

Definition of terms

Breakthrough point: Is a point on a sorption curve when 0.1 mg $P.l.^{-1}$ is released in the filtrate.

Durability: The duration the filter can treat water before releasing 0.1 mg $P.l.^{-1}$ in filtrate. It is measured in terms of the amount of P sorbed until a breakthrough point when 0.1 mg $P.l.^{-1}$ is in filtrate.

Efficieney: The proportion of P removed by the filter in relation to P supplied in the inlet solution. Mathematically, efficieney (%) = (Inlet P concentration/outlet P concentration)*100%

Saturation point: A point on a sorption curve when there is no further increase in the amount of P sorbed.

Sorption capacity: Is the total amount of P that can be removed (sorbed) by a filter. Two types of sorption capacity are distinguished.

- **Sorption capacity at breakthrough point** - represents the cumulative amount of P sorbed from the start of the filtration to breakthrough point.
- **Sorption capacity at saturation point** - represents the cumulative P sorbed from the start of filtration until saturation point.

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Abstract

Flanders (Belgium) is confronted with reactive phosphorus concentrations in streams and lakes which are three to four times higher than the 0.1 $mg.l^{-1}$ environment limit set by the Water Framework Directive. Much of the excessive P input in surface waters is derived from agriculture. Specifically, direct P input from artificially installed subsoil drainage pipes which short-circuits the buffering capacity of the subsoil is suspected to be one of the major sources. In this study, we aim to develop simple and cheap filters that can be directly installed in the field to reduce P concentration from farm drain water. To achieve this, our specific objectives included: (1) determining the link between physical size distribution, bulk density and initial saturated hydraulic conductivity (Ksat) of filter materials, (2) evaluating P removal efficiency and durability of the filter materials, (3) determining the cumulative P sorption until saturation point and subsequently test P desorption efficiency and (4) assessing the performance of the filters under a pilot field trial. The filter materials used were made of iron coated sand and mixtures of iron coated sand with glauconite. We determined Ksat using the constant head method and Darcy's equation, particle size distribution by sieving the materials through sieves of 0-5 mm mesh size and bulk density by measuring dry mass per volume. The method of Murphy and Riley was employed to analyse P using a spectrophotometer. We found that Ksat is linked to particle size distribution and bulk density by the equation: Ksat =0.004 + 0.004*D20 +0.010*D10 – 3.013*EXP-06*BD. We also found that the filter with the highest P removal efficiency was Grobbendonk 90/10% with 98.84% P removal efficiency but had a lower saturated sorption capacity of 538.9 $mg.kg^{-1}$. The most durable filter was Grobbendonk 100% with P sorption capacity at breakthrough point of 942.2 mg $P.kg^{-1}$. We estimated that Grobbendonk 100% was able to realise 62% of its total sorption capacity in the laboratory experiment (942.2 mg $P.kg^{-1}$ out of 1500 mg $P.kg^{-1}$). Therefore, our best filter in terms of both efficiency and durability was Grobbendonk 100%. Similarly, our field trial identified Grobbendonk 100% as the best filter with estimated sorption capacity at breakthrough point of 985 mg $P.kg^{-1}$, P removal efficiency of 74% and achieving 65.7% of its estimated saturated sorption capacity. Based on these findings, we suggested that the experiment to determine the maximum sorption capacity of the filters be concluded so that we can compare the capacity of the filters used in relation to their total capacity at saturation. We also suggested that a comprehensive large scale field trial be conducted for best performing filters to validate both the laboratory and pilot trial results.

Chapter 1: Introduction

1.1 Background information and justification

Phosphorus (P) is the most important macro-nutrient required for plant growth and productivity next to nitrogen. Though P may be abundant in soils, it is a major limiting nutrient as it is mainly in unavailable form for plant uptake (Kumar et al., 2014). This is because P in soils is highly fixed. Therefore, despite the high dosage of P that may be applied, only small quantities are removed by crops and most becomes unavailable to growing plants (Derau et al., 2010; Shen et al., 2011; Buda et al., 2012).

To ensure optimum productivity of crops, farmers make use of mineral fertilizers and manure to replenish plant available P and increase crop productivity. Surplus P inputs in farmlands have recently been exacerbated by intensification of agriculture which took place due to industrial revolution and growing populations (Buda et al., 2012). Agriculture intensification consequently led to more mineral P fertilizer being used, more animal feeds and manure being produced. As animals inefficiently utilize P in feeds (only 30% is retained), most of the P consumed ends up in manure, which is usually applied locally over the fields (Sharpley et al 2001). This led to accumulation of P in the soil profile in North and west Europe due to higher P inputs than outputs (Lemercier et al., 2008).

P accumulation in farmlands enabled increased agricultural productivity; however it also permitted build-up of P in soil profile above amounts sufficient for optimal crop yields subsequently escalated the potential for P losses in runoff as well as in leachate (Haygarth et al., 1998; Heckrath et al., 1995; Sharpley et al., 1996). Unfortunately, P losses from farmlands through surface and subsurface transport culminate into fresh water eutrophication (Csatho et al., 2011; Odum, (1997)).

Surface and subsurface transport of P from fertilised agricultural fields to open waters are common through surface erosion and subsurface percolations (leaching and sub surface artificial drainage) (Azevedo et al., 2015). These are major causes of non-point (diffuse) P losses to the environment (Ballantine and Tanner 2010).

Erosion is a mechanism of P transport that preferentially removes finer-sized soil particles (Haygarth and Sharpley, 2000). Run-off is caused by water flowing over the soil and P loss through runoff is initiated by the release of P from soil, plant material, and suspended

sediments (Sharpley, 1985). Leaching involves P loss through subsurface water flow percolating through the soil (Sharpley, 2001). Subsurface flow includes artificial and natural drainage, where artificial drainage includes percolating water intercepted by installed drainage systems, such as pipe drains.

There is usually low potential of P losses through subsurface drainage (Sharpley, 2001); however, subsurface P losses can be high in organic, sandy or in soils with structure prone to preferential drainage (Sims and Sharpley., 1998). Furthermore, subsurface P loss is exacerbated through installation of subsoil artificial drainage which short-circuits the buffering capacity of the soil profile (Bengston et al., 1992; Sims and Sharpley., 1998).

In Flanders, sandy soils with low P sorption capacity are common and their buffering capacity is short-circuited by installation of artificial drainage pipes in the subsoil. This increases P losses through subsurface drainage (Harrison et al., 2010). The pipe drains practice effectively connects farmland water to open waters, streams, lakes and seas (Ule'n et al., 2007). P losses cause eutrophication which subsequently creates undesired effect like reduced biodiversity and fish mortality in water bodies (Ballantine and Tanner 2010, Azevedo et al., 2015).

Due to the undesired effects of eutrophication, attempts have been made to mitigate eutrophic waters in Europe through legislations like Water Framework Directive (2000) and proper household or industrial wastes management (Harrison 2001). However, despite the efforts, the water quality is still not good and non-point (diffuse) pollution has been "earmarked" as a major cause (Ballanite and Tanner, 2010; Sharpley et al., 2003). To reach the goal of "good" water quality defined in the Water Frame Directive (WFD, article 2) or attain a P concentration below 0.1 $mg.L^{-1}$ (Environmental Protection Agency (EPA), 1986; Smil, 2000, WFD, 2000) requires a substantial reduction of diffuse P losses from farmlands in many parts of Europe (Kaasik et al., 2008).

Currently, recommendations have been made to reduce use of P fertilizers on crop lands with highest P supply which covers regions mostly in Belgium and Netherlands (Toth et al., 2013; Hermann, 2013). Following these recommendations, Belgium's, current application standards of P are restricted between 65 and 95 kg P_2O_5/ha/year. The limits depend on the type of crop and it's calculated to achieve P mining of soils. Maximum phosphorus application standards are approximately 5 kg P_2O_5/ha/year smaller than the general phosphorus export by the crop.

resulting in a small negative phosphorus input into the soil (Manure Action Plan (MAP), 2012; Amery and Schoumans, 2014).

Whereas this is a good gesture to mitigate eutrophic waters in the long run, it's mandatory that Flanders urgently complies with Water Framework Directive (WFD) required by European Union, lest Belgian agriculture may have to take the consequence. Therefore reduction of P fertilisation alone is not sufficient but also an immediate improvement of water quality is needed (WFD, 2000). Reduction of P losses from farmland via pipe drains to open water using P sorbing materials may be one way to urgently improve water quality (Penn et al., 2007; Ballantine and Tanner 2010).

A number of P filter materials have been tested to reduce P concentrations in surface runoff (Hoffman et al., 2009). Similar studies have shown reduction of P in subsurface transport by installing P filters at the outlet of drainage pipes (Penn et al., 2007). This approach was suggested to be carried out in connection with small scale constructed wetland (Reinhardt et al., 2005) or flow through filter structures in ditches (Penn et al., 2007). Additionally, some filter materials for P retention have been described for retention of P for high concentrations (above 40 mg $P.L^{-1}$) in waste water (Penn et al., 2007; Vohla et al., 2011).

However, the efficacy of these filters in retaining P under low P concentrations (below 0.5 mg $P.L^{-1}$) as in farmland drainage water is unclear because filters are known to behave differently at high and low P concentrations (Adam et al., 2007; Andriamanantena, 2014). Fortunately, an attempt has been made at University of Ghent laboratory to screen potential P filter materials under different solution concentrations.

Promising P filter materials found at small scale laboratory level includes iron sludge and acid pre-treated glauconite (Andriamanantena, 2014). However the usability and efficacy of these potential P filters is untested under actual large scale laboratory and field conditions. The aim of this Master thesis is therefore to evaluate the efficacy and stability of these filters under large scale laboratory and field conditions in artificially drained farmland in Belgium.

1.2 Objectives of the study

1.2.1 General objective

To measure the usability, effectiveness and durability of P sorbing materials in filter systems to reduce P losses from artificially drained agricultural fields in Belgium.

1.2.2 Specific Objectives

1. To determine the link between physical size distribution, bulk density and initial hydraulic conductivity of filter materials
2. (i) To evaluate P removal efficiency of the filter materials
   (ii) To evaluate the amount of P that can be sorbed by the filters at breakthrough point
3. To determine the cumulative P sorption until saturation point and subsequently test P desorption efficiency
4. To assess the performance of the filters under a pilot field trial

1.3 Research hypothesis

1. Initial saturated hydraulic conductivity of the filter materials is dependent on particle size distributions because of the influence of particle sizes on distribution of the pores
2. Initial saturated hydraulic conductivity is negatively related to Ksat because an increase in bulk density reduces porosity.
3. The amount of P that can be sorbed by a filter material is dependent on the surface area available for P sorption and contact time. The more contact time and/or the total surface area available the more P is sorbed.
4. P desorption is dependent on ionic interaction, contact time and pH of the solution

Chapter 2: Literature Review

2.1 Importance and fixations of P in soil

P is the most important element in the nutrition of plants next to nitrogen (Kumar et al., 2014). It plays an important role in plant metabolism like photosynthesis, energy transfer, signal transduction, macromolecular biosynthesis and respiration and nitrogen fixation in legumes (Khan et al., 2010). It is a component of key molecules such as nucleic acids, phospholipids, and ATP, and, consequently, plants cannot grow without a reliable P supply (Schachtman etal., 1998). P deficiencies in plants results in stunted growth, slower ripening, delayed harvest, lower yields.

Though P may be abundant in soils both in organic and inorganic forms, it is a major limiting nutrient for plant growth because it is mainly in unavailable form for plant uptake (Kumar et al., 2014). This is due to P fixation in soils which results in removal of available P from soil solution into the soil solid phase. These fixations involves two reactions; phosphate sorption on the surface of soil minerals and phosphate precipitation by free Ca^{2+}, Al^{3+} and Fe^{2+} in soil solution (Buda et al., 2012).

In acidic soils inorganic P occurs predominantly as insoluble complexes of aluminium and iron while in calcareous soils it occurs as insoluble complexes of calcium. These insoluble P forms cannot be directly absorbed by plants (Reinhardt et al., 2005). Further, organic matter also immobilises 20% to 80% of P in soils (Harrison, 1987). Due to these various forms of P fixations in soils, only 0.1% of total soil P exists in a form available for plants uptake (Parfitt, 1989).

2.2 Soil Phosphorus cycle and dynamics

As already mentioned, plant available P is a limiting factor for plant productivity. This is because P is highly fixed and has slow diffusion in soils (Shen et al., 2011). A continuous input of P in soil is thus inevitable to counter the fixations. A summary of P cycle in soils in figure 1.1 highlights some of these soil processes for organic and inorganic P as well as the rhizosphere and plant processes.

Within soils, P can cycle between different forms depending on several processes. Two P forms are Inorganic and organic P each with different cycle. The organic and inorganic (Pi)

forms of P differ in their behaviour in soils (Turner et al., 2007) and Pi contributes up to 35% to 70% of total P in soil (Harrison, 1987).

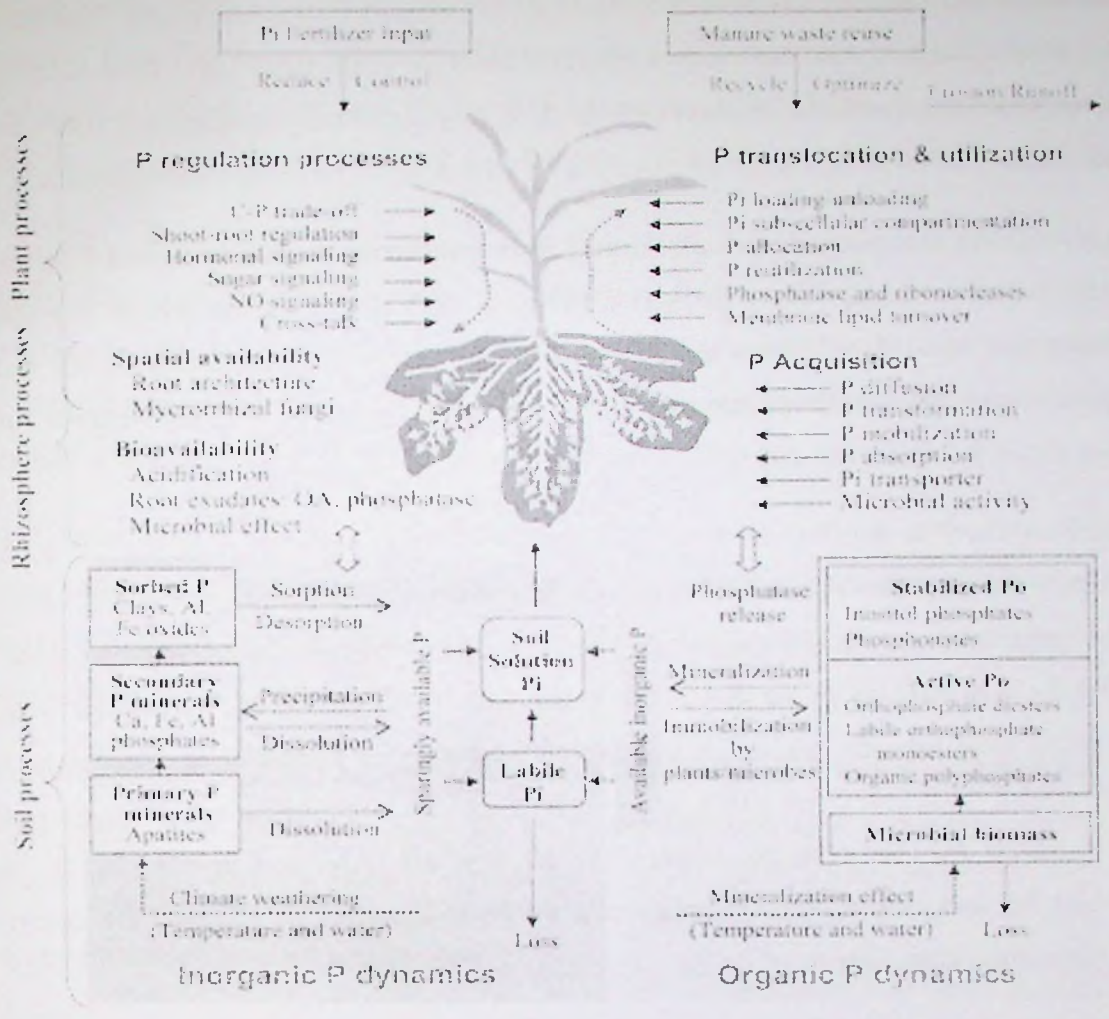


Figure 1.1: P dynamics in the soil/rhizosphere-plant continuum (C-P is Carbon to Phosphorus, NO is Nitrous oxide, OA is Organic acid (extracted from Shen et al., 2011)

In summary, P inputs in soils include: application of chemical P fertilizers and animal manure which have been used to improve soil P fertility and crop productivity (Shen et al., 2011). On the other hand, P outputs include runoff, leaching, plant uptake and various P fixation processes in soils.

P is released as a result of weathering of P primary minerals in soils (apatites, strengite, variscite). This results in formation of secondary minerals and sorbed P in Fe and Al oxides. However, the weathering process is very slow because the minerals are stable and cannot release P fast enough to cope with crop demand. In some instances, direct application of

phosphate rocks (apatite) has proven to be relatively efficient for crop growth in acidic soils (Shen et al., 2011). P can be released through desorption reactions that yields soluble and labile P which are available for plant uptake. Similarly, these labile and soluble P can also be fixed via desorption or precipitation reactions by silicates, Al, Fe oxides and hydroxides.

In addition, the secondary P minerals formed from weathering as well as sorbed P forms like Ca, Fe and Al phosphate vary in their dissolution rates depending on size of the mineral particles and soil pH (Oelkers and Valsami-Jones, 2008). The solubility of Fe and Al Phosphates increases with increase in soil pH but Ca phosphate decreases except for pH values above 8 (Hinsinger, 2001).

In acidic soils, P is dominantly adsorbed by Al/Fe oxides and hydroxides such as gibbsite, haematite and goethite (Parfitt, 1989). In neutral to calcareous soils, P retention is dominated by precipitation reactions (Lindsag et al., 1989) although P can also be adsorbed on surface of $CaCO_3$ as well as clay minerals (Derau et al., 2010). Phosphate can precipitate with Ca generating dicalcium phosphate (DCP) which is available for plant uptake. Ultimately, DCP can be transformed into more stable forms such as octocalcium phosphate and hydroxyapatite (HAP) which are less available to plants at alkaline pH (Arai and Sparks, 2007). The P adsorbed on surfaces of clay minerals and Al/Fe oxides can be released by desorption reactions (Shen et al., 2011).

P immobilised in organic form mineralises from organic matter due to microbial activities. This yields both active and stabilised Po from which P can be realised by mineralisation and removed by immobilisation processes (Tunner, et al 2007).

2.3 Intensification of agriculture and its consequences

To overcome this problem of P fixation in soils, farmers make use of P fertilizers and manure to increase levels of available P and achieve high crop productivity (Buda et al., 2012). Although raising P levels in soils is beneficial for crop yield, continuous P inputs in agricultural fields allows for build-up of soil P beyond crop requirements. This increases potential for P losses to the environment (Harrison et al., 2010). P losses to environment can occur through erosion, surface runoff, leaching and subsurface artificial drains (Sharpley et al 2001).

There can be a high potential for P losses in surface runoff arising from transport of dissolved P. This is initiated by the release of P from soil, plant material and suspended sediments

(Sharpley et al., 2001).This process occurs when rainfall interacts with a thin layer of surface soil (1–5 cm) before leaving the field as surface runoff (Sharpley, 1985). The potential of P losses in water percolating through the soil profile by leaching is generally small due to sorption of P by P-deficient sub-soils. However, there are exceptions in organic soils, where the adsorption affinity and capacity for P sorption are low due to the predominance of negatively charged surfaces (Duxbury and Peverly, 1978; Miller, 1979; White and Thomas, 1981).

Notably, other soils that are susceptible to subsurface drainage P losses include waterlogged soils where Fe (III) has been reduced to Fe (II), and well structured soils prone to preferential flow through macro-pores and earthworm burrows and finally sandy soils with low P sorption capacities (Bengston et al., 1992; Sims and Sharpley., 1998).

Factors controlling P loss in subsurface flow are more complex than for surface runoff due to variable paths and time of water flow through a soil with subsurface drainage. For instance subsurface P losses in sandy soils are exacerbated when buffering capacity of the soil is short-circuited by installing subsoil artificial drains (Csatho et al., 2011, Penn et al., 2009).

P loss from soil to water is responsible for eutrophication of fresh waters which poses a risk to fresh water biota (Azevedo et al., 2015). P concentration of 0.1 mg $P.L^{-1}$ in water is sufficient to trigger eutrophication of surface water (WFD, 2000; EPA, 1998).

2.4 Eutrophication control legislations

2.4.1 European legislations

The issue of increasing the efficient use of phosphorus was lately tackled by the European Commission (Anon., 2013). European Member States address the agricultural phosphorus losses via national or regional legislation restricting the application of phosphorus. Most of this legislation concerns implementations of the Nitrates Directive (91/676/EEC) in terms of National Action Plans, the Water Framework Directive (2000/60/EC) in terms of River Basin Management Plans and the Industrial Emissions Directive (2010/75/EU).

Policies to reduce nutrient losses to fresh and coastal waters have been developed by the European Union and international conventions since the beginning of the 1990s. Table 1. highlights legislation related to eutrophication which was enacted by the European commission to abate water pollution.

