Filter beds for on-site wastewater treatment

Towards more reliable estimations of phosphorus retention

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Phosphorus (P) is an important plant nutrient and essential for life. However, the phosphate rock used for fertilizer production is a non-renewable resource and its production is expected to peak. At the same time, the discharge of P into natural waters is causing eutrophication, a severe problem in areas such as the Baltic Sea. On-site wastewater treatment facilities in Sweden contribute substantially to this discharge because of their inadequate retention of P. Filter beds are a potentially useful technique to capture P in on-site facilities. However, many variables need to be considered when the P retention of potential filter materials is estimated in laboratory tests prior to designing full-scale filters. The overall aim of this thesis was therefore to increase the reliability of forecasting P retention in full-scale filters by increasing the understanding of P retention in P filters under varying conditions and by identifying measures that could lead to more reliable methods of testing filter materials at laboratory scale.

The effects of influent type, influent P concentration, loading rate and ambient temperature on the filter materials *FILTRA P*, *Filtralite P*, *Top16* and *Polonite* were investigated in filter column experiments using 2^4 factorial designs. Furthermore, the P binding mechanism was studied using mineral phase investigations and by determining the reaction time of the P in the filter. In addition, filter performance was estimated by means of hydro-geochemical transport modelling.

The investigated factors significantly ($\alpha = 0.05$) affected the retention of P in the filter materials showing that it is important to consider those factors when designing laboratory filter experiments and full-scale filters. Using secondary wastewater as an influent instead of P solution decreased the P binding capacity of *Filtralite P*, probably due to organic compounds contained in the wastewater. Increasing influent P concentration decreased the number of bed volumes treated before breakthrough in *FILTRA P* by 82%. The loading rate was shown to be an important design parameter. Increasing the loading rate, something commonly done in the laboratory to accelerate the testing, significantly increased the amount of washed-out particulate P in *FILTRA P* and *Filtralite P*. However, the residence time was also shown to be important; it should be maximised in filter tests as far as practical constraints allow.

Increasing the temperature from 4.3 to 16.5°C increased the P binding capacity in both *Top16* and *Polonite* which was attributed to an enhanced precipitation of calcium phosphates. This indicates that results obtained from experimental filters at room temperature might overestimate filter performance in the field where the temperature can be lower. In addition, full-scale filters might function better in warm rather than cool climates. The results further showed that it is crucial to measure both the concentration of dissolved P and particulate P in the filter effluent, as P-containing particles were observed to escape from the experimental filters in this study.

Hydroxylapatite was detected in the outflow hose of the *FILTRA P* columns indicating that this mineral phase may form in the filters under certain conditions. The geochemical models, however, indicated that the only precipitated calcium phosphate compound was amorphous tricalcium phosphate.

Two hydro-geochemical transport models were developed that satisfactorily described the experimentally derived P breakthrough curves and effluent pH of the filter columns with *Filtralite P*. The simulations suggested that calcium oxide, calcite and the calcium-silicate phase wollastonite supplied the Ca$^{2+}$ and OH$^{-}$ ions required for the precipitation of phosphate.
SAMMANFATTNING


De undersökta faktorerna påverkade P retentionen signifikant ($\alpha = 0.05$) vilket betyder att det är viktigt att ta hänsyn till dem när ett filter utformas, både i laboratoriet och i fält. Användning av biologiskt förbehandlat avloppsvatten istället för P lösningsledde till att P retentionen minskade i Filtralite P. Detta berodde troligtvis på de organiska föreningarna i avloppsvattnet. Därför är en välfungerande biologisk förbehandling av avloppsvattnet viktig. När P koncentrationen ökade från 12 till 50 mg L$^{-1}$ i lösningen kunde 82% färre baddvolymer behandlas innan utgående P koncentration översteg 1 mg L$^{-1}$. Filtrets hydrauliska belastning visades vara en viktig parameter. En högre belastning ökade mängden partikulärt P i utloppet från Filtra P och Filtralite P filtren. Dock var uppehållstiden också viktig och borde maximeras så mycket som praktiskt möjligt i laboratorieförsök.

Vid en temperatur av 16.5°C var fosforretentionskapaciteten i både Top16 och Polonite högre än vid 4.3°C vilket troligtvis berodde på att kalciumfosfat-utfällningen fungerade bättre. Därför kan resultat från laboratorieförsök utförda i rumstemperatur överkasta filtrets fosforretentionsförmåga i fält. Fullskalefilter fungerar möjligtvis bättre i varmare klimat. Resultaten av denna studie tyder på att präknarkärt fosfor kan sköljas ur filtret. Därför är det viktigt att mäta både lös och totalt fosfor i filtrets utgående vattnet.

I utgående slangen från Filtra P kolonnerna hittades hydroxylapatit vilket visar att detta mineral kan bildas i filtret under vissa förutsättningar. De geokemiska modellerna tydde dock på att den enda mineralfasen som fälldes ut var amorf trikalciumfosfat.