The European Commission took action to reduce nutrient losses to surface waters with the implementation of the Nitrates Directive (Directive 91/676/EEC) which was targeted on diffuse pollution from agriculture. There is also the Urban Waste Water Treatment Directive (Directive 91/271/ EEC), aiming at reducing nutrients in urban waste water discharges.

In 2000, with the Water Framework Directive (WFD, Directive 2000/60/EC) a comprehensive regulation for water was enforced. The WFD aims to achieve a "good" ecological status for all European fresh and coastal waters by 2015, and requires the development of river basin plans including strategies to reduce nutrient losses. Finally, the Marine Strategy Directive (Directive 2008/56/EC) was enacted in 2008 to protect the marine environment (Amery and Schouman, 2014).

Table 1: European Directives in relation to phosphorus aspects (extracted from Amery and Schouman, 2014)

Bathing Water Directive	**76/160/EEC amended by 2006/7/EC**
Directive on Dangerous Substances	76/464/EEC = 2006/11/EC
Urban Waste Water Directive	91/271/EEC
Nitrates Directive	91/676/EEC
Water Framework Directive	2000/60/EC
Groundwater Directive (daughter directive of Water Framework Directive	2006/118/EC
Marine Strategy Framework Directive	2008/56/EC
Waste Framework Directive	2008/98/EC
Industrial Emissions Directive (replaces IPPC Directive 96/61/EC)	2010/75/EU

2.4.2 Flanders Legislations

In Flanders, the Water Framework Directive to ensure good water quality is enforced through manure decree and implemented through Manure Action Plan (MAP) which restricts on the maximum total phosphorus application standards as listed in the Manure Decree (Table 3).

In 2014, the permitted application standard ranges between 65 and 95 kg P_2O_5/ha/year depending on the crops P demand. The Indicative limits for the current Manure Decree (2015-2018) are mentioned (5–10 kg P_2O_5/ha/year and set lower than the standards of 2014) (MAP, (2012).These maximum phosphorus application standards are approximately 5 kg P_2O_5/ha/year lower than the general phosphorus export by the crop, resulting in a small negative phosphorus input into the soil. Phosphorus can be applied in the form of manure, organic materials or chemical fertilisers (only derogation farms cannot use chemical P fertilisers).

Table 3: Maximum total phosphorus application standards in Flanders (limits for 2015-2018 are indicative) extracted from Manure Action Plan (MAP), 2012.*

Crop	Application limits(kg P_2O_5/ha/year)			
	2011-2012	**2013-2014**	**2015-2016***	**2017-2018***
Grassland (only mowing)	95	95	95	90
Grassland (not only mowing)	90	90	90	90
1 cut grass/rye + maize	95	95	95	90
Maize	80	80	75	70
Winter wheat-triticale	75	75	70	70
Other cereals	75	70	70	70
Other crops	75	65	55	55

2.5 Impacts of eutrophication control legislation and remaining problems

Eutrophication is the enrichment of natural water bodies by nutrients particularly nitrogen and phosphorus and the undesirable changes in water quality which accompany the process. Dangers of eutrophication includes: increase in biomass of phytoplankton and macrophyte, depletion of oxygen, change in species composition and diversity; and the shift to bloom-forming algal species, some of which are toxic; as well as the increase of fish kill, problems for drinking water and aesthetic of the water body (Smith & Schindler, 2009).

Following the interventions to control P losses to water bodies, there was improvement in the ecological status of surface waters in the last decades, though water quality is still poor in many European lakes and waterways (Kristensen, 2012). The improvement of water quality resulted from reduction of P inputs from point sources and scattered dwellings. This was due to increasing proportions of the population connected to urban wastewater treatment plants and improved waste water treatment with more tertiary treatment (Anon, 2013; Buda et al., 2012).

The prevention of pollution at source, the precautionary principle and the prior licensing of wastewater discharges by competent authorities have become key elements of successful policies for preventing, controlling and reducing inputs of hazardous substances, nutrients and other water pollutants from point sources into aquatic ecosystems (Harrison et al., 2010). For instance, in Flanders in the year 2003, it was estimated that households contributed 49% to the total-P load to surface water in Flanders, agriculture 39%, and industry 12%. For 2004 it was calculated that, compared to 1992, the contribution of households decreased by 35%, agriculture by 4%, and industry by 78% (MIRA, 2005).

Figure 4 shows that the orthophosphate concentration in surface water in Flanders is higher than the limits for surface waters (MIRA, 2012). Despite efforts to reduce P pollution, orthophosphate concentration in surface water in Flanders is still three to four times above the 0.1 mg $P.L^{-1}$ environment limit (Ballantine and Tanner; 2010 and non-point (diffuse) P losses is now the major cause.

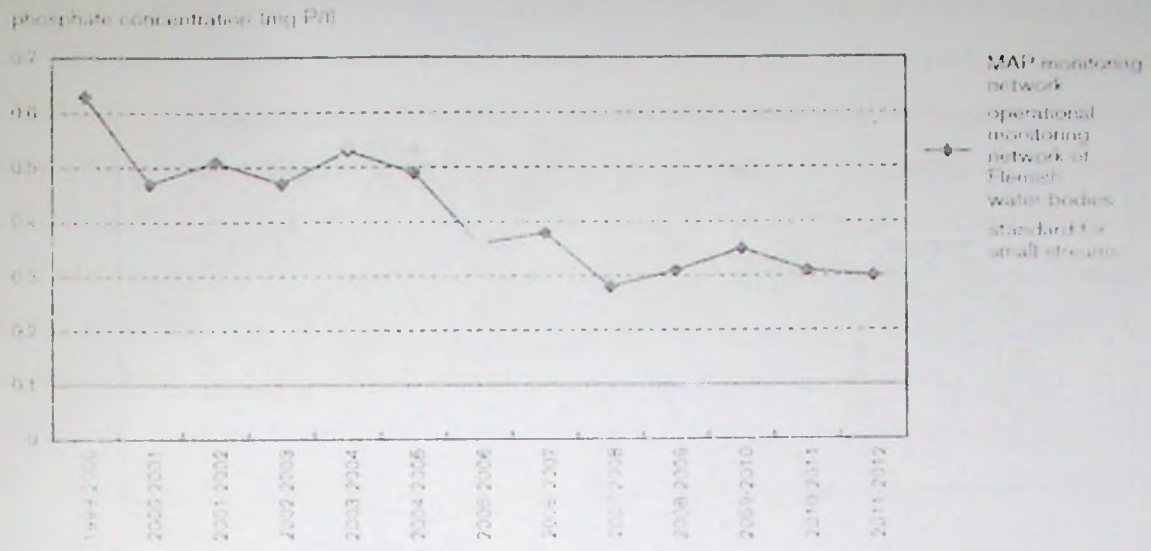


Figure 4: Evolution of orthophosphate concentration and percentage of measuring points in surface water that meet their specific basic quality norm in Flanders (adapted from MIRA 2012)

Due to the reduction in point sources (industry and waste water treatment plants) agriculture is now often the main contributor of phosphorus losses to surface waters (Harrison et al., 2010). This fact has been highlighted in figure 5, which is a map of Belgium showing large parts of Flanders with phosphorous saturation degree above the 25% limit (Van Meirvenne et al., 2008). A high P saturation degree poses a threat for a high potential of P losses which is undesirable because of eutrophication and also the fact that P is a finite resource (Ballantine and Tanner, (2010). Though P leaching from soil is not entirely a function of phosphorus saturation degree (PSD) in soils but also hydrological conditions (Schoumans et al., 2013), its commonly accepted that for acidic sandy soils (common in Flanders), PSD correlates with P leaching to shallow ground water and seepage into surface water (Chardon and Schoumans, 2007).

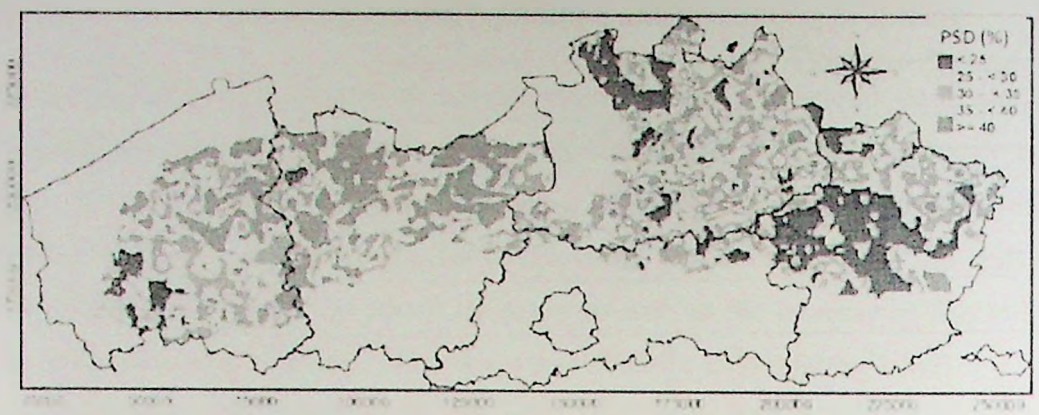


Figure 5: Classification of Phosphorus saturation degree (PSD) of soils in Flanders with a probability of 95% (source: Van Meirvenne et al., 2008)

Innovative measures that can reduce losses of P from farmlands through surface erosion and subsurface discharge are needed (Penn et al., 2007). The potential of P filters in reducing P losses from farmlands drainage is still unclear yet it may be one way to improve water quality (Penn et al., 2007; Ballantine and Tanner 2010).This study therefore attempts to address this gap so as to reduce the input of P from farmland pipe drains to open water by using P sorbing materials.

2.6 Potential of P filter materials

2. 6.1 Cost, Capacity, reactivity and stability

Lyngsie, (2013) study observed that, the technique of using filters to sorb P is dependent on the filters' costs, effectiveness (capacity), and stability. Materials proposed as efficient drainage water filters must be cheap, possess high capacity, reactivity and stability to retain P from rather low (0.3-0.5 mg $P.l.^{-1}$) concentrations.

Proposed filter materials must be readily available and cheap so that it is easily accessible and affordable to farmers who may not have sufficient profits from agriculture to invest (Ballanite and Tanner, 2010; Cucarella and Renman, 2009).

Materials with high reactivity allows for sorbing P at a fast rate. This is relevant for field application especially in a flow through system design or during fast leaching events (Lyngsie, 2013; Penn et al., 2007). Similarly, a stable material is able to consistency maintain its P sorption over time. This is relevant in determining the usability in field application in terms of durability and possibility of recycling when saturated with P (Ballanite and Tanner, 2010; Shen et al., 2011).

In addition, filter materials with high capacity and efficiency is preferred so that it is capable to sorb high P concentration before saturation point while reducing P concentrations in filtrate to below the environmental limit (Ballanite and Tanner, 2010; Lyngsie, 2013). This is important to allow for usability of the material in terms of increasing its durability and efficiency in field applications. High capacity of a material is a function of number of available cations to fix P and the total surface area available for P fixations (Weng et al., 2012). Such higher surface area is a function of particle size distribution of the material: finer materials have higher the surface area (Nair et al., 1984; Mann, 1996; Zhu et al., 1997). Generally, proposed filters must reduce inorganic P (Pi) concentrations in drainage water as Pi concentrations higher than 0.1mg $P.L^{-1}$ may cause eutrophication (Smil, 2000; WFD, 2000; EPA, 1998).

There is a consensus among authors about the variability of sorption capacity of P filters (Andriamanantena, 2014; Lyngsie, 2013; Vohla et al., 2011; Ballanite and Tanner, 2010; Cucarella and Renman, 2009). In his study, Cucarella and Renman (2009) documented numerous materials for P removal. The P sorption capacity of the materials he documented ranged from 30 $mg.kg^{-1}$ to $113*10^{3}$ $mg.kg^{-1}$ (table 4). Boujelben et al., 2008, found a sorption capacity of iron coated sand and iron coated brick at 1500 and 1750 mg $P.kg^{-1}$ filter material respectively (table 4).

The sorption capacity is a function of the total surface area available for P sorption. Therefore, numerous studies agree that P sorption increases with decrease in particle size of the filter material (Ballanite and Tanner, 2010; Vohla et al., 2011; Lyngsie, 2013). The mechanism of P sorption was found to rely on metal ion competitors, Ca concentration and also pH dependent (Weng et al., 2012). The metal cations bind mobile ion phosphate by adsorption and/or precipitation, a reaction which is dependent on concentration of the metal cations, pH and concentration of calcium ions (Weng et al., 2012).

Table 4: Sorption capacity of some P filters compiled by Cucarella and Renman, (2009)

Material	P sorption capacity (mg $P.kg^{-1}$)	Reference
Blast furnace slag	420	Mann and Bavor, 1993
Fly ash	260	
Granulated slag	160	
Black oxide	890	Cheung et al., 1994
Red mud gypsum	507	
Blast furnace slag	44250	Sakadevan and Bavor, 1998
Steel furnace slag	1430	
Zeolite	2150	
Bauxite	610	Drizo et al., 1999
Limestone	680	
Shale	650	
Opoka	100	Johansson, 1999
Spodosol	1000	
Filtralite P	2500	Ádám et al., 2007
Shell sand	9600	
Fe-coated sand	1500	Boujelben et al., 2008
Fe-coated brick	1750	

2.6.2 Ksat of filter materials

It is noted that under field conditions, filters must be able to process large volume of water during peak flow, heavy leaching events such as rainstorms or when transition between frost and thaw is very short (Lyngsie, 2013). Therefore, the study of P filters for field application requires understanding of its saturated hydraulic conductivity (Ksat). A high Ksat is important to permit processing of large volumes of water (Canga et al, 2013). For instance, in Flanders, there is an estimated peak flow of 8000 L of water per day; appropriate filters must be able to process this volume within a small area. Additionally, in the study of P filter media, it's known that Ksat influences P sorption (Lyngsie, 2013).

There is a consensus among authors that Ksat has a relation with bulk density and particle sizes. Researchers found that Ksat decreases with increase in bulk density (Richard et al., 2001). Other authors also agree that P sorption increases with decrease in particle size of filter materials (Ballanite and Tanner, 2010; Vohla et al., 2011; Lyngsie, 2013). Ksat also influences the sorption efficiency of the filters, the lower the Ksat the more the contact time for P sorption (Andriamanantena, 2014). Therefore we need to strike a balance between sorption efficiency and capacity to process large volumes.

However, direct measurement of Ksat in the lab or in the field is often very costly and time consuming. It is therefore convenient to find simple and reliable functions to predict Ksat (Canga et al, 2013). In soil science, Ksat has always been predicted from using functions that relate to physical size distribution, bulk density or particle density of the soil (Iversen et al., 2011, Arya et al., 2010). Unfortunately, these functions cannot be used for our coarse filter materials as the particle sizes are different from the ranges found in soil. To address this, we need to develop predictive function that links Ksat to particle size distribution and bulk density of the filter materials.

2.6.3 Pollution free and recycling through P desorption

It's also mandatory that P filter materials should not contain pollutants otherwise its unacceptable to cause other environmental problems. In addition, the filters are preferred if they are easily recycled after saturation with sorbed P (Ballanite and Tanner, 2010). Recycling of P filters can be done through desorption reactions (Lyngsie, 2013). P sorption reaction can be reversible and knowledge of the degree of reversibility of the adsorption of phosphate by P filters is of great significance for the recycling of filters (Cabrera et al., 1981).

Desorption can be done by altering equilibrium between phosphate ions in solution and solid surfaces. This can be done by changing: (1) the concentration of phosphate ions in solution; (2) the pH of the suspension; (3) other variables of less influence (e.g., ionic strength, temperature, etc.). (Hingston et al., 1972, 1974; Barrow and Shaw, 1975; Cabrera et al., 1977). Cabrera et al. (1981) conducted P desorption from iron oxide using a strong base (NaOH) and NaCl salt at pH 3 and 7 to alter ionic strength in the solution. Up to 96% of the sorbed P was desorbed from iron oxide. Desorption, using NaOH solution, was found to be predominantly a surface reaction, at which hydroxyl ions replace the adsorbed phosphate ions only at the surface outer biding sites (Zack-Moar et al., 2011).

2.7 Types of filters materials

Natural potential filter materials which meet standard P sorption filter criteria includes: silica rich materials, gypsum and lime and some have been commonly used in studies to remove P from wastewater (Vohla et al., 2011) (table 2 and 3 describes some of the filters used to retain P in wastewater and P solutions studies under laboratory experiments respectively).

In addition, synthetic filtration products like iron hydroxide, allophane and wollastonite have been used in P retention studies. In addition, waste materials and/or by-products from industries (Iron humates, coal) and man-made products (expanded clay aggregates and lanthanum modified clay (Ballanite and Tanner 2010; Vohla et al., 2011).

A Master thesis laboratory study at Ghent University by Andriamanantena (2014) also found that P sorption varies for different filter materials but generally increases with increasing contact time. The study highlighted iron sludge as best filter material with P sorption of 550 and 15520 mg $P.kg^{-1}$ for 30 mg $P.L^{-1}$ and 100 mg $P.L^{-1}$ solution respectively. The sorption reduces to 215 mg $P.kg^{-1}$ for 2 mg $P.L^{-1}$ solution. Generally P sorption was three times higher in iron sludge compared to other filters for 30 mg $P.L^{-1}$ solution concentration and ten times higher for 100 mg $P.L^{-1}$ solution (Andriamanantena, 2014). Though iron sludge need to be mixed with sand to improve its usually low hydraulic conductivity in order to be used under field conditions to process large volumes of water. Under field application, a higher Ksat represents capacity of the filter to process large volumes of water in a small area (Canga et al. 2013). Therefore in this study we addressed the challenge of low Ksat of iron sludge by using iron coated sand materials.

Table 2. Some selected filter materials for removal of P from wastewater (Extracted from Vohla et al., 2011).

Material	Study type	Description of the study	Retention calculation	P retention	Ca (CaO)	pH	References
Alunite (calcinated)	Batch	Adsorption: 1 g of material with 1 L of phosphate solution (25–150 $mg.L^{-1}$), contact time 29.1 min	Calculated	Average of over 80% removal	-	5	Özacar. (2006)
Apatite (igneous and sedimentary)	Batch/Column	35 g of material in a 1 L glass flask filled with 700 mL of solution (5–150 mg $P.L^{-1}$) 24 and 96 h isotherms	Langmuir/Freundlich	0.28–1.09 g $P.kg^{-1}$ material in 24 h isotherms	7–31.4%		Bellier et al., (2006)
Bauxite	Batch	2.5–40 mg $P.L^{-1}$, 20 g and 24 h and column study (40d + 40d): HLR 3 $L.d^{-1}$	Langmuir	Adsorption 0.612 $g.kg^{-1}$. Column: 160 mg $P.kg^{-1}$, longer study: 355 mg $P.kg^{-1}$			Drizo et al., (1999)
Bauxite	Batch	1 g substrate and 100 dm^{-3} solution, 10 mg $P.dm^{-3}$ and shaken for 2 h	Calculated	Maximal PO_4^{3-} removal 67.3% at pH 4.45		8	Altundoğan and Tümen (2002)
Bauxites (raw and activated)	Batch	1 g substrate and 100 dm^{-3} solution, 10 mg $P.dm^{-3}$ and shaken for 2 h	Calculated	Adsorption for raw and activated bauxite: 0.82 and 2.95 mg $P.g^{-1}$, removal >95% for activated bauxite		5.9	Altundoğan and Tümen (2003)
Dolomite and sand	Batch	10 g sorbate in 50 mL solution with 0–100 $mg.L^{-1}$, 24 h	Langmuir	0.168 g $P.kg^{-1}$	28.7%	4.5–5.2	Prochaska and Zouboulis (2006)
Laterite	Batch	Sorption test with leachate (10g granular laterite, solution with 5-50 mg PO_4^{3-} L^{-1}) and pilot CW, 2 years	Calculated	99% removal of phosphates in lab and 96% in pilot CW			Wood and McAtamney (1996)

Table 3: Some P filters that have been used in laboratory studies to extract P from P solution

Filter materials	Description	Author
Filtrate P*	Light expanded clay aggregates resembling material calcinated at 1200°C provided by Weber Norway. Porous material consisting of granules of Ca/Mg oxides. Has minerals calcite, Ca/Mg oxides and clay silicates	Lyngsie et al., 2013
Limestone	Consist of a mixture of bryozo and coral chalk from the Danian formation at Faxe. Dried material provided by Faxe Kalk Aps. Denmark. Contain mineral calcite	
Calcinated Diatomaceous Earth (CDE)	From the Fur formation calcinated at 750°C, was provided by Damolin Aps. Denmark. It's a mixed calcinated clay silicate	
Shell-sand	Consist of crushed sea shells. It was provided by Danshells Aps. Denmark. Contain minerals calcite, aragonite and dolomite	
CFH-12	Consist of dried iron oxides. It was provided Kemira Oyj. Finland. Has mineral iron oxide	
Bauxite	Oxides of aluminium, iron and silica	Andriamanantena, 2014
Biotite	Iron oxide, silicon oxide, aluminium oxide	
Olivine	Magnesium oxide, silicon oxide, Iron oxide	
Fe sludge	Iron oxide, Calcium oxide, Silicon oxide	

Chapter 3: Materials and methods

3.1 Checking the link between physical size distribution, bulk density & initial hydraulic conductivity of the filter materials

We checked the link between physical size distribution, bulk density and hydraulic conductivity of the filter materials. In this study, the filter materials used were two types of iron coated sand and glauconite (figure 3.1). These materials are non-pollutants, cheap and readily available. The filter materials used were all rich in iron because of the reported high P sorption capacity of iron (Andriamanantena, 2014; Caurella, 2009; Arias et al., 2001, Ballaux and Peaslee, 1975).The iron coated sand is a brownish iron-rich waste material acquired from drinking water processing companies. Glauconite is a greenish iron-rich micaceous clay mineral (McRae, 1972). It is very friable, weakly resistant against weathering and is a readily available soil mineral commonly formed under reduced soil conditions. In this study, glauconite was pre-treated with acid in order to speed up weathering and release iron for P fixation (Martinez et al., 2014). HCl was used in the pre-treatment because it results into more iron being released than treatment with H_2SO_4 (Wilson 2013).

Balen Fe coated sand | Grobbendonk Fe coated | Acid pre-treated glauconite

Figure 3.1: Iron coated sand from Balen, Grobbendonk and acid pre-treated glauconite

3.1.1 Particle size distribution of the materials

We determined the particle size distributions by preparing different filter material mixtures. These mixtures consisted of iron coated sand and 0.1M HCl pre-treated glauconite. The ratios (on weight basis) in which they were mixed are given in table 3.1.

Table 3.1: Mixing ratio of filter materials consisting of iron coated sand and acid pre-treated glauconite

Filter material mixture		Percentage of iron coated sand	Percentage of glauconite
Balen	100%	100%	0%
	90/10%	90%	10%
	80/20%	80%	20%
	70/30%	70%	30%
	60/40%	60%	40%
Grobbendonk	100%	100%	0%
	90/10%	90%	10%
	80/20%	80%	20%
	70/30%	70%	30%
	60/40%	60%	40%

Particle size distribution of the filter materials was determined by sieving 100 g of each filter material mixture through sieves with mesh sizes varying from 0.05 to 5.00 mm. For each filter material, the experiment was replicated three times and the average weight percentage of the particles passing each sieve was considered. Cumulative particle size distributions of each filter material were then determined. From the graphs of the cumulative particle size distribution of the filter materials, "Dx" values were calculated by linear interpolation ranging from D10 to D90 (Dx is the mesh size of the sieve which allows x% of the particles to pass).

3.1.2 Bulk density of the filter mixtures

To determine the bulk density of each filter material, 100 g of dry material mixture was mixed and shaken manually in a plastic beaker to homogenous the particle distributions. The 100 g mixtures were filled successively in a graduated tube until a height of 20 cm was reached. Bulk density was determined as the mass of the dry material divided by the volume it occupied.

Bulk density ($kg.m^{-3}$) = mass of dry filter material (kg)/Volume (m^3)

3.1.3 Determination of initial saturated hydraulic conductivity (Ksat)

Saturated hydraulic conductivity (Ksat) was determined using the constant head method (Klute, 1965) and calculated using Darcy equation. In this method a constant water head was kept on top of the filter material by ponding water. In the simplest form, the constant head method is illustrated in figure 3.2. In the set up water is supplied from a reservoir to the plastic tube whose length L was filled with filter material to a height of 20 cm. Above the filter material, a constant water head H of about 4 cm is maintained .

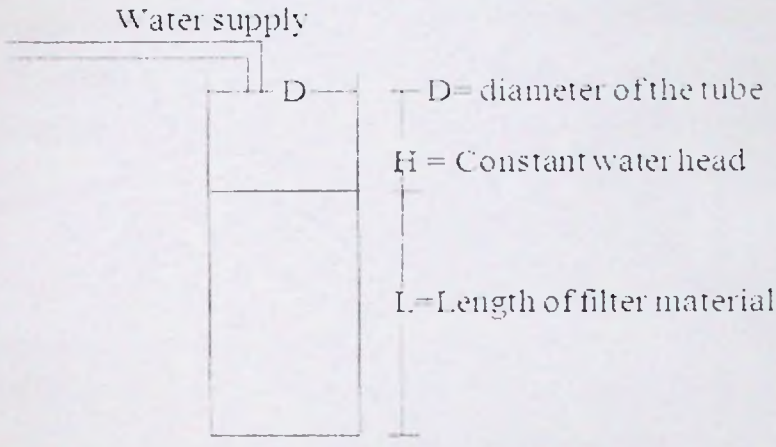


Figure 3.2: Schematic sketch of a constant head method used to determine initial Ksat

Discharge per minute (V) was then determined and Ksat calculated using Darcy's equation.

$Ksat = (V*L) / (A*T*\Delta H)$

Where Ksat = Saturated hydraulic conductivity (m/s)
V = discharge volume (m^3)
L = Length of the filter column (m)
T = time taken for discharge V (s)
ΔH = the head difference between inlet and outlet (m)
A = cross sectional area occupied by the filter material (m^2)

The final Ksat was calculated at a standard temperature for conductivity determinations (20°C) by taking into consideration effect of viscosity (Kestin et al., 1978)

$$Ks_{(20^oC)} = (Ks_{(t)} * \eta_{(t)} / \eta_{(20^oC)})$$

Where, $Ks_{(20^oC)}$ is saturated hydraulic conductivity at 20°C
$Ks_{(t)}$ is saturated hydraulic conductivity at a measured temperature (°C)
$\eta_{(t)}$ is viscosity at measured temperature and $\eta_{(20^oC)}$ is viscosity at 20°C.

However, in our experiment the system used to determine Ksat was slightly adjusted (though the main principles remained the same). The adjustment was necessary because the same system had to be used to assess P removal efficiency and durability of the filters.

In order to achieve this, we used a system where ponding water was maintained by a continuous flow which was designed through a system of communicating vessels. This was also vital to allow several filter materials to be run concurrently. The adapted system as illustrated in a schematic sketch, figure 3.3 (a) and figure 3.3 (b) consists of a main water supplier container, a reservoir, filter material tube and filtrate collector. All the compartments are connected through plastic tubes.

The system works by pumping water from the main supplier to the reservoir. The reservoir has an outlet to allow excess water to flow back into the main supplier and to keep constant water head on top of the filter materials. From the reservoir, water is supplied to several filter material tubes via communicating vessels. To initiate the flow, a small pump is switched on for a few seconds to allow water to fill the tube with filter materials so that communication between the reservoir and the filter material tube is established. Once the communication is established the pump is turned off and the continuous water flow is sustained voluntarily. This maintains constant water head on top of the filter materials.

Prior to the start of the experiment, as much air as possible was evacuated by vertical displacement. This was done by slowly supplying drops of water from outlet of the tube connected to the filter material. Initial discharges of filtrate through the filter materials per minute were recorded and the temperature of water noted as well. Ksat at a measured temperature was calculated using Darcy equation.

The flow system is however turned off at the end of each day and only re-stated the following day. Such intermittent break periods though inevitable in practice are undesired since they may result in fluctuations of Ksat and/or P sorption curve.

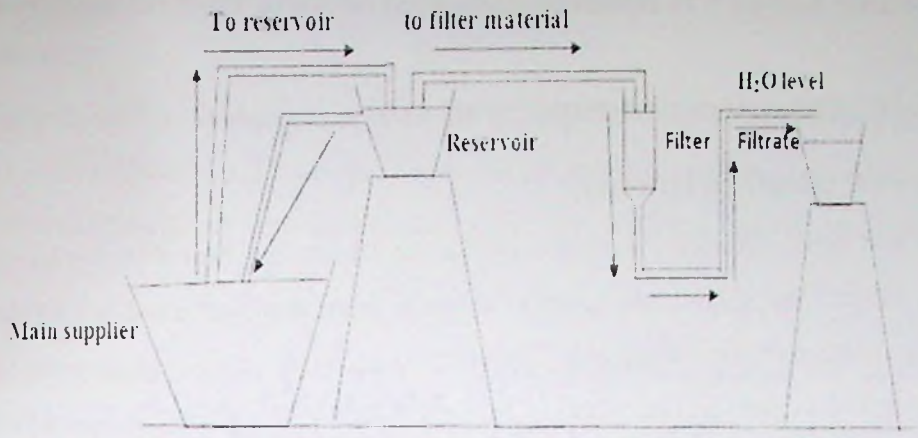


Fig 3.3 (a)

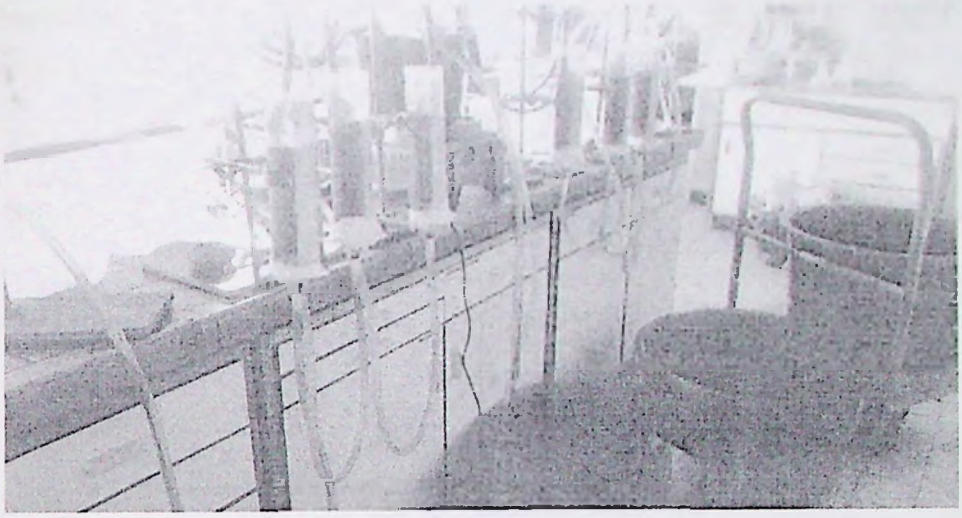


Fig 3.3 (b)

Figure 3.3 (a) & (b): A schematic sketch of the set up adapted to measure Ksat (Fig 3.3 a) and a picture of the actual set up (fig 3.3 b). A continuous flow set up designed by a system of communicating vessels with a main supplier for supplying solution into a reservoir which distributes the solution to the different tubes containing filter materials.

3.1.4 Link between physical size distribution, bulk density and hydraulic conductivity of filter materials

The obtained Dx values and bulk densities were subjected to normality test in SPSS software. Having satisfied the normality assumption, a step wise forward and backward regression analysis were used to select predictors of Ksat. However, stepwise forward regression was preferred in order to select a simple model which includes only the most important variables.

3.2 P removal efficiency and durability of the filter materials

3.2.1 P removal (sorption) efficiency

In order to test how efficient P is removed by the filters and how P removal changes over time when filters are used continuously at maximum rate, we designed a continuous P solution flow system in the laboratory. The continuous flow set up was designed by a system of communicating vessels as described in Ksat determination above (fig 3.3 (a) & (b)). In the same system used for Ksat determination, a 0.5 mg $P.L^{-1}$ in 0.01 M $CaCl_2$ solution was supplied continuously to maintain constant flow. We used 0.5 mg $P.L^{-1}$ P solution in order to mimic the concentration of P in field drain water. P solution was prepared in 0.01 M $CaCl_2$ to account for dissolved ions in field drain water. Samples of filtrate passing through the filters were collected right from the start of the flow and every 10 litres of filtrate. Standard P solutions of 0, 0.04, 0.1, 0.2, 0.4, 0.6 and 0.8 mg $P.L^{-1}$ were also prepared. P in filtrate samples and standards were determined using the method of Murphy and Riley (1963). The colour intensity of the standards and the samples were measured with Cary 50 UV-visible spectrophotometer at 880 nm wavelength.

P concentration in filtrate was used to calculate P removal efficiency of filter material until the environmental limit breakthrough point of 0.1 mg $P.L^{-1}$.

However, concentration of P in filtrate for some filters did not reach the 0.1 mg $P.L^{-1}$ environment limit even after processing up to 870 L of P solution. Therefore we had to predict evolution of P sorption efficiency for larger volumes by fitting a logistic regression in R software to generate P sorption curve for the filters. From the sorption curve, P sorption efficiency of each filter was calculated from the start of the experiment until the 0.1 mg $P.L^{-1}$ environment breakthrough point.

The fitted logistic regression equation is: $Y = 0.5 * [EXP (a + b * x)] / [1 + EXP (a + b * x)]$

Where Y is the residual P concentration in filtrate
a and b are coefficients that best describes changes in Y in relation to x
x is the volume of P solution filtered

3.2.2 Durability of the filter material (cumulative amount of P sorbed until 0.1 mg $P.L^{-1}$ is in the filtrate)

Sorption capacity at breakthrough point (when 0.1 mg $P.L^{-1}$ is in filtrate) was estimated from the sorption curve fitted in 3.2.1 above. From the fitted sorption curve, cumulative amount of P sorbed was calculated from the start of the experiment until the environment limit point.

3.2.3 Checking for Stability of Ksat

Ksat of the filter material was continuously followed up after every 10 L of filtrate. At the end of experiments, the filter materials were removed from the plastic tube and oven dried for 24 hours. The materials were sieved for the second time to determine their particle size distributions. This was done to check whether there were changes in particle sizes and whether it has an effect on Ksat.

3.3.1 Determining cumulative maximum Phosphorus sorption capacity until saturation

This study was to determine maximum sorption capacity of filter materials at saturation point. This allows for comparison with sorption capacity realised when the filters are functioning at maximum rate. In previous study, Andriamanantena, (2014) noted that sorption is positively related with contact time.

In this experiment we used filter materials consisting of 100%, 90/10% and 80/20% iron coated sand/acid pre-treated glauconite on weight basis. For each filter material, two treatments consisting of 0.4 mg $P.L^{-1}$ 0.5 mg $P.L^{-1}$ solution were used and replicated twice. We used 0.5 and 0.4 mg $P.L^{-1}$ solution because they are within the range of P concentrations in drainage water from agricultural fields.

In this experiment, 5 g of filter materials were filled in a porous bag (figure 3.4 (a)) and immersed in 50 ml of the 0.5 and 0.4 mg $P.L^{-1}$ solution (figure 3.4 (b)). The set up was shaken at 100 rotations per minute for 24 hours. The 24 hours shaking period was to give sufficient contact time for P sorption reaction. Remaining P concentration in the solution was determined using the method of Murphy and Riley (1962) and analysed with a Cary 50 UV-visible spectrophotometer at 880nm wavelength. The experiment was repeated by adding fresh P solutions for subsequent analysis until P saturation point is attained.

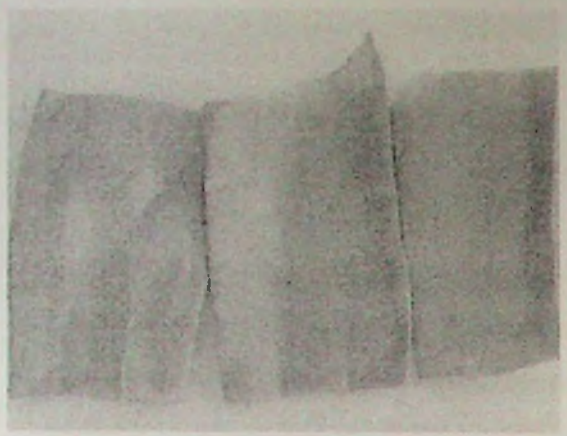


Fig 3.4 (a)

Fig 3.4 (b)

Figure 3.6: Porous bag designed to contain 5g of filter materials (fig 3.6 (a)) and Filtering of 50ml of 0.5 mgP.l.$^{-1}$ *solution after 24 hours of shaking to determine P (fig 3.2 (b))*

3.3.2 Theoretical approach for P removal (desorption)

As no saturation point has been reached yet by any filter material, desorption test that was supposed to be done couldn't be performed. Therefore we proposed a theoretical approach for P removal. In this proposal, we intend to desorb the adsorbed P from iron coated sand using desorption solution of 0.1M NaCl and 0.1M NaOH at pH 4 and 7. After the saturation point is reached from the previous maximum sorption experiment, the 5g of filter material will be immersed in 50ml of 0.1M NaOH and 0.1M NaCl. P concentration will be equilibrated by preparing NaOH and NaCl in the same amount of P solution as the one that saturated the filters. The pH is adjusted by adding required amount of HCl or NaoH to keep it at pH 4 and 7. All the experiments will be done in duplicate. The set up will be shaken for 24hours at 100 rotations per minute. P concentration in the solution will be measured using the method of Murphy and Riley (1962) and analysed with a Cary 50 UV-visible spectrophotometer at 880nm wavelength. Desorbed P will be determined as the difference in P concentration in the resultant solution from an initial P in the extraction solution. The experiment is repeated by refreshing extraction solutions (0.1M NaCl and 0.1M NaOH) and correcting pH to 4 and 7. This will be done continuously until no more desorption is feasible.

3.4 Field trial

Our intention was to assess amounts P can be removed by the filter when P concentration is 3-4 times above the environment limit and also test whether P concentrations can still be reduced when it's slightly above or below the 0.1mg $P.l^{-1}$ environment limit.

Field trials were conducted at three sites, Anzegem, Shriek A and Shriek B. Anzegem is a municipality located in the Belgian province of West Flanders at 50°50' North, 03°28' East and Schriek is situated in Antwerpen, Vlaanderen at 51°2' North, 4°41' East.

At installation, P concentration was 0.31 $mg.l^{-1}$ at Anzegem, 0.09 $mg.l^{-1}$ at Schriek A and 0.12 mg $P.l^{-1}$ at Schriek.

All the pilot field trials were conducted concurrently at the time of running the laboratory experiments. They were therefore not based on laboratory results but only intended for preliminary comparison of the performance of the filters in the field.

Three different filter materials were installed. Filter Grobbendonk 100% was used at site Anzegem, Grobbendonk 75/25% at Schriek A and Balen 100% at Schriek B. Two designs of the filters container were used. Balen 100% and Grobbendonk 100% containers were designed such that the head difference between the water surface in the container and the outlet of filtrate is small, only about 5 cm (figure 3.5). This is important to reduce the Ksat so that more P is sorbed. However, with this design, there was no outflow for filter Grobbendonk 75/25%. Therefore we adapted the design such that the head difference is increased to about 25 cm.

To form reactive barrier, thirty kilograms of each filter material mixture on weight basis were filled in a plastic container of diameter 0.53 m (0.2206 m^2) through a height of 0.2 m. The set up was installed in the field to allow drainage water from agricultural field to flow through the filters (figure 3.5). Samples were taken after every week at the inlet and outlet of the filters to analyse P concentrations. P concentrations were determined by the method of Murphy and Riley (1962) using Cary 50 UV-visible spectrophotometer at 880nm wavelength.

Figure 3.4: Field installed filter at site Anzagem to allow drainage water from the field to flow through the filter before being released into the drainage channels.

Chapter 4: Results and discussion

4.1 Link between physical size distribution, bulk density and hydraulic conductivity of the filter materials

4.1.1 Particle size distribution of the filters

Analysis of particle size distribution as shown in figure 4.1 revealed that, iron coated sand from Balen has coarser particles (diameter between 0 - 5.0 mm) and is less homogenous than Grobbendonk materials. The Balen material has 98.4% of the particles within a diameter of 4mm and only 1.6% above 4 mm. On the other hand, Grobbendonk have particles ranging between 0-3.00 mm of which 99.4% of the particles have a diameter below 2 mm and only 0.6% above 2 mm.

We also noted that pure (100%) filter materials have on average coarser particles compared to filter materials mixed with glauconite. The particle size distribution is found to shift to the finer diameter sizes with increasing percentage of glauconite in the mixture since glauconite has finer particles between 0.05-0.5 mm.

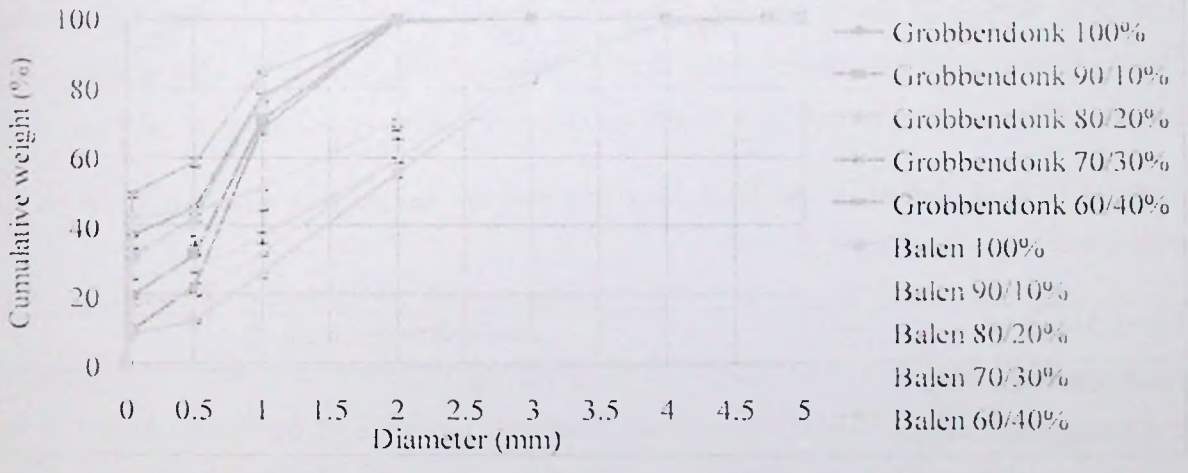


Figure 4.1: Particle size distributions of the filter materials for Grobbendonk & Balen filters

Dx values calculated from the cumulative particle size distribution curve (Appendix 1) shows that Balen 100% has the largest D50 value (the median particle size) of 1.82 mm and Grobbendonk 60/40% has the smallest size (0.08mm). It is further revealed that Dx values decrease with increase in glauconite in the mixture. (Dx is the mesh size diameter of the sieve which allows x% of the particles to pass). (see appendix 1 for the calculated Dx values from D10 to D90).

4.1.2 Bulk density of the filter materials

Bulk density of the filters shown in table 4.1 was found to be between 1138 kg.m^{-3} (Grobbendonk 100%) and 1534 kg.m^{-3} (Balen 60/40%). Bulk density of Balen filters are between 79 to114 kg.m^{-3} higher than their corresponding mixture of Grobbendonk filter. This is because Balen materials are coarser and less homogenous (are poorly sorted).

The sorting coefficient of Balen 100% calculated using equation by Stuart and Elliot (2009) as (D84-D16)/2 is 1.22 which is higher than Grobbendonk 100% of 0.62 (value below 0.5 implies better sorting and above 1 implies poor sorting)

While sorting coefficient calculated from Trask 1932 equation (SQRT (D75/225) gives a value of 1.70 for Balen and 1.52 for Grobbendonk. Using this equation both values are below 2.5 implying well sorted particles. However, Grobbendonk is still showing a lower value meaning it is better sorted than Balen 100% material.

The poor sorting of Balen material allows for higher packing density than Grobbendonk filters. Consequently, a higher bulk density is associated with decreased porosity (high packing density) and shifts of pore shape and size distributions (Richard et al., 2001).

Table 4.1: Bulk density of the filter materials and the weight that filled up to 20 cm of a plastic tube

Filter Material	Bulk density (kg.m^{-3})
Grobbendonk 100%	1138
Grobbendonk 90/10%	1176
Grobbendonk 80/20%	1294
Grobbendonk 70/30%	1371
Grobbendonk 60/40%	1432
Balen 100%	1235
Balen 90/10%	1260
Balen 80/20%	1372
Balen 70/30%	1485
Balen 60/40%	1534

4.1.3 Initial Ksat of filter materials

Initial Ksat of the filter materials is shown in figure 4.2, and ranges from 0.000023 to 0.0063 $m.s^{-1}$. Initial Ksat of Balen 100% is about twice higher than that of their corresponding Grobbendonk 100%. The initial Ksat of Balen is in most cases higher than of corresponding Grobbendonk mixture. This is due to Balen materials being coarser; hence have more macro-pores for water conduction than the finer Grobbendonk materials.

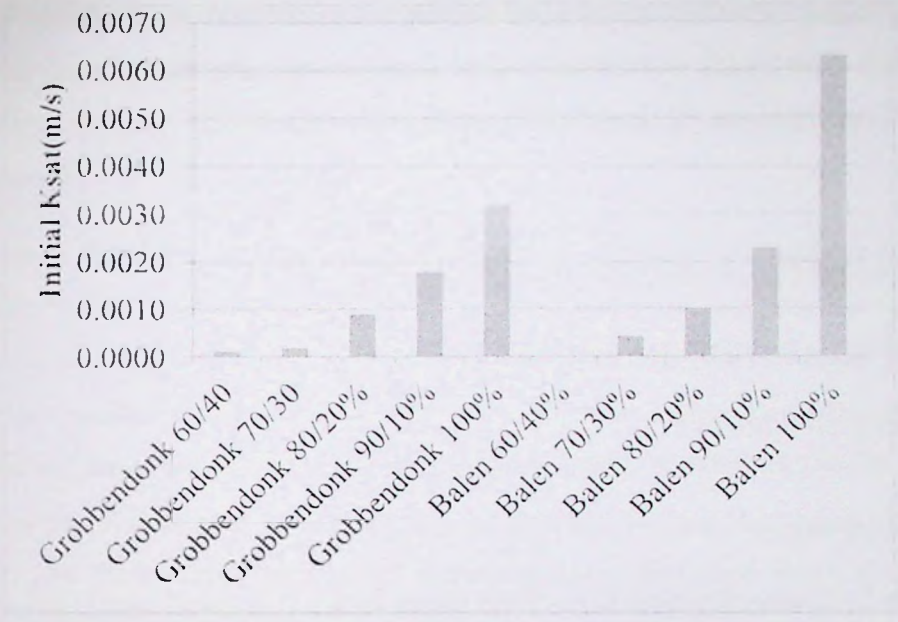


Figure 4.2 Initial Ksat (m/s) of the filter materials

In addition, the result also shows that initial Ksat increases with increase in particle sizes. Ksat is mainly influenced by smaller Dx values; finer materials have lower initial Ksat than coarser materials. This finding agrees with Canga et al. (2013), study which found that Ksat of the filters increased positively with increasing mean particle diameter (D50).

However, the only exception is the Ksat of Balen 60/40% (Ksat 0.000023 m/s) and Grobbendonk 60/40% (Ksat 0.0001 $m.s^{-1}$). Where the finer material of Grobbendonk 60/40% (D50 value of 0.08 mm) has a higher Ksat, four times that of the coarser material of Balen 60/40% (D50 value of 1.14 mm (Appendix 1). In this case, the effect of packing density on Ksat appears to be dominant than effect of particle size. The lower Ksat of Balen 60/40% could possibly be explained by its higher bulk density of 102 $kg.m^{-3}$ more than Grobbendonk

60/40%. Several authors indeed associated increased bulk density with decreased porosity and shifts of pore shape and size distributions (Richard et al., 2001).

4.1.4 Link between physical size distribution, bulk density and Ksat of the filters

A forward step wise multiple regression analysis in SPPS software used to link initial Ksat, bulk density and particle size distribution (Dx) revealed that, the best predictors of Ksat are D20, D10 and bulk density (Appendix 4.1). This suggests that the initial Ksat is greatly controlled by the finest particles (D10 and D20) and bulk density.

The equation of the multivariate regression model fitted is:

$$Y = 0.004 + 0.004*D20 + 0.010*D10 - 3.013*EXP\text{-}06*BD$$

Where Y = the predicted Ksat ($m.s^{-1}$)
D20 and D10 is the sieve diameter (mm) when 20 % and 10% of the particles are finer respectively
BD is the bulk density ($kg.m^{-3}$)

The fitted equation accurately predicts Ksat of the filters with a R squared value of 0.953 (see Appendix 2 for the SPSS multiple regression output). Previous study by Canga et al (2013) predicted Ksat using the equation log Ksat = 4.66 +0.63* log (D20) + 0.94*log (D50). This predictive model also indicates that Ksat depends on narrow grain size (D20) and medium grain-size (D50). However our model included both D10 and D20 further emphasizing the importance of small-sized grain in determining Ksat. The difference in the predictive equation is probably due to differences in particle sizes and bulk densities. Canga et al. (2013) particle sizes ranges from 0.5 -15 mm compared to ours which is between 0-5 mm and the bulk density was between 230 - 1420 $kg.m^{-3}$ compared to ours, which is between 1138-1534 $kg.m^{-3}$. Possibly since we had a narrow range of particle sizes and bulk density as well, we are probably in a linear range of effect of particle size distribution and bulk density on Ksat.

4.2 P sorption efficiency and durabilty of the filters

4.2.1 P sorption efficiency

In our laboratory experiments, the filters processed different volumes of P solution. (920 L, 740 L and 580 L for Balen 100%, 90/10% and 80/20% respectively and 870 L, 680 L, 400 L for Grobbendonk 100%, 90/10% and 80/20% respectively) (fig 4.4 (a)-(f)). This was dependent on their own hydraulic conductivity. Filter materials of 30-40% glauconite mixtures were not used in the continous flow experiement because of their very low hydraulic conductivities. Within the time of data collection for this thesis, they could not process a reasonable volume of solution to generate sufficient P sorption data for any realistic comparison.

We noticed that there are fluctuations in P sorptions through the experiments possibly due to changes in Ksat and intermitten break periods when the supposedly "continously" flow system is turned off. The break period or lower Ksat increases contact time for P sorption reactions. Similar studies have shown that P sorption increases positively with increase in contact time (Andriamanantena, 2014, Lyngsie, 2013). Nonetheless, there is a general trend of increasing P in filtrate with increasing volumes of filtered P solution. As more P solution volumes are processed, the worked zone increases and unworked zone reduces, hence sorption efficiency is reduced.

Generally, as demonstrated in(fig 4.4 (a)-(f)): P removal was high initially with more or less no P in the filtrate This is the region when the filters were still effective due to availability of free P binding surfaces. Grobbendonk filters maintained higher P removal efficiency, P concentrations in filtrate were below 0.1 mg $P.L^{-1}$ throughout the experiment. However for Balen filters P concentration in filtrate exceeded 0.1 mg $P.L^{-1}$. This point was reached after 350L, 200L, and 90L for Balen 100%, 90/10% and 80/20% respectively.

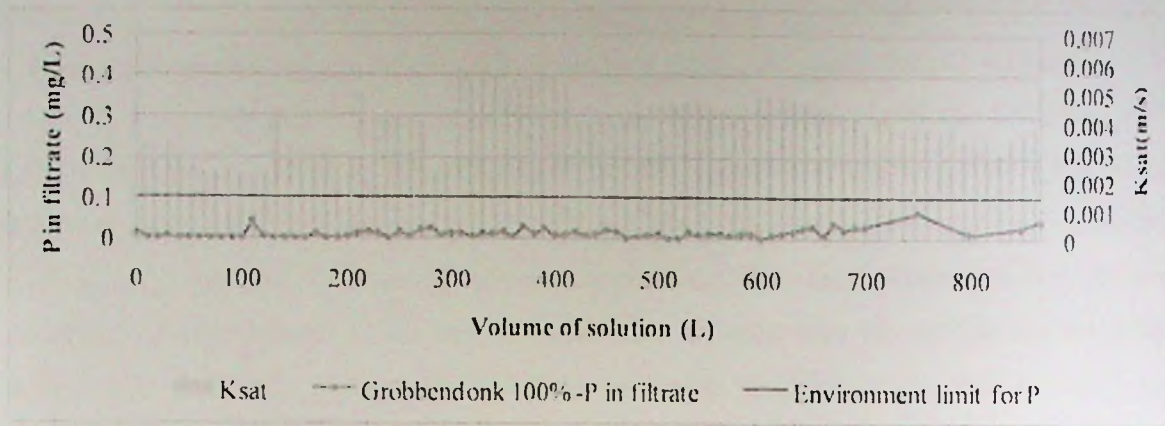


Fig.4.4(a)

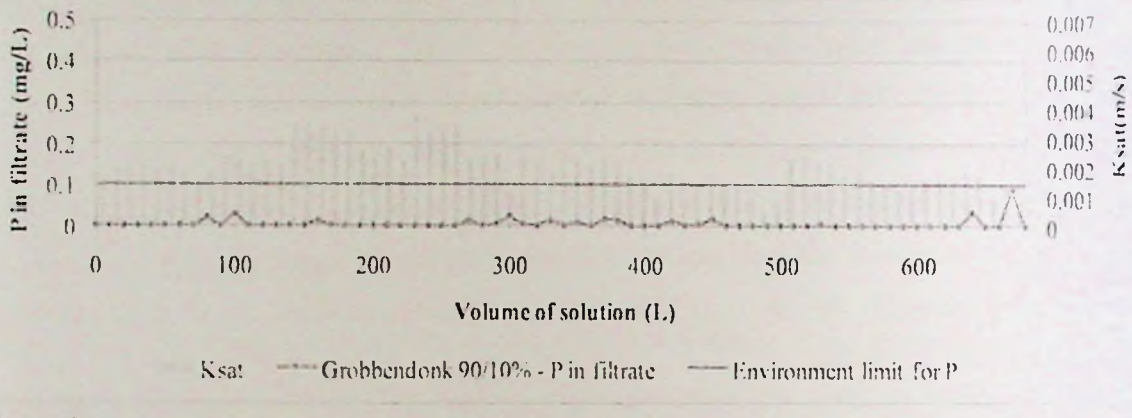


Fig.4.4(b)

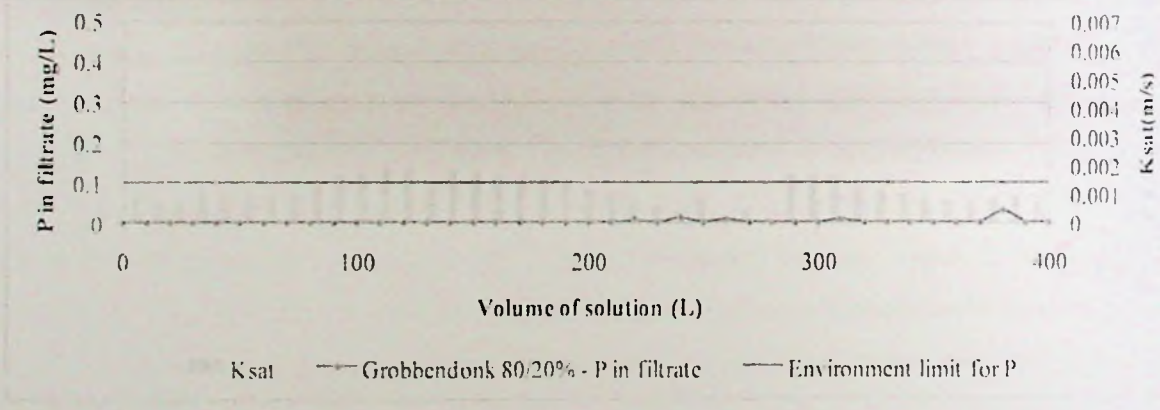


Fig.4.4(c)

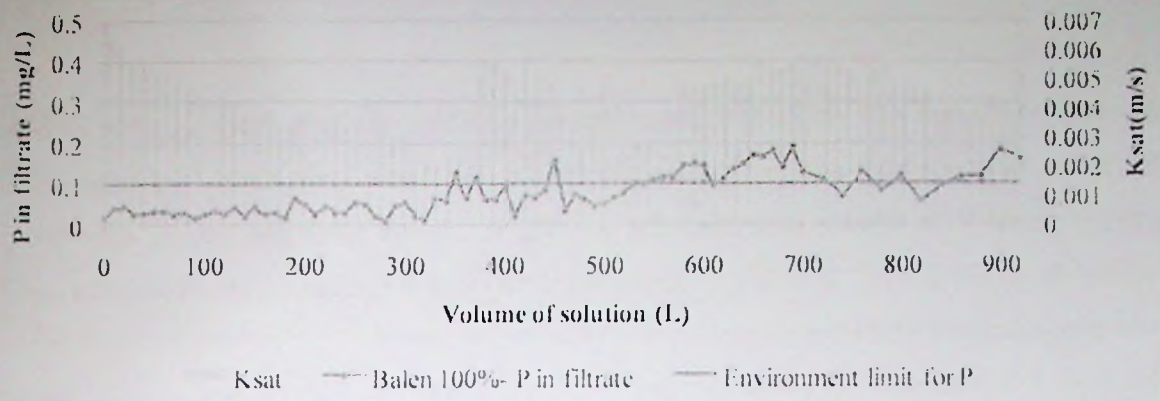


Fig 4.4(d)

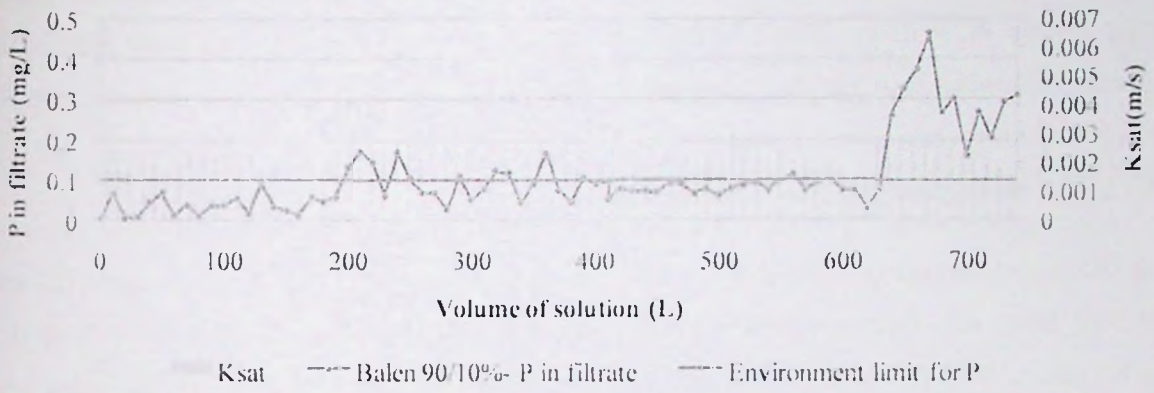


Fig 4.4(e)

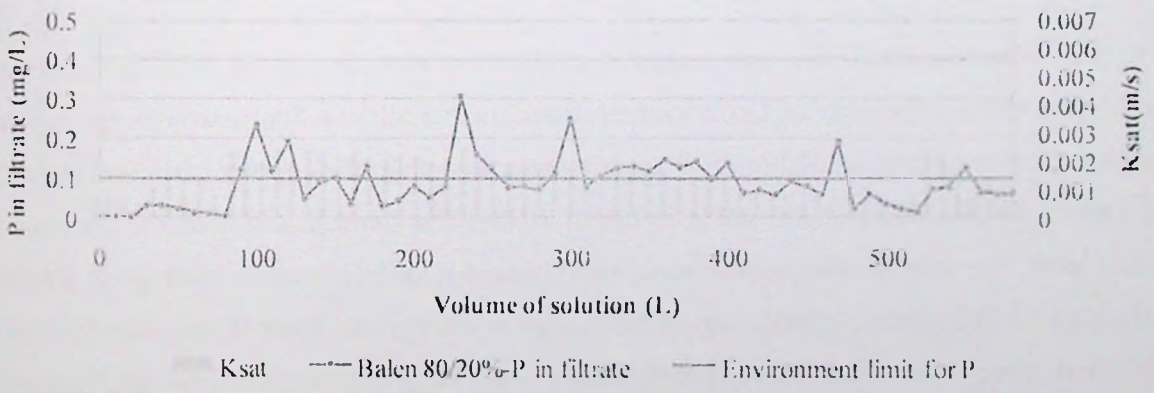


Fig 4.4(f)

Figure 4.4 (a)-(f): P concentration in filtrate in relation to Ksat and volume of the P solution filtered for Grobbendonk filter materials (fig 4.4 a, b & c) and Balen filter materials (fig 4.4 d, e & f). the residuals P were compared against the environment limit.

However, we noted that residual P concentration of Balen 80/20% filter material is heavily fluctuating between high and low values (figure 4.4 (f)). More surprisingly for Balen 80/20% filter, residual P in filtrate exceeded the 0.1 mg $P.L^{-1}$ just after processing only 90 L of treating the 0.5 mg $P.L^{-1}$ P solution. There after residual P concentration drops low again at even high volume of 500 L.

The highly inconsistent P concentration in filtrate could be due to preferential flow that evades filtration through the whole filter material volume. Such preferential flow has been blamed for the escape of pollutants well below the buffering capacity of the soil into ground water (Stone & Wilson, 2006; Lindahl & Bockstaller, 2012). This can arise due to non homogenous mixing of the fine glauconite materials with the coarser iron coated sand. Non uniform mixing may allow formation of layered structure of finer and coarser materials which permits preferential flow (Zhang Jian-feng et al. 2003).

The fitted sorption curve displayed in figure 4.5 and summarised in table 4.2 shows the most efficient filter was Grobbendonk 90/10% with sorption efficiency of 98.84%, followed by Grobbendonk 80/20% with 96.58% and Grobbendonk 100% with 94.04%. On the other hand, Balen 90/10% had a sorption efficiency of 89.92%, Balen 100% had 87.91% and Balen 80/20% with 81.88% (figure 4.6).

Generally, sorption efficiency was negatively related to particle size of the filter materials. The high sorption efficiency of Grobbendonk filters is due to their finer particles and hence a higher total surface area available for P sorption reactions than the coarser particles (Ballanite and Tanner, 2010; Vohla et al., 2011; Lyngsie, 2013). The particle sizess define the specific surface area, the smaller the particle size, the larger the surface area to undergo P sorption (Nair et al., 1984; Mann, 1996). In addition, due to their finer particle size, Grobbendonk filters had lower Ksat than Balen filters. This allows for more contact time for P sorption reactions hence improving their sorption efficiency compared to coarser Balen filters.

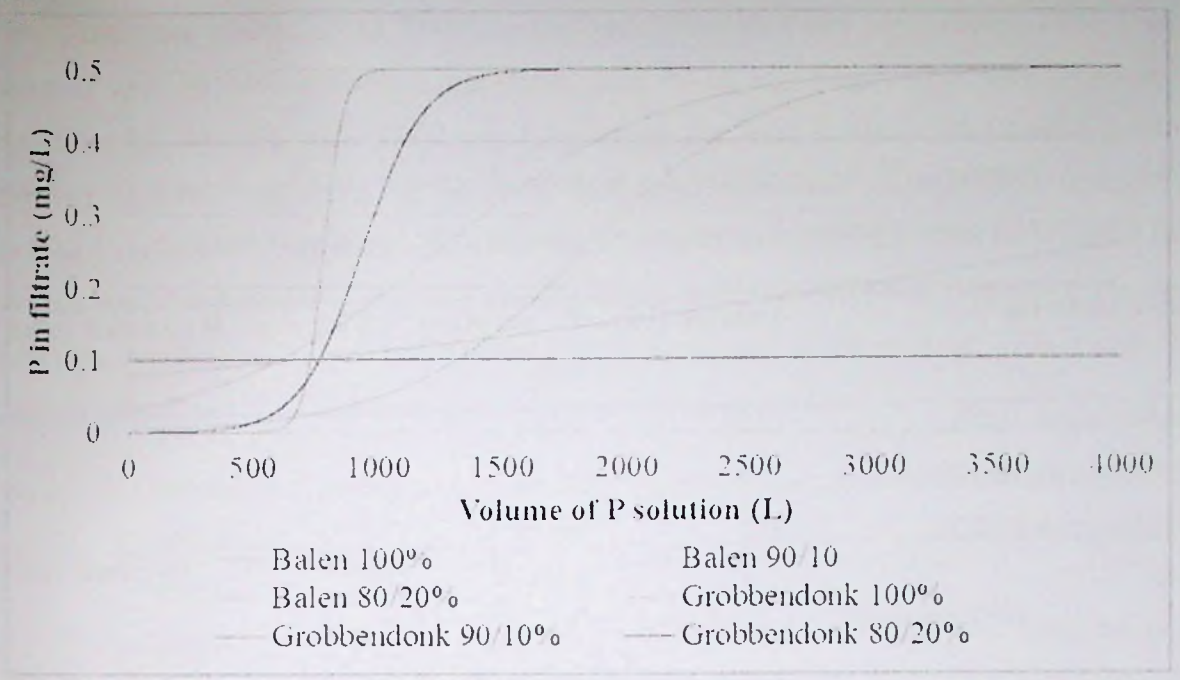


Figure 4.5: P sorption curves of the filters, a more durable and efficient filter is the one that processes more volume and keeps P concentration below 0.1 mg P.L^{-1} environment limit.

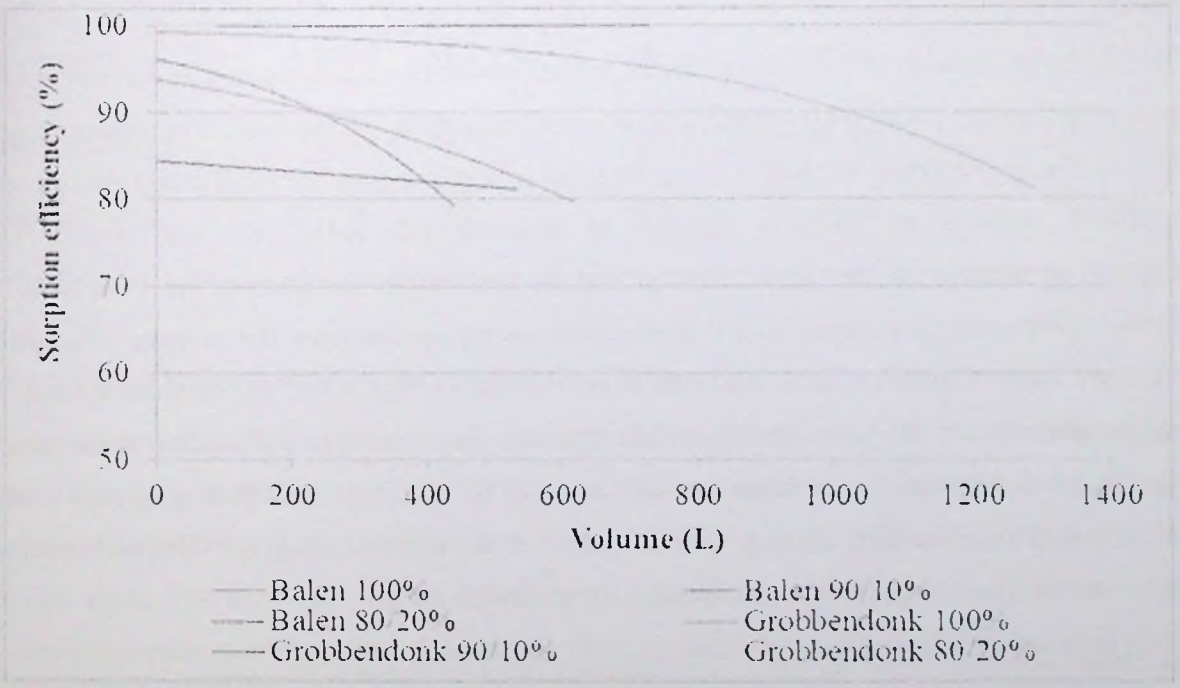


Figure 4.6: Evolution of P sorption efficiency with volume of 0.5 mg P.L^{-1} solution filtered

Table 4.2: Summary of the predicted break through points showing volume of solution processed to this point, average P sorption efficiency and the model correlation

Filter material	Volume (L)	P sorption efficiency (%)	R squared value
Grobbendonk 100%	1292	94.04	0.521
Grobbendonk 90/10%	727	98.84	0.190
Grobbendonk 80/20%	753	96.58	0.301
Balen 100%	615	87.91	0.789
Balen 80/20%	532	81.86	0.650
Balen 90/10%	438	89.92	0.105

4.2.2 Durability of filter materials (cumulative P sorbed until 0.1 mg $P.L^{-1}$ breakthrough point)

The maximum volume of P solution filtered when the filters are functioning at maximum rate until breakthrough point gives information about the durability of the filter. The breakthrough point is that point when 0.1 mg $P.L^{-1}$ is realised in the sorption curve. By determining the maximum volume of solution filtered to breakthrough point, we can predict the longevity/durability of the filters. This is can be realised by converting the volume of P solution processed into amounts of P sorbed and taking into account the average efficiency. Since we used a solution of a uniform P concentration, the more the volume treated to breakthrough point, the more the P sorbed and the more durable is the filter. Since some filters had not yet reached the breaktheough point of 0.1 mg $P.L^{-1}$ in filtrate (figure 4.5 a-f), we estimated this point by fitting sorption curve in R software using our observed data to predict sorptions at larger volumes (figure 4.5 and table 4.3).

The fitted sorption curve for each filter demonstrated in figure 4.5 reavealed variations in maximum volumes of P solution processed to break through points and hence the amount of P sorbed. The volume of P solution filtered to breakthrough point ranges from 438 L to 1292 L, this translates into amount of sorbed P between 613 to 942.2 mg $P.kg^{-1}$ of filter material depending on the average P sorption efficiency of a filter. Therefore, more durable filters are those that filtered the largest volumes before breakthrough point with high P removal percentage hence translating into higher amount of P sorbed.

We found that Grobbendonk 100% is the best filter, its 0.645 kg filtered 1292 L of P solution with 94.04% efficeincy translating into 942.2 mg $P.kg^{-1}$. This was followed by Grobbendonk 90/10% with 538.9 mg $P.kg^{-1}$) and the least is Balen 90/10 with sorption capacity of 275.7 mg $P.kg^{-1}$ table (4.3). Similarly, maximum sorption is a function of availabel surface for P sorption. The more finer Grobbendonk materials thus have higher total surface area for P sorption than the coarser Balen materials. Sorption capacity is found to generally decrease with increase in percentage of glauconite in the mixture. This reveals that the iron coated sand has higher sorption capacity than glauconite.

Table 4.3: Cumulative P sorption until breakthrough point to determine durability of filters

Filter material	Weight (kg)	Volume (L)	P sorbed ($mg.kg^{-1}$)	Sorption efficiency (%)	Model R^2
Grobbendonk 100%	0.6450	1292	942.2	94.04	0.521
Grobbendonk 90/10%	0.6667	727	538.9	98.84	0.190
Grobbendonk 80/20%	0.7334	753	495.8	96.58	0.301
Balen 100%	0.7000	615	386.2	87.91	0.789
Balen 80/20%	0.7143	532	279.9	81.86	0.523
Balen 90/10%	0.7778	438	275.7	89.92	0.105

4.2.2.2 Effect Ksat fluctuation on durability of filters

As demonstrated in figure 4.5 (a-f), Ksat of the filter materials showed continuous up and down fluctuations throughout the continuous flow experiment. Pure Balen 100% and Grobbendonk 100% filters generally have higher Ksat up to twice that of their corresponding 90/10% filter. The Ksat decreases with increase in glauconite percentage in the mixture. This is due to decrease in particle size distribution since glauconite is a fine material between 0-0.5 mm.

Balen filters have higher Ksat than corresponding Grobbendonk filter, for instance Ksat of Balen 100% is twice that of Grobbendonk 100%. This is due to Balen filter being coarser and

hence has more conducting pores. Over all, the Ksat of all our filters ranged between 0.0009 m/s ($7.8x10^3$ cm.day^{-1}) and 0.0063 (54.410^3 cm.day^{-1}).

The Ksat values obtained are within the magnitude of those found as adequate for processing large volumes of water (Canga et al., 2013). However, upper limits of those of Canga et al., 2013), of $38x10^3$ to $2,643\times10^3$ cm.day^{-1}) and Arias, 2001 ($2.2x10^3$ to $112x10^3$) appear to be higher. The differences arise due to higher Dx values for the materials used in these studies compared to ours. For instance, D10 value of Canga et al., 2013) range between 0.5 mm and 11.6 mm. The D50 ranged between 1.1 mm to 16.5 mm compared to our study that has D10 ranging from 0.01 mm to 0.09 mm and D50 ranging from 0.08 mm to 1.82 mm.

The fluctuations in Ksat throughout the experiment could be due to a number of reasons including the effect of entrapped air that forms bubbles in the pores and the narrow conducting tubes. We observed that when the air bubbles are ejected, the flow improves and Ksat increases. In addition, surface sealing by dust sized particles combined with standing water head on top of the material creates some surface compaction which hinders infiltration rates (Moore, 1981).

Another reason could be due to a recurring clogging and clearance of pores. This results from transportation of the finest dusty particles within and out of the column. Analysis of particle size distribution after the experiment demonstrated in figure 4.7 (a) & (b) revealed evidence of particle movement. We found that, such transportation resulted into a decrease of particles (0-0.5mm) at the end of the experiment.

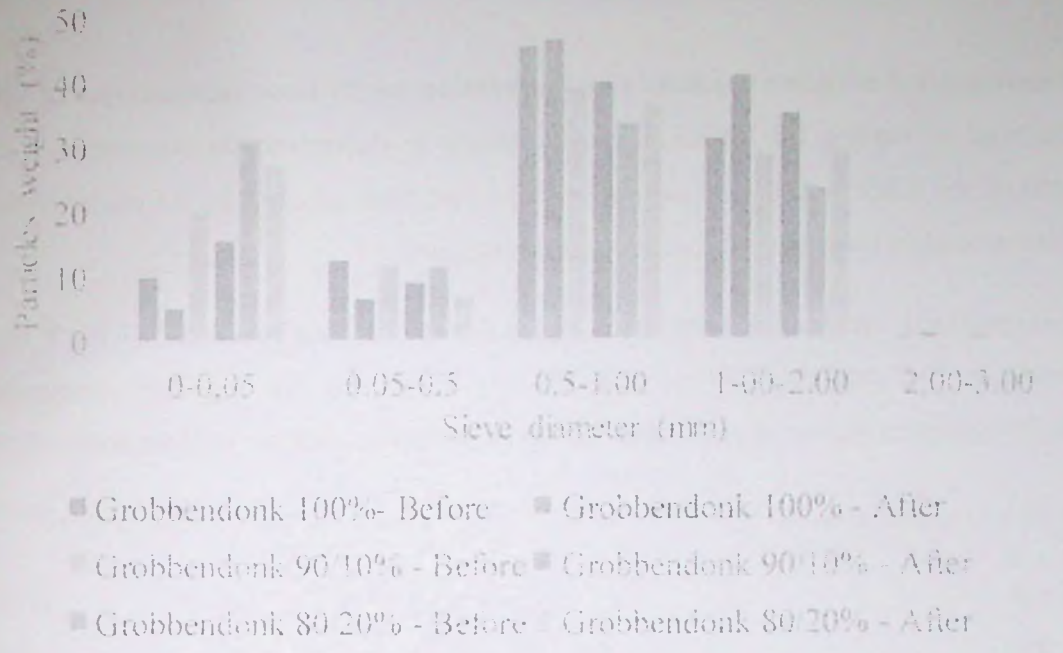


Fig 4.7(a)

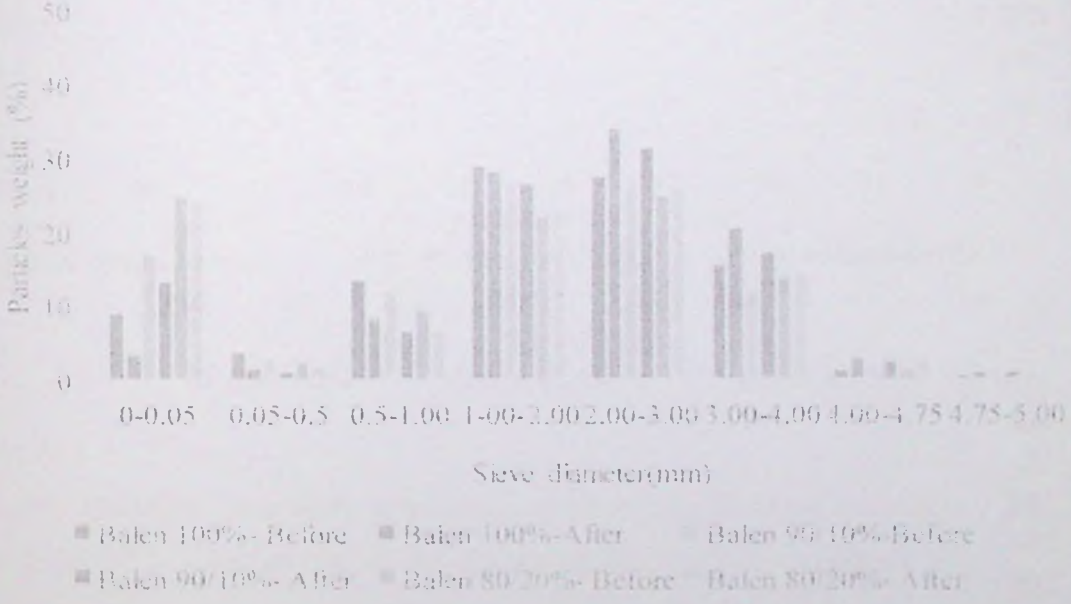


Fig 4.7(b)

Figure 4.8 a & b: Particle size distribution before and after the continuous flow experiment (a for Grobbendond and b for Balen filters)

4.3 Cumulative P sorption capacity until saturation for 24 hour contact time of filters

At the time of writing this thesis, the experiments to determine the maximum P sorption capacity of the filter materials at saturation point had been running for 85 days. However all the filter materials have not yet reached saturation point.

As demonstrated, cumulative sorption in figure 4.9 (a)-(d), has reached 417 mg $P.kg^{-1}$ filter materials for 0.5 mg $P.L^{-1}$ filters and 331 mg $P.kg^{-1}$ for 0.4 mg $P.L^{-1}$ treatment. The cumulative sorption curve of each filter still shows a steady increase in P sorbed with time.

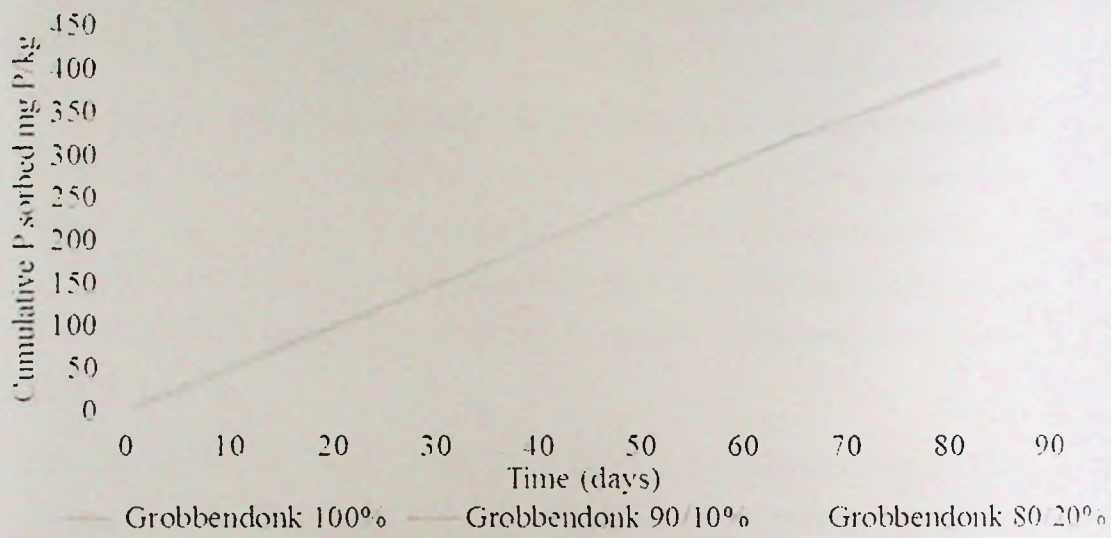


Fig 4.9 (a)

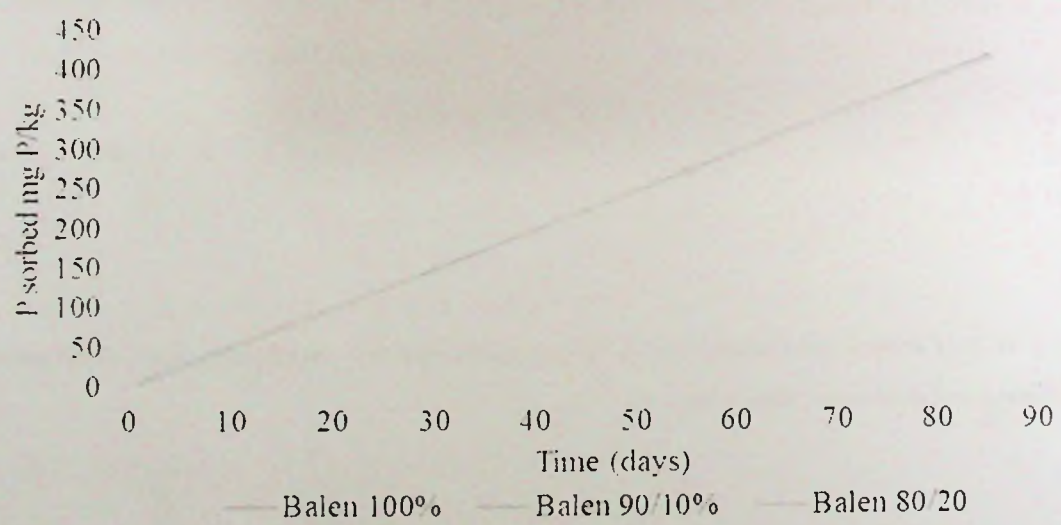


Fig 4.9 (b)

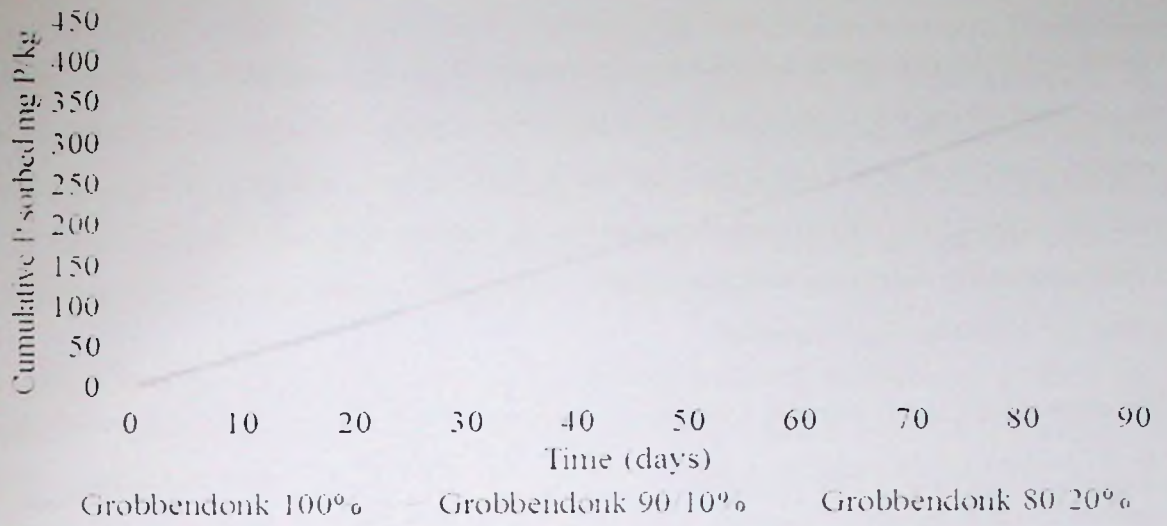


Fig 4.9 (c)

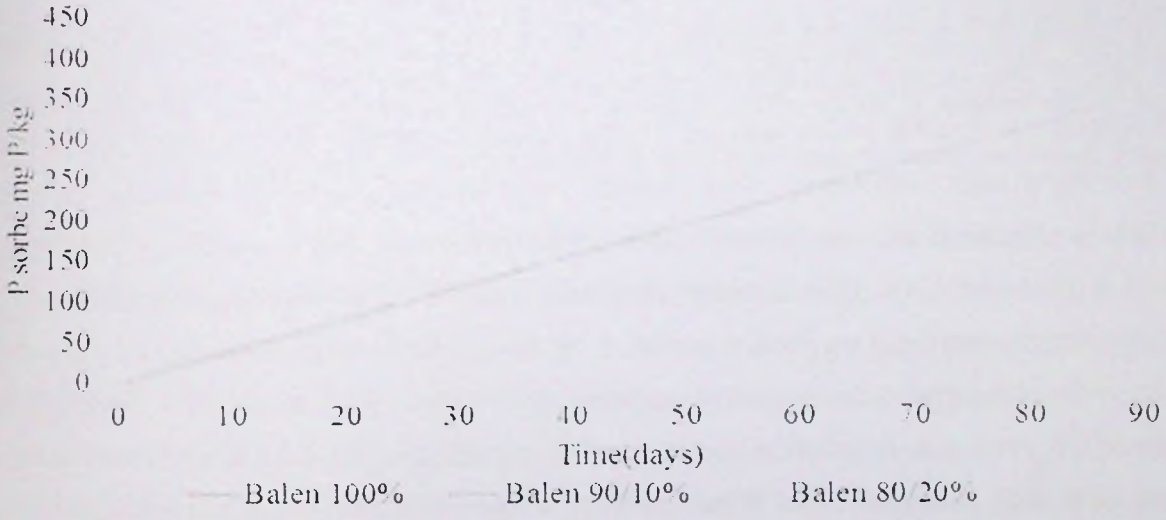


Fig 4.9 (d)

Figure 4.9: Maximum cumulative sorption capacity of Grobbendonk and Balen filters using 0.5 and 0.4 mg P.L^{-1} solution (fig. 4.9 (a) & (b) and fig. 4.9 (c) & (d) respectively).

Though saturation point has not yet been attained, the sorption capacity of all the filters is already higher or within the range of some filters reported in literature. Andriamanantena (2014) reported P sorption between 10 - 215 mg P.kg^{-1} using 2 mg P.L^{-1} concentrations. He found that iron sludge has the highest sorption capacity of 215 mg P.kg^{-1} and acid pre-treated glauconite has a sorption capacity of 60 mg P.kg^{-1}.

Cucarella (2009) documented numerous materials for P removal and their P sorption capacity ranged from 30 mg $P.kg^{-1}$ to $113*10^3$ mg $P.kg^{-1}$. Interestingly, Boujelben et al. (2008) found a sorption capacity of iron coated sand and iron coated brick at 1500 and 1750 mg $P.kg^{-1}$ filter material respectively. Given that Boujelben et al. (2008) study used iron coated sand, we would expect the maximum sorption capacity of our similar iron coated sand material to be within the 1500 mg $P.kg^{-1}$ reported.

Therefore, using the maximum sorption capacity of 1500 mg $P.kg^{-1}$ reported, we compared the proportion of the sorption surface used by our filters at the point of breakthrough in relation to their potential sorption capacity to saturation when sufficient contact time is allowed (table 4.4).

The comparison in table 4.4 revealed that Grobbendonk 100% is most efficient, it realised 62.8% of the estimated potential saturated (maximum) sorption capacity followed by Grobbendonk 90/10% which attained 35.9% and Grobbendonk 80/20% with 33.1%. Balen filters show high inefficiency, they attained only between 18 to 25.7% of the estimated potential saturation sorption capacity. These differences could also be attributed to the higher total surface area of the finer Grobbendonk filters as well as its lower Ksat which allows for more contact time for P sorption than Balen. However, these comparisons have assumed the same potential sorption to saturation point for all the filters at 1500 $mg.kg^{-1}$. Although this may not be the case, therefore a precise cumulative sorption capacity to saturation point of each filter will be known after the experiment is completed and better comparisons will be performed.

Table 4.4: P sorption capacity at breakthrough point when the filters are functioning at maximum rate in comparison to the assumed saturation sorption capacity of 1500 mg $P.kg^{-1}$

Filter material	Saturated sorption capacity ($mg.kg^{-1}$)	Breakthrough sorption capacity ($mg.kg^{-1}$)	Sorption capacity realised (%)
Grobbendonk 100%	1500	942.2	62.8
Grobbendonk 90/10%	1500	538.9	35.9
Grobbendonk 80/20%	1500	495.8	33.1
Balen 100%	1500	386.2	25.7
Balen 80/20%	1500	279.9	18.7
Balen 90/10%	1500	275.7	18.4

4.4 Pilot field trial of the filters

The pilot field trial included three filters: Grobbendonk 100% at site Anzegem, Grobbendonk 75/25% at site Schriek A and Balen 100% at site Schriek B. At filed Anzegem, filter Grobbendonk 100% was installed on 16/02/2016. The trial was run throughout the water outflow season for a period of about 70 days. As demonstrated in figure 4.2.1 and table 4.6, the volume of water flowing from the outlet was 6048 L per day in the first two weeks. The initial inlet P concentration was 0.31 $mg.L^{-1}$.

The filter was able to reduce this concentration to 0.05 achieving an efficiency of 83%. The P removal efficiency increased to 91% when the outflow reduced to 2274 L per day. The highest efficiency of 95% was attained when the outflow was at 480 L per day. It's therefore clear that sorption efficiency is negatively related with outflow volumes. The average outflow throughout the trial was 2596 L per day and average sorption efficiency was at 74%.

Cumulative sorption capacity was estimated to be 985 mg $P.kg^{-1}$ (table 4.6.). The high sorption capacity and efficiency of the Grobbendonk 100% filter is explained by high sorption capacity of iron, high total surface area due to its finer particle sizes and lower Ksat.

In comparison with our laboratory experiment, the sorption efficiency of Grobbendonk 100% in laboratory was experiment (94.04%) is higher than in the field trial (74%). This could possibly be attributed to the lower average P concentration in the field (0.22 $mg.L^{-1}$) compared to 0.5 $mg.L^{-1}$ in the laboratory experiment. P sorption is known to behave differently depending on P concentration of the solution (Andriamanantena 2014; Ballantine and Turner 2010; Penn et al., 2007). Another possible reason is the larger out flow volume in the field trial.

There was no outflow from the drain from 26/04/2016 until first week of July when he had a sample on 07/07/2016. At this point P concentration exceeded 0.1 mg $P.L^{-1}$. Therefore, to estimate P sorption capacity, we used average cumulative P sorption from 16/02/2016 until 26/06/2016 when the flow was continuous. Cumulative P sorption for Grobbendonk 100% filter was estimated at 985 mg $P.kg^{-1}$ on 26/04/2016; this is fairly within the predicted capacity in the laboratory (942 mg $P.kg^{-1}$). However, it's important to note that we only had weekly data for the field experiments, therefore we cannot account for any daily changes in outflow volumes, P concentrations or P sorption efficiency. This makes the comparison with the laboratory results only a rough estimation.

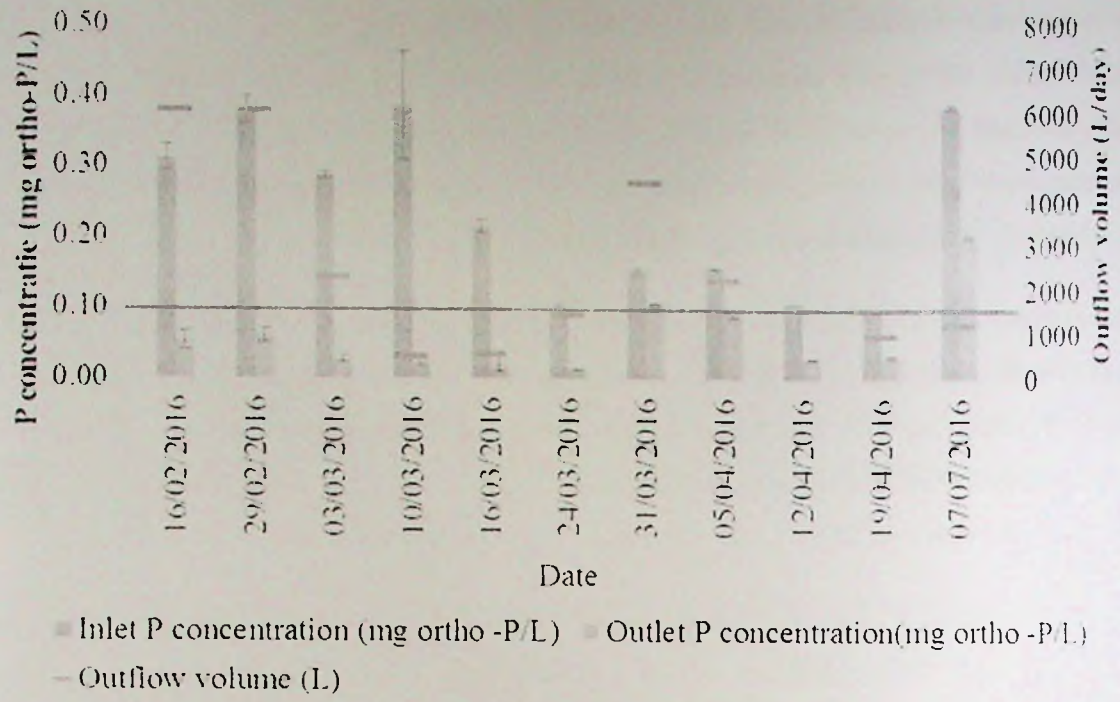


Fig 4.2.1: P concentration in inlet and outlet of the filter and the volume of water flowing through the outlet for field trial filters Grobbendonk 100% at Anzegem

For filter Grobbendonk 75/25% that was installed at Schriek A field, the trial run for about 64 days. As demonstrated in figure 4.2.2 (a), and table 4.6, the average outflow rate was at 2333 L per day, average P concentration in the inlet was 0.122 $mg.L^{-1}$ and 0.056 $mg.L^{-1}$ in the outlet with average P sorption efficiency of 51%. However, this mixture was not used in our laboratory experiment because of lower Ksat of mixtures having more than 20% glauconite

Filter Balen 100% was installed at Schriek B on 16/02/2016 and also run for 70 days. As shown in figure 4.2.2 (b) and table 4.5, the average water outflow was 5939 L per day, average P concentration in inlet was 0.09 $mg.L^{-1}$ and in the outlet it was 0.05 $mg.L^{-1}$. The average sorption efficiency was 41%. It's observed that the concentration of P in filtrate first exceeded 0.1 mg $P.L^{-1}$ on 28/03/2016 after about 41 days of running. At this point the estimated cumulative sorption realised was 351 mg $P.kg^{-1}$. For the same filter, our laboratory continuous flow experiment predicted a sorption capacity of 387 mg $P.kg^{-1}$. The predicted sorption capacity is quite close to the realised capacity in the field trial. Nonetheless, we would not expect to get a very precise value because this was an estimate since field samples were collected weekly and we cannot tell the exact time breakthrough occurred, the daily changes in outflow volumes, inlet and outlet P concentrations, or P sorption efficiency.

Fig *4.2.2 (a)*

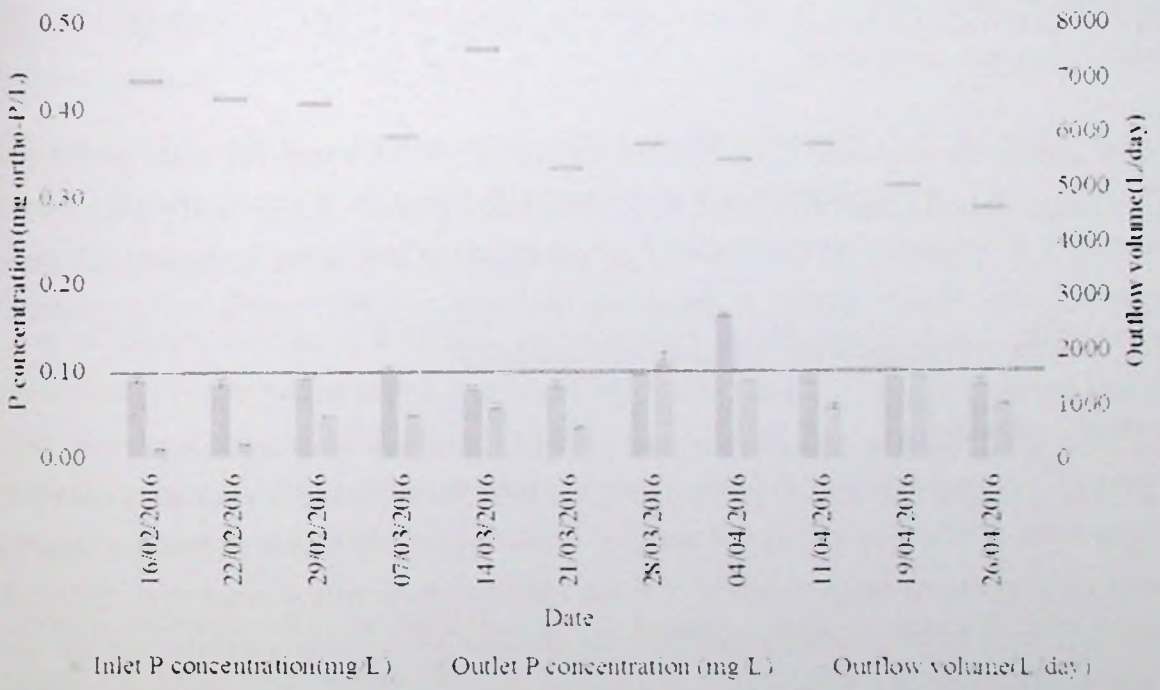


Fig 4.2.2 (b)

Fig 4.2.1:P concentration in inlet and outlet of the filter and the volume of water flowing through the outlet for field trial filters Grobbendonk 75/25% at Schriek A (fig 42.1 (a)) and Balen 100% at Schriek B (fig 4.2.1 (b))

Table 4.5: A summary of average outflow volume, P sorption efficiency and cumulative p sorption capacity throughout the field trial for each filter

Filter	Average outflow volume (L)	Average P in inlet (mg/L)	Average efficiency (%)	P sorbed (mg/kg^{-1})
Grobbendonk 100%	2594.6	0.22	74	985
Balen 100%	5939	0.1	41	511
Grobbendonk 75/25%	2332.8	0.12	51	315

It is therefore consistent that Grobbendonk 100% always outperformed other filter material mixture both in laboratory and field trial. It's high sorption capacity and efficiency is explained by high sorption capacity of oxidised iron, high total surface area due to its finer particle sizes and lower Ksat.

It's also clear that the filters were able to reduce P concentrations to below the environment limit of 0.1 $mg.L^{-1}$ enshrined in the Water Framework Directive. It's noted that the filters can still reduce P concentration even when P concentration in inlet were lower than 0.1 $mg.l^{-1}$. Generally, the results depict a promising potential of this innovation to reduce P concentration in drainage water and abate eutrophication.

General discussion

In actual field application of P filters, there is a need to strike a balance among parameters such as Ksat, sorption efficiency and sorption capacity (durability). For instance, a high Ksat allows for processing large volumes of water within a small area (Canga et al. 2013). We found that Ksat is link with Dx and bulk density and its the finer particles that are more important in determining Ksat than coarser particle; Ksat = 0.004 + 0.004*D20 +0.010*D10 – 3.013*EXP-06*BD.

In table 4.6 we calculated area required to treat an estimated 8000L of water at peak flow for each filter. This resulted in elimination of filters having 30% and 40% of glauconite because of its low Ksat of 0.000023 and 0.0001 $m.s^{-1}$. With such low Ksat, they would not be conviniently used in the field. This is because they would require a container of surface area of upto 1.16 to 4.63 m^2 to conduct an estimated 8000 $L.day^{-1}$ of water during peak flow.

Table 4.6: Diameter of the container each filter would require in order to process the estimated peak water flow of 8000 L.day^{-1} in the field (calculations are based on Darcy equation, with H = 0.04 m, L = 0.2 m)

Filter	Ksat (m/s)	Diameter (m)	Weight (kg)
Grobbendonk 60/40	0.0001	2.4	1296
Grobbendonk 70/30	0.00019	1.76	667
Grobbendonk 80/20%	0.0009	0.81	133
Grobbendonk 90/10%	0.0018	0.57	60
Grobbendonk 100%	0.0032	0.43	33
Balen 60/40%	0.000023	5.06	6169
Balen 70/30%	0.0004	1.2	335
Balen 80/20%	0.0010	0.77	128
Balen 90/10%	0.0023	0.51	52
Balen 100%	0.0063	0.31	19

A higher Ksat therefore represents the capacity of the filter to contact large volume of water within a small area.

Another important parameter is the maximum amount of P that can be sorbed before breakthrough point (sorption capacity and durability); a filter with high sorption capacity can be used for a longer period of time before saturation.

In term of highest amount of P sorbed, our laboratory experiment revealed that our most durable filter is Grobbendonk 100%, it treated 1292 L of 0.5 mg P.L^{-1} solution. Given that the weight used in making the filter was 0.645 kg, and it's average sorption efficiency was 94.045; this means that the amount of P that can be sorbed by 1 kg is 942 mg P.kg^{-1} ((1292 L *0.5 mg.L^{-1})/(0.645)*94.04/100.

In addition, P sorption efficiency of a filter should be high enough to reduce P concentration in filtrate below the environment limit of 0.1 mg.L^{-1}. Otherwise it cannot be employed to control environmental P pollution (WFD, 2000; Ballanite and Tanner, 2010; Lyngsie, 2013).

Anzegem site with average daily P in inlet of 0.22 mg P.L^{-1} and an average daily outflow volume of 2595 L, each kilogram of Grobbendonk filter material would last for 1.65 days before breakthrough point. Therefore the 30 kg of materials used in the field trial would last

for approximately 50 days. Although the number of days it lasted in the field trial exceeded 50, it could be due to either a lower average P in inlet or a lower volume of treated water than the estimated average.

In our Anzegem field trial, P sorbed was 985 mg $P.kg^{-1}$ on 26/04/2016; this is fairly within the predicted capacity in the laboratory (942 mg $P.kg^{-1}$). Note that on 07/07/2016, when the Anzegem drain had an outflow again, P concentration in the outlet exceeded the breakthrough point. P in inlet was 0.385 and 0.202 in outlet which is above the environment limit and the efficiency reduced from the average of 74% before breakthrough point to only 47.5%. Therefore our logistic regression fit is a good guide of the expected sorption capacity to breakthrough point of the filter materials.

Similarly, durable filters should be stable and capable to maintain flow at a rate sufficient to process an estimated volume of water at peak flow. It's preferable that such filters can be easily recycled after saturation and be re-used (Lyngsie, 2009).

The design of the filter should be such that the head difference between the outlet and the inlet is small (about 5 cm). This helps to reduce flow rate and increase contact time for reaction.

The total weight needed to form a reactive barrier should be at least 45-50 kg so that it can be used for a whole year without saturation.

Given the lack of sufficient space for installation in the field, filters should be preferably small: a surface area may not exceed 0.51 m^2 or 0.81 m diameter. Fortunately, this may not be a major bottleneck since several filters can be installed within one hectare, this will also help to improve P sorption efficiency of the filters by controlling the volume of water flowing through the filter. Sub-dividing the flow could be very benefiting in terms of P sorption efficiency, durability and processing larger total volumes.

Given our results, ideal filters that can be installed in the field to reduce P losses to open waters should be Grobbendonk filters (100% and 90/10%) since increasing glauconite amounts lowers sorption capacity, Ksat, and increases area of filters' container

Conclusion

Flanders is confronted with high P concentration in surface waters of up to 3-4 times above the 0.1 $mg.l^{-1}$ environment limit. Non-point pollution from agriculture has been earmarked as a major cause. Particularly, direct P input from artificially drained fields has been identified as one important contributor. Our research was intended to develop cheap easily available P filters made of P sorbing materials that can easily be installed in the field. From the results we obtained, the following conclusions can be drawn.

We found that Ksat is linked to particle size distribution and bulk density by the equation: Ksat = 0.004 + 0.004*D20 +0.010*D10 – 3.013*EXP-06*BD.

Filters consisting of iron coated sand and acid pre-treated glauconite in ratios of 100/0 to 80/20 % on weight basis has sufficient Ksat to process the estimated volume of water at peak flow within a suitably small area.

P sorption efficiency is positively related to the amount of iron in the filter material mixture and negatively related to Ksat.

P sorption capacity is positively related to amount of iron in the mixture and negatively related to particle size distribution. It is also negatively related to outflow volume of water treated.

Recommendations

We suggest that experiment to determine the sorption capacity until be run until saturation point is attained for the filters. After saturation of the filters, desorption assessment should also be done to answer the question of recyclability of the filters.

Based on results both from the large scale laboratory experiment and pilot field trial, we recommend that a comprehensive large scale field trial be conducted using filters of Grobbendonk 100%, 90/10%, 80/20%. This would generate adequate data to validate and confirm the potential of the filters for field applications.

References

Adam et al., (2007). K. Adam, T. Krogstad, L. Vrale, A.K. Sovik, P.D. Jenssen. (2007). Phosphorus retention in the filter materials shell sand and filtralite P® — batch and column experiment with synthetic P solution and secondary wastewater. Ecol. Eng., 29 (2) (2007), pp. 200–208

Altundoğan and Tümen, (2002). H.S. Altundoğan, F. Tümen, (2002). Removal of phosphorus from aqueous solutions by using bauxite. I. Effect of pH on the adsorption of various phosphates J. Chem. Technol. Biotechnol., 77 (2002), pp. 77–85

Altundoğan and Tümen, (2003). H.S. Altundoğan, F. Tümen, (2003). Removal of phosphates from aqueous solutions by using bauxite. II. The activation study. Journal of Chem. Technol. Biotechnol., 78 (2003), pp. 824–833

Amery and Schouman (2014); F. Amery and O. Schoumans (2014). Agricultural phosphorus legislation in Europe

Andriamanantena (2014). Effectiveness of filtering materials for reducing phosphorus losses from drained agricultural fields in Flanders, Belgium

Anon., (2013). Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Consultive communication on the sustainable use of phosphorus. European Commission, Brussel.

Arias et al. (2001). C.A. Arias, Del Bubba, M. and Brix, H. (2001). Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. Water Research. 35(5):1159-1168.

Arai and Sparks (2007). Y. Arai and D.L Sparks, (2007). Phosphate reaction dynamics in soils and soil minerals: a multiscale approach. Adv Agron 94: 135–179

Arya et al. (2010). L. M Arya, J. I. Heitman, B. B Thapa, & D. C Bowman (2010). Predicting saturated hydraulic conductivity of golf course sands from particle-size distribution. Soil Science Society of America Journal, 74(1), 33–37. doi:10.2136/ sssaj2009.0022.

Azevedo et al., (2015). L. Azevedo, R. Van Zelm., S.E.W. Leuven, A. Hendriks, A.J. Huijbregts, (2015). Combined ecological risks of nitrogen and phosphorus in European waters. Elsevier, environmental pollution 200(2015) pg 85-92

Ballantine and Tanner, (2010). D.J. Ballantine, C.C. Tanner, (2010). Substrate and filter materials to enhance phosphorus removal in constructed wetlands treating diffuse farm runoff: a review N.Z. J. Agric. Res., 53 (1) (2010), pp. 71–95

Ballaux and Peaslee (1975). J. C. Ballaux and D. E. Peaslee (1975). Relationships between Sorption and Desorption of Phosphorus by Soils. Soil Science Society of America Journal. 39:275-278.

Barrow and Shaw (1975). N.J Barrow and T.C. Shaw (1975). The slow reactions between soil and anions: 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. Soil Science, 119:167–177.

Bellier et al., (2006). N. Bellier, F. Chazarenc, Y. Comeau (2006). Phosphorus removal from wastewater by mineral apatite Water Res., 40 (2006), pp. 2965–2971

Bengston et al.(1992). L. Bengston, P. Seuna, A. Lepisto and R.K Saxena (1992) Particle movement of meltwater in a subdrained agricultural basin. J. Hydrol. 135, 383–398.

Boujelben et al. (2008). N. Boujelben, J. Bouzid, Z. Elouear, F. Jamoussi and A. Montiel (2008). Phosphorous removal from aqueous solution using iron coated natural and engineered sorbents. Science Direct Journal oh hazardous mataerails 151 (2008) 103-110.

Buda et al., (2012). A.R. Buda, G.F. Koopmans, R.B. Bryant, W.J. Chardon, 2012). Emerging technologies for removing nonpoint phosphorus from surface water and groundwater: introduction J. Environ. Qual., 41 (3) (2012), pp. 621–627

Cabrera et al. (1981). F.Cabrera, P. de Arambarri, L. Madridand C. G Toca (1981) Desorption of phosphate from iron oxides in relation to equilibrium pH and porosity: Geoderma 26, 203- 216

Canga et al. (2013). E. Canga et al. B.V. Iversen and C. Kjaergaard (20013). A Simplified Transfer Function for Estimating Saturated Hydraulic Conductivity of Porous Drainage Filters. Springer Science+Business Media Dordrecht (2013).

Chardon and Schoumans, (2007). W. J. Chardon & O. F. Schoumans (2007). Soil texture effects on the transport of phosphorus from agricultural land in river deltas of Northern Belgium, The Netherlands and North-West Germany, journal of Soil Use and Management Volume 23, Issue Supplement s1, pages 16–24, September 2007

Cheung et al. (1994). K.C Cheung,T.H. Venkitachalam, and W.D. Scott. 1994. Selecting soil amendment materials for removal of phosphorus. Water Sci. Technol. 30:247–256.

Csathó et al., (2011). Csathó, P., Radimszky, L., Németh, T. (2011). N and P turnover studies on European and on Danube basin levels. Conference on Mitigation Options for Nutrient Reduction in Surface Water and Groundwaters, Keszthely, Hungary. Proceedings, p. 22

Cucarella and Renman, 2009. V. Cucarella and G. Renman (2009). Phosphorus Sorption Capacity of Filter Materials Used for On-site Wastewater Treatment Determined in Batch Experiments–A Comparative Study. J. Environ. Qual. 38:381–392 (2009).

Devau et al., (2010). N. Devau, E. Le Cadre, P. Hinsinger, F. Gérard (2010). A mechanistic model for understanding root-induced chemical changes controlling phosphorus availability. Ann Bot (Lond) 105: 1183–1197

Directive 2000/60/EC (2000) establishing a Framework for Community Action in the Field of Water Policy. (OJ (2000) L327/1). (Water Framework Directive).

Directive 2008/56/EC (2008) establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive) (OJ L 164, 25.6.2008, p. 19-40).

Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (integrated pollution prevention and control) European Commission - Off. J. Eur. Union, 2010

Directive 91/271/EEC (1991) concerning urban waste water treatment. (OJ (1991) L271/40). (Urban Waste Water Directive)

Directive 91/676/EEC (1991) concerning the protection of waters against pollution caused by nitrates from agricultural sources (OJ (1991)L375/1).(Nitrates Directive).

Drizo et al., (1999). A. Drizo, C.A. Frost, J. Grace, K.A. Smith, (1999). Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. Water Res., 33 (17) (1999), pp. 3595–3602

Duxbury J M and Peverly J H (1978) Nitrogen and phosphorus losses from organic soils. J. Environ. Qual. 7, 566–570.

EPA, (1988). Environmental Protection Agency (EPA), (1988). Phosphorus water quality standards criteria summaries: A compilation of state /Federal criteria. United States Environmental Protection Agency.

European Commission (EC), (2006). EC of the European Parliament and of the Council of 15 February (2006) concerning the management of bathing water quality and repealing Directive 76/C Directive - EEC Official Journal L, 2006

European Commission (EC), (2006). European Commission (EC) Directive 2006/118/EC of the European Parliament and the Council of 12th of December 2006 on the protection of ground water against pollution and deterioration Off. J. Europ. union., L (2006) 372/19, 27/12/2006

European Council Directive 67/548/EEC. Official Journal of the European Communities, 16-08-1967, no. L 196 (dangerous substances).

European Union, (2008). Directive 2008/98/EC of the European Parliament and the Council of 19 November 2008 on Waste and Repealing Certain Directives. Official Journal of the European Union, 22/11/2008

Haygarth et al. (1998). P. M Haygarth, P. J Chapman, S. C Jarvis, and R. V. Smith. (1998). Phosphorus budgets for two contrasting farming systems in the UK. Soil Use and Management 14, 160-167.

Haygarth and Sharpley (2000). P.M Haygarth, and A.N Sharpley. (2000): Terminology for phosphorus transfer. J. Environ. Qual., 29, 10-15.

Harrison (1987). A.F Harrison, (1987). Soil Organic Phosphorus—A Review of World Literature. CAB International, Wallingford, Oxon, UK, p 257

Harrison et al., (2010). J.A. Harrison, A.F. Bouwman, E. Mayorga, S. Seitzinger. (2010). Magnitudes and sources of dissolved inorganic phosphorus inputs to surface fresh waters and the coastal zone: a new global model Glob. Biogeochem. Cycles, 24 (2010)

Heckrath et al. (1995). G. Heckraeth, P. C Brookes, P .R Poulton and K.W.T Goulding (1995). Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. J. Environ. Qual. 24, 904–910.

Hingston et al. (1972) F. J Hingston, R. J Atkinson, A. M Posner and J. P Quirk. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. J. Soil Sci. 23, 177 -92.

Hoffmann et al., (2009). C.C. Hoffmann, C. Kjaergaard, J. Uusi-Kämppä, H.C.B. Hansen, B. Kronvang, (2009). Phosphorus retention in Riparian buffers: review of their efficiency J. Environ. Qual., 38 (5) (2009), pp. 1942–1955

Iversen, B. V., Borgesen, C. D., Laegdsmand, M., Greve, M. H., Heckrath, G., & Kjaergaard, C. (2011). Risk predicting of macropore flow using pedotransfer functions, textural maps, and modeling. Vadose Zone Journal, 10(4), 1185–1195. doi: 10.2136/vzj2010.0140.

Johansson (2007), Johansson, L. Westholm, 2007. Substrates for phosphorus removal-Potential benefi ts for on-site wastewater treatment? Water Res. 40:23–36.

Kaasik et al., (2008), A. Kaasik, C. Vohla, R. Mõtlep, Ü. Mander, K. Kirsimäe, (2008). Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands Water Res., 42 (4–5) (2008), pp. 1315–1323

Khan et al (2010), A. Khan[1], W. Akram[1,*], M. Ashfaq[1], K. Kim[2] and J. Lee, (2010). Effects of optimum doses of nitrogen, phosphorus, potassium and calcium on silkworm, *Bombyx mori* L., growth and yield. Entomological ResearchVolume 40, Issue 6, pages 285–289, November 2010

Klute, A. (1965). Laboratory measurement of hydraulic conduc-tivity of saturated soil. In C. A. Black (Ed.), Methods of soil analysis, part 1. Agronomy 9 (pp. 210–221). Madison: American Society of Agronomist.

Kristensen, (2012), P. Kristensen, (2012). European waters - assessment of status and pressures. European Environment Agency, Copenhagen.

Kumar et al., (2014), A. Kumar, C.S Choudhary, P. Diwaka, K. Brijesh and A. Anjana (2014). Sustainable way for enhancing P efficiency in agricultural soils through phosphate solubilising microbes. An Asian journal of soil science (2014)

Lemercier et al., (2008), B. Lemercier, L. Gaudin, C. Walter, P. Aurousseau, D. Arrouays, C. Schvartz, N.P.A. Saby, S. Follain, J. Abrassart, (2008). Soil phosphorus monitoring at the regional level by means of a soil test database Soil Use and Management, 24 (2) (2008), pp. 131–138

Lindahl, A., Bockstaller, C. (2012). An indicator of pesticide leaching risk to groundwater. *Ecological Indicators*, *23*, 95-108.DOI: 10.1016/j.ecolind.2012.03.014 http://prodinra.inra.fr/record/184512

Lyngsie et al., (2014), G. Lyngsie O.K. Borggaard, H.C.B. Hansen (2014). A three-step test of phosphate sorption efficiency of potential agricultural drainage filter materials, Elsevier Science direct journal of water research

Mann and Bavor (1993). R.A Mann and H.J. Bavor. 1993. Phosphorus removal in constructed wetlands using gravel and industrial waste substrata. Water Sci. Technol. 27:107–113. McBride. M.B. 1994. Environmental chemistry of soils. Oxford Univ. Press. New York.

MAP (2012). VCM-Enquete Operationele Stand Van Zaken Mestverwerking In Vlaanderen 2012 http://www.vcm-mestverwerking.be/publicationfiles

Martinez et al. (2014) R. E.Martinez. S. Weber and K. Bucher (2014). Quantifying the kinetics of olivine dissolution in partially closed and closed batch reactor systems. Chemical Geology. 367 (2014) 1–12.

McRae. (1972). S.G. (1972). Glauconite. Earth-Science Reviews. 8 (4): 397–440

Stuart and Eliot (2009). J. Staurt and M. Elliot (2009). Ecology of marine sediments pg 25

MIRA. (2005). Milieurapport Vlaanderen. Achtergrond document (2005). kwaliteit oppervlaktewater. Vlaamse Milieumaatschappij. Meche- len. Belgium

MIIRA (2012). Milieurapport Vlaanderen. Achtergrond document (2005). kwaliteit oppervlaktewater. Vlaamse Milieumaatschappij. Meche- len. Belgium

Moore (1981). Runoff. Infiltration and Subsurface Flow of Water in Arid and Semi-Arid Regions. edited by S. Aries. Springer Science + Business media B.V

Murphy and Riley. (1962). J. Murphy and J.P Riley. (1962). A modified single solution method for the determination of phosphate in natural waters. department of oceanography. the University of Liverpool. Great Britain

Nair et al (1984). P.S Nair.T.J. Logan. A.N. Sharpley. L.E. Sommers. M.A. Tabatabai. and T.L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. J. Environ. Qual. 13:591–595.

Odum et al., (1979). E.P. Odum. J.T. Finn. H.F. Eldon. (1979). Perturbation theory and the subsidy-stress gradient Bioscience. 29 (1979). pp. 349–352

Oelkers and Valsami-jones (2008). E.H Oelkers. E. Valsami-Jones (2008) Phosphate mineral reactivity and global sustainability. Elements 4: 83–87

Özacar. (2006). M. Özacar. (2006). Contact time optimization of two-stage batch adsorber design using second-order kinetic model for the adsorption of phosphate onto alunite. J. Hazard. Mater. B. 137 (2006). pp. 218–225

Parfitt (1989). R.L. Parfitt. (1989). Phosphate reactions with natural allophone, ferrihydrite and goethite. J Soil Sci 40: 359–369

Penn et al., (2007). C.J. Penn, R.B. Bryant, P.J.A. Kleinman, A.L. Allen. (2007). Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials J. Soil Water Conserv., 62 (4) (2007), pp. 269–276

Penn et al., (2011). C.J. Penn, R.B. Bryant, M.P. Callahan, J.M. McGrath. (2011). Use of industrial by-products to sorb and retain phosphorus Commun. Soil Sci. Plant Anal., 42 (6) (2011), pp. 633–644

Prochaska and Zouboulis. (2006). C.A. Prochaska, A.I. Zouboulis, Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate, Ecol. Eng., 26 (2006), pp. 293–303

Reinhardt et al., (2005). M. Reinhardt, R. Gächter, B. Wehrli, B. Müler. (2005). Phosphorus retention in small constructed wetlands treating agricultural drainage water J. Environ. Qual., 34 (4) (2005), pp. 1251–1259

Richard et al. (2001). G Ricahrds, I Cousin, J.F Bruand, J. Guerif. Effect of compaction on porosity of a silty soil-influence on unsaturated hydraulic properties

Schachtman et al(1998). D. P Schachtman, R. J. Reid and S. M. Ayling, (1998). Phosphorus uptake by plants: from soil to cell. Plant Physiol. 116, 447-453.

Smith, F. W., Ealing, P. M., Dong, B. and Delhaize, E. (1997). The cloning of two Arabidopsis genes belonging to a phosphate transporter family. Plant J. 11, 83-92.

Schoumans et al., (2013). O. F. Schoumans, C.van der salm & P. Groenendijk. (2013). PLEASE: a simple model to determine P losses by leaching, Journal of Soil Use and Management, March 2013, 29 (Suppl. 1), 138–146

Sharpley et al., (2002). A.N. Sharpley, P.J.A. Kleinman, R.W. McDowell, M. Gitau, R.B. Bryant. (2002). Modelling phosphorus transport in agricultural watersheds: processes and possibilities Journal of Soil and Water Conservation, 57 (6) (2002), pp. 425–439

Shen et al., (2011). J. Shen, L. Yuan, J. Zhang, H. Li, Z. Bai, X. Chen, W. Zhang, F. Zhang. (2011). P dynamics from soil to plants. Journal of Plant physiology. Vol 156. pp. 997-1005

Sharpley (1985). A.N Sharpley (1985). Depth of surface soil-runoff interaction as affected by rainfall, soil slope, and management. Soil Sci. Soc. Am. J. 49, 1010–1015.

Sharpley et al. (1996) A.N Sharpley T.C Daniel. J. T Sims and D. H Pote 1996. Determining environmentally sound soil phosphorus levels. J. Soil Water Conserv. 51. 160–166.

Sharpley et al.(2003) A.N Sharpley, T. Daniel, T. Sims, J. Lemunyon, R. Stevens, and R. Parry. 2003. Agricultural Phosphorus and Eutrophication, 2nd ed. U.S. department of Agriculture, Agricultural Research Service, ARS.149, 44 pp.

Sharpley and McDowell (2001). AN Sharpley and R.W McDowell (2001) Approximating phosphorus release from soils to surface runoff and subsurface drainage

Smil. (2000). V. Smil. (2000). Phosphorus in the environment: natural flows and human interferences Annual Review of Energy and the Environment. 25 (2000). pp. 53–88

Sims and Sharpley (1998). J.T and A.N Sharpley (1998) .Managing agricultural phosphorus for water quality protection: future challenges. In Soil Testing for Phosphorus: Environmental Uses and Implications. Ed. J T Sims. pp. 41–43. Southern Cooperative Series Bulletin No. 389, SERA-IEG 17. University of Delaware, Newark, DE.

Smith and Schindler. (2009). VH Smith and DW Schindler. (2009). Eutrophication science: where do we go from here? Trends in Ecology and Evolution. 24. 201–207.

Stone and Wilson. 2006.W. Stone. J.T Wilson (2006). Preferential Flow Estimates to an agricultural Tile Drain with Implications for Glyphosate Transport. J Environ Qual. 2006 Aug 9:35(5):1825-35. Print 2006 Sep-Oct.

Torrent. (1997) J. Torrent (1997). Interactions between phosphate and iron oxide K. Auerswald, H. Stanjek, J.M. Bigham (Eds.). Soils and Environment. Adv. GeoEcol., vol. 30Catena Verlag, Reiskirchen, Germany (1997). pp. 321–344

Tóth et al.. (2013). G. Tóth, A. Jones, L. Montanarella. (2013). The LUCAS topsoil database and derived information on the regional variability of cropland topsoil properties in the European Union Environmental Monitoring and Assessment. 185 (9) (2013). pp. 7409–7425

Tóth et al.. (2014). G. Tóth, R. Guicharnaud, B. Tóth, T. Hermann. (2014). Phosphorus levels in croplands of the European Union with implications for P fertilizer use. Elsevier. European journal of Agronomy vol 55 (2014) pg 42-52

Trask (1932). Geological Survey Bulletin pg 71-72

Turner et al., (2007). B. Turner, A.E Richardson, E. Mullaney, (2007). Inositol Phosphates: Linking Agriculture and the Environment. CAB International, Wallingford, UK, p 304

Ulén et al., (2007). B. Ulén, M. Bechmann, J. Folster, H.P. Jarvie, H. Tunney, (2007). Agriculture as a phosphorus source for eutrophication in the north-west European countries, Norway, Sweden, United Kingdom and Ireland: a review Soil Use Management, 23 (2007), pp. 5–15

Van Meirvenne, M., Tariku, M., De Neve, S., Hofman, G.,Salomez, J. & De Bolle, S., (2008). Afbakening van de fosfaatverzadigde gebieden in Vlaanderen op basis van een kritische fosfaatverzadigingsgraad van 35%. Ghent University, Ghent.

Vohla et al., (2011). C. Vohla, M. Kõiv, H.J. Bavor, F. Chazarenc, Ü. Mander, Filter materials for phosphorus removal from wastewater in treatment wetlands—a review Ecol. Eng., 37 (1) (2011), pp. 70–89

Weng, L., van Riemsdijk, W.H. and Hiemstra, T. (2012). Factors controlling phosphate interaction with iron oxides. Journal of Environmental Quality, 41:628–635

White and Thomas (1981). R.E White and G.W Thomas (1981). Hydrolysis of aluminium on weakly acidic organic exchangers: implications for phosphorous adsorption. Fert. Res. 2 159-167

Wilson (2003). M.J Wison (2013). Rock-forming Minerals: Sheet silicates: clay minerals. Vol. 3C. 2nd Ed. Geological Society, London, - Science - 736 pages.

Wood and McAtamney, (1996). R.B. Wood, C.F. McAtamney, (1996). Constructed wetlands for waste water treatment: the use of laterite in the bed medium in phosphorus and heavy metal removal, Hydrobiologia, 340 (1996), pp. 323–331

Zach-Maor et al.(2011). A. Zach-Maor, R. Semiat, A. Shemer (2011). Adsorption-desorption mechanism of phosphate by immobilized nano-sized magnetite layer: interface and bulk interactions. J Colloid Interface Sci. 2011 Nov 15:363(2):608-14. doi: 10.1016/j.jcis.2011.07.062. Epub 2011 Jul 27.

Appendix 1: Table of calculated Dx values (mm) of the filter materials ranging from D10 to D90

Filter material	D10	D20	D30	D40	D50	D60	D70	D80	D90
Grobbendonk 60/40%	0.01	0.02	0.03	0.04	0.08	0.53	0.72	0.91	1.37
Grobbendonk 70/30%	0.01	0.03	0.04	0.20	0.57	0.73	0.88	1.11	1.56
Grobbendonk 80/20%	0.02	0.03	0.05	0.05	0.61	0.76	0.91	1.16	1.59
Grobbendonk 90/10%	0.03	0.06	0.44	0.44	0.73	0.86	0.99	1.32	1.67
Grobbendonk 100%	0.05	0.41	0.58	0.58	0.80	0.91	1.06	1.38	1.70
Balen 60/40%	0.01	0.02	0.04	0.05	0.92	1.47	2.00	2.58	3.25
Balen 70/30%	0.01	0.03	0.04	0.72	1.23	1.70	2.18	2.67	3.31
Balen 80/20%	0.02	0.09	0.64	0.64	1.59	2.03	2.43	2.83	3.42
Balen 90/10%	0.03	0.49	0.91	0.91	1.67	2.05	2.42	2.79	3.36
Balen 100%	0.19	0.78	1.14	1.14	1.82	2.17	2.54	2.90	3.46

Appendix 2: Stepwise forward regression in SPSS to determine the link between Ksat, particle size distribution (Dx) and bulk density

Correlations

		Ksat	D10	D20	D30	D40	D50	D60	D70	D80	D90	BD
Pearson Correlation	Ksat	1.000	.834	.940	.865	.763	.504	.456	.373	.330	.280	-.673
	D10	.834	1.000	.742	.604	.524	.386	.350	.291	.251	.224	-.421
	D20	.940	.742	1.000	.894	.801	.586	.556	.483	.436	.393	-.572
	D30	.865	.604	.894	1.000	.861	.693	.674	.588	.535	.484	-.624
	D40	.763	.524	.801	.861	1.000	.762	.789	.725	.686	.643	-.415
	D50	.504	.386	.586	.693	.762	1.000	.973	.962	.957	.939	-.017
	D60	.456	.350	.556	.674	.789	.973	1.000	.992	.977	.966	.071
	D70	.373	.291	.483	.588	.725	.962	.992	1.000	.995	.990	.185
	D80	.330	.251	.436	.535	.686	.957	.977	.995	1.000	.997	.226
	D90	.280	.224	.393	.484	.643	.939	.966	.990	.997	1.000	.292
	BD	-.673	-.421	-.572	-.624	-.415	-.017	.071	.185	.226	.292	1.000
Sig. (1-tailed)	Ksat	.	.000	.000	.000	.000	.002	.006	.021	.038	.067	.000
	D10	.000	.	.000	.000	.001	.018	.029	.060	.090	.117	.010
	D20	.000	.000	.	.000	.000	.000	.001	.003	.008	.016	.000
	D30	.000	.000	.000	.	.000	.000	.000	.000	.001	.003	.000
	D40	.000	.001	.000	.000	.	.000	.000	.000	.000	.000	.011
	D50	.002	.018	.000	.000	.000	.	.000	.000	.000	.000	.464
	D60	.006	.029	.001	.000	.000	.000	.	.000	.000	.000	.355
	D70	.021	.060	.003	.000	.000	.000	.000	.	.000	.000	.164
	D80	.038	.090	.008	.001	.000	.000	.000	.000	.	.000	.115
	D90	.067	.117	.016	.003	.000	.000	.000	.000	.000	.	.059
	BD	.000	.010	.000	.000	.011	.464	.355	.164	.115	.059	.
N	Ksat	30	30	30	30	30	30	30	30	30	30	30
	D10	30	30	30	30	30	30	30	30	30	30	30
	D20	30	30	30	30	30	30	30	30	30	30	30
	D30	30	30	30	30	30	30	30	30	30	30	30
	D40	30	30	30	30	30	30	30	30	30	30	30
	D50	30	30	30	30	30	30	30	30	30	30	30
	D60	30	30	30	30	30	30	30	30	30	30	30
	D70	30	30	30	30	30	30	30	30	30	30	30
	D80	30	30	30	30	30	30	30	30	30	30	30
	D90	30	30	30	30	30	30	30	30	30	30	30
	BD	30	30	30	30	30	30	30	30	30	30	30

Variables Entered/Removed[a]

Model	Variables Entered	Variables Removed	Method
1	D20	.	Forward (Criterion: Probability-of-F-to-enter <= .050)
2	D10	.	Forward (Criterion: Probability-of-F-to-enter <= .050)
3	BD	.	Forward (Criterion: Probability-of-F-to-enter <= .050)

a. Dependent Variable: Ksat

Model Summary[d]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.940[a]	.884	.880	.000652505	.884	212.912	1	28	.000
2	.962[b]	.925	.920	.000533270	.041	14.921	1	27	.001
3	.976[c]	.953	.947	.000430937	.028	15.349	1	26	.001

a. Predictors: (Constant), D20

b. Predictors: (Constant), D20, D10

c. Predictors: (Constant), D20, D10, BD

d. Dependent Variable: Ksat

ANOVA[d]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	1	.000	212.912	.000[a]
	Residual	.000	28	.000		
	Total	.000	29			
2	Regression	.000	2	.000	166.844	.000[b]
	Residual	.000	27	.000		
	Total	.000	29			
3	Regression	.000	3	.000	175.444	.000[c]
	Residual	.000	26	.000		
	Total	.000	29			

a. Predictors: (Constant), D20

b. Predictors: (Constant), D20, D10

c. Predictors: (Constant), D20, D10, BD

d. Dependent Variable: Ksat

Coefficients[a]

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.	Correlations		
	B	Std. Error	Beta			Zero-order	Partial	Part
1 (Constant)	.000	.000		1.851	.075			
D20	.007	.000	.940	14.592	.000	.940	.940	.940
2 (Constant)	.000	.000		1.311	.201			
D20	.005	.001	.715	9.098	.000	.940	.868	.479
D10	.010	.003	.303	3.863	.001	.834	.597	.203
3 (Constant)	.004	.001		4.054	.000			
D20	.004	.001	.598	8.514	.000	.940	.859	.362
D10	.010	.002	.305	4.804	.000	.834	.686	.204
BD	-3.013E-6	.000	-.203	-3.917	.001	-.673	-.609	-.167

a. Dependent Variable: Ksat

Excluded Variables[d]

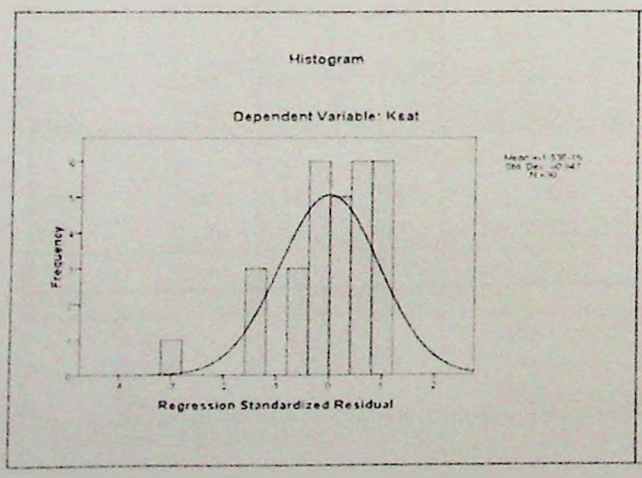
Model		Beta In	t	Sig.	Partial Correlation	Collinearity Statistics
						Tolerance
1	D10	.303[a]	3.863	.001	.597	.449
	D30	.120[a]	.830	.414	.158	.200
	D40	.028[a]	.256	.800	.049	.359
	D50	-.072[a]	-.901	.375	-.171	.656
	D60	-.096[a]	-1.252	.221	-.234	.691
	D70	-.106[a]	-1.468	.154	-.272	.766
	D80	-.098[a]	-1.394	.175	-.259	.810
	D90	-.105[a]	-1.542	.135	-.284	.846
	BD	-.202[a]	-2.884	.008	-.485	.673
2	D30	.220[b]	1.922	.066	.353	.192
	D40	.090[c]	1.014	.320	.195	.348
	D50	-.049[b]	-.751	.459	-.146	.651
	D60	-.069[b]	-1.091	.285	-.209	.683
	D70	-.080[b]	-1.340	.192	-.254	.756
	D80	-.072[b]	-1.236	.228	-.236	.799
	D90	-.082[b]	-1.456	.157	-.275	.836
	BD	-.203[b]	-3.917	.001	-.609	.673
3	D30	.113[c]	1.106	.279	.216	.173
	D40	.117[c]	1.664	.109	.316	.345
	D50	.065[c]	1.081	.290	.211	.501
	D60	.069[c]	1.107	.279	.216	.458
	D70	.076[c]	1.189	.246	.231	.440
	D80	.084[c]	1.365	.185	.263	.464
	D90	.083[c]	1.308	.203	.253	.439

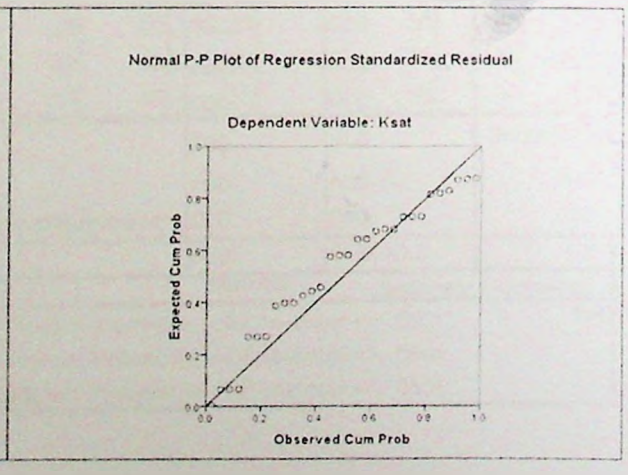
a. Predictors in the Model: (Constant), D20

b. Predictors in the Model: (Constant), D20, D10

c. Predictors in the Model: (Constant), D20, D10, BD

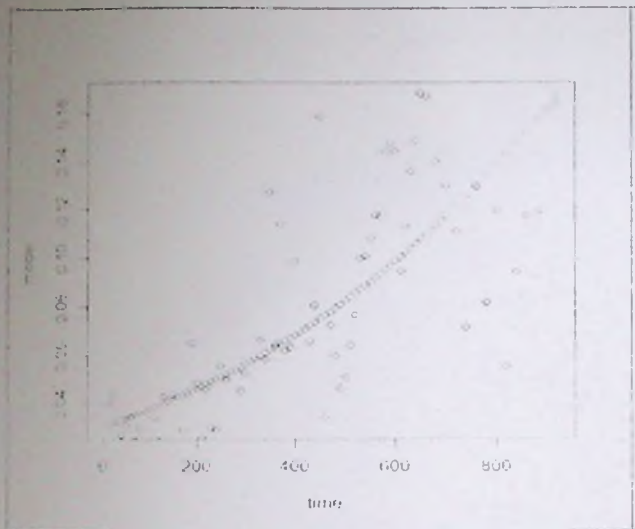
d. Dependent Variable: Ksat



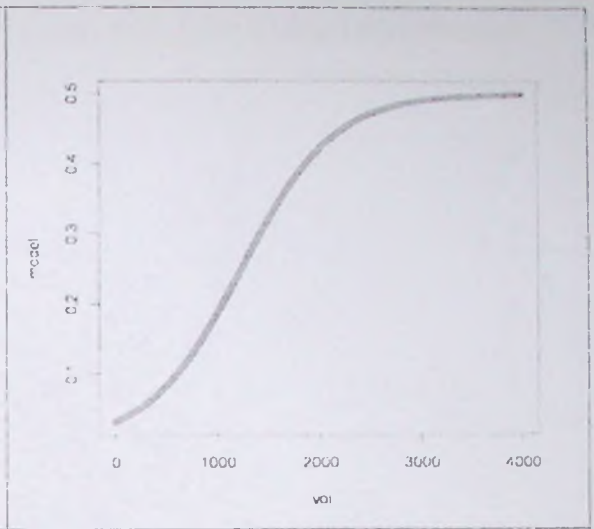


Appendix 3: R output to predict P sorption curve

Balen 100% model prediction (sorption curve); P in filtrate versus volume

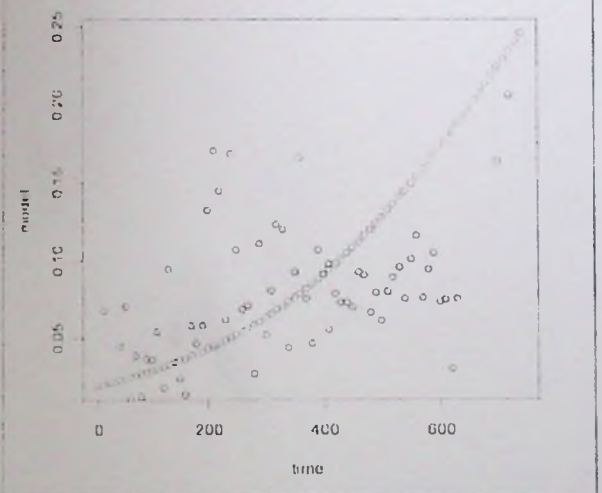


Observations = blue; prediction = red

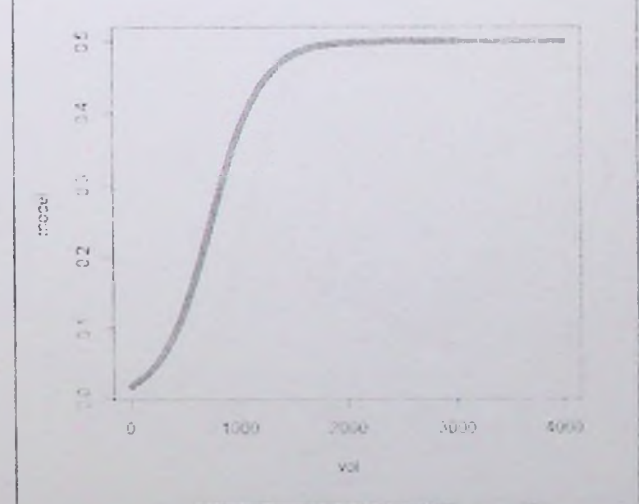


Prediction for larger volume of 4000l.

Balen 90/10% % model prediction (P sorption curve); P in filtrate versus volume

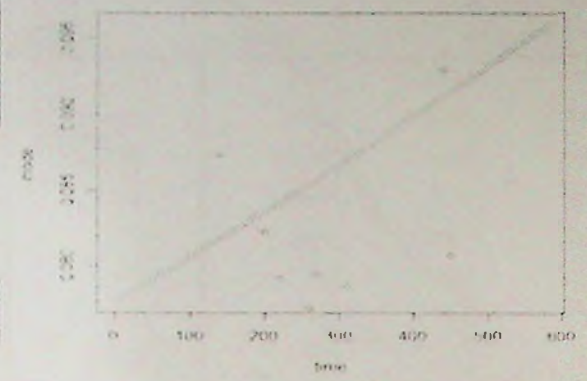


Observations = blue; prediction = red

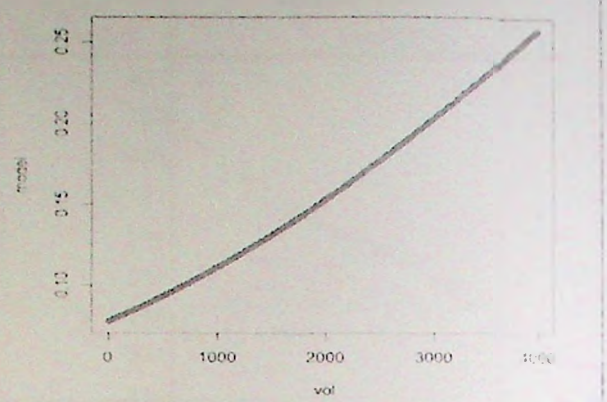


Predictions for large volume, 4000L

Balen 80/20% model prediction (P sorption curve); P in filtrate versus volume

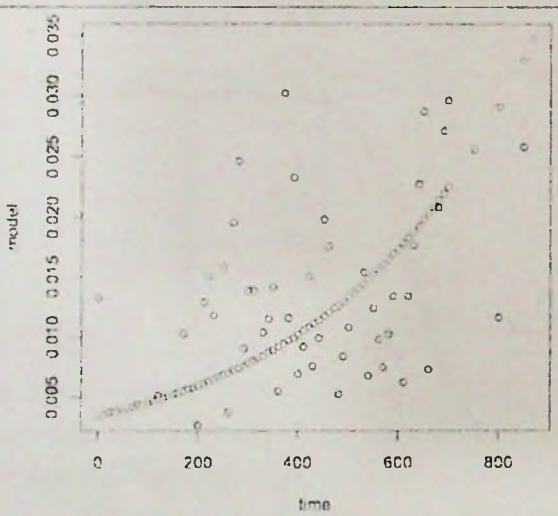


Observations = blue; prediction = red

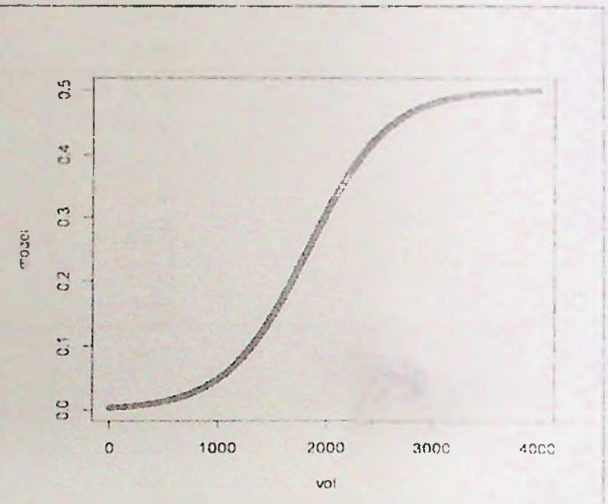


Predictions for large volume, 4000L

Grobbendonk 100% model prediction (P sorption curve); P in filtrate versus volume

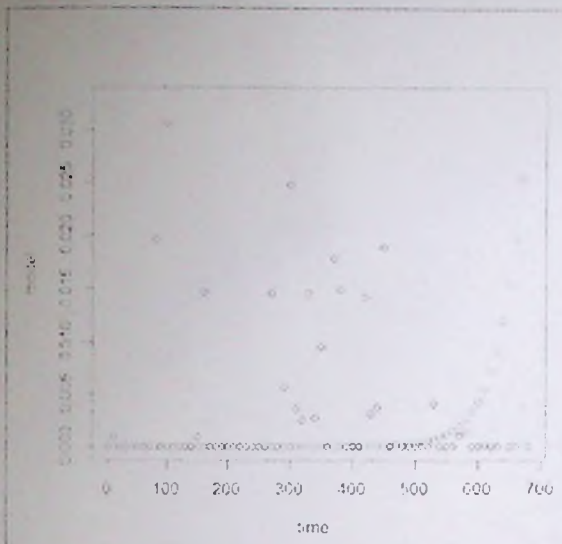


Observations = blue; prediction = red

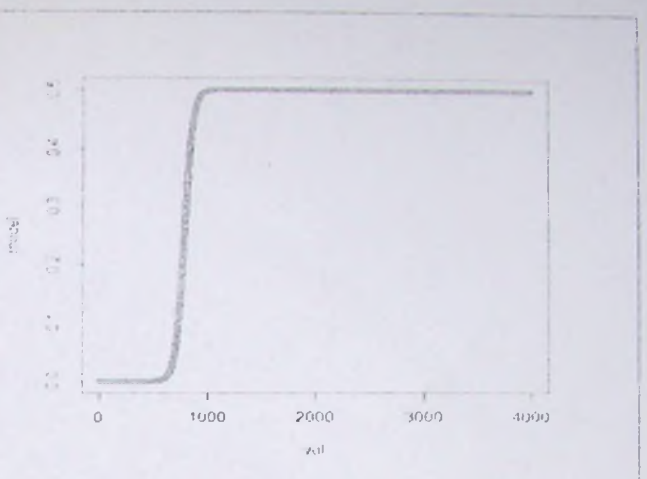


Predictions for large volume, 4000L

Grobbendonk 90/10% model prediction (P sorption curve); P in filtrate versus volume

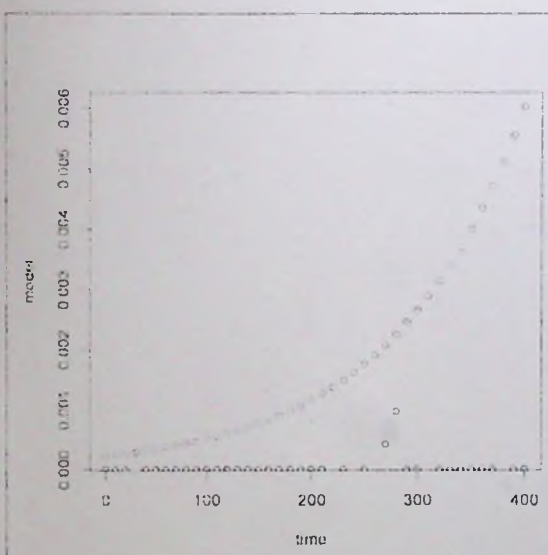


Observations = blue; prediction = red

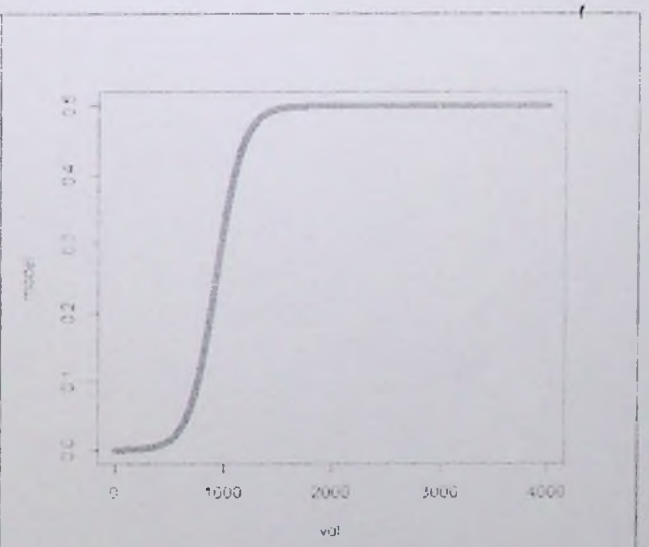


Predictions for large volume, 4000L

Grobbendonk 80/20% model prediction (P sorption curve) ; residual P versus volume



Observations = blue; prediction = red



Predictions for large volume, 4000L