Två hydro-geokemiska transportmodeller utvecklades som väl beskrev fosforkoncentrationen samt pH i utgående vattnet av Filtralite P kolonnerna. I modellen inkluderades kalciumoxit, kalciumkarbonat och kalciumsilikatfaseten wollastonit vilket indikerar att de kalciumioner som behövs för reaktionen med fosfor löses ut ur dessa faser.


Die untersuchten Faktoren hatten einen signifikanten (α = 0.05) Einfluss auf die Phosphorretentionskapazität der Filtermaterialien. Daher sollten sie bei der Bemessung eines Filters sowohl im Labor als auch im Feld beachtet werden. Die mit Abwasser betriebenen Filtra P-Filter wiesen eine geringere Retentionskapazität auf als die mit Phosphatlösung betriebenen, was wahrscheinlich auf den Gehalt organischer Substanzen im Abwasser zurückzuführen ist. Ein Anstieg der Phosphorkonzentration im Zulauf eines Filtra P-Filter von 12 auf 50 mg L⁻¹ führte zu einem früheren Anstieg der Phosphorkonzentrationen im Ablauf (die Anzahl der behandelten Filtervolumen sank um 82%). Des Weiteren wurde eine Auswaschung von partikulärem Phosphor aus den Filtern beobachtet, die durch eine erhöhte hydraulische Belastung des Filters, wie sie oft in Laboruntersuchungen der Fall ist, verstärkt wurde. Daher ist die hydraulische Belastung eine wichtige Bemessungsgröße. Jedoch war auch die Retentionszeit von Bedeutung, die, soweit praktisch möglich, in Laboruntersuchen maximiert werden sollte. Die Auswaschung von partikulärem Phosphor zeigt außerdem, dass es wichtig ist, die Konzentration von sowohl gelöstem als auch partikulärem Phosphor im Ablauf zu messen.

Die Filter, die bei einer höheren Temperatur (16.5°C) betrieben wurden, wiesen eine höhere Phosphorretentionskapazität auf als die Filter bei niedrigerer Temperatur (4.3°C), vermutlich weil die Ausfällung von Calciumphosphaten begünstigt war. Daher kann die Funktion des Originalfilters je nach Umgebungstemperatur deutlich unter der bei Raumtemperatur gemessenen Funktion liegen.

Ausfällungen, die sich im Ablaufschlauch der Filtra P-Filter abgesetzt hatten, konnten als Hydroxylapatit identifiziert werden, was darauf hinweist, dass sich dieses Mineral im Filter bilden kann. Die geochemischen Modelle deuten allerdings an, dass amorphe Tricalciumphosphat das einzige Calciumphosphat war, das ausgefällt wurde. Es wurden zwei hydrogeochemische Transportmodelle entwickelt, die die kinetische Auflösung von CaO, CaCO₃ und Wollastonit simulierten und die Phosphorkonzentrationen und den pH im Ablauf der Filtra P-Filter zufriedenstellend darstellten.


IV. Inga Herrmann, Kerstin Nordqvist, Annelie Hedström, Maria Viklander. Effect of temperature on the performance of laboratory-scale phosphorus-removing filter beds in on-site wastewater treatment. Submitted to *Chemosphere* (under review).


### My contribution to the papers

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INTRODUCTION

Phosphorus (P) is currently receiving increasing attention because the phosphate rock used for fertiliser production is a non-renewable resource and P, being an important plant nutrient, is essential for life. At the same time, the discharge of P into natural waters is causing eutrophication, a severe problem in areas such as the Baltic Sea (HELCOM, 2005). Cordell et al. (2012) pointed out that the wastewater sector is, along with mining inefficiencies and diffuse discharges from agriculture, the largest source of P losses from the global P cycle. Therefore, enhanced P recovery from wastewater is essential. About 11 % of the P contained in Swedish wastewater arrives at on-site treatment facilities, potentially generating 730 tons per year of recoverable P (Linderholm et al., 2012). As on-site P treatment is poor, 620 tons of this P are released to soil or water each year, more than twice the emissions from all Swedish municipal wastewater treatment plants put together (Linderholm et al., 2012). Thus, there is a substantial quantity of potentially recoverable P in on-site wastewater currently discharged to receiving waters, aggravating the problem of eutrophication.

Filtration in a bed of granular material which can both mechanically and chemically retain P is a potentially useful technique for capturing P in on-site wastewater treatment because it is a robust, low-maintenance option that can also facilitate the recovery of P. P filter beds could be retro-fitted downstream of existing non-infiltration on-site treatment facilities such as constructed wetlands (e.g. sand filtration beds), or could be integrated as a final treatment step in small-scale wastewater treatment units. However, the function of the filters over time and under varying conditions is uncertain and difficult to predict.

The process of P retention in filter beds is influenced by many variables, both in the laboratory and under field conditions: the properties of the filter material, the surface loading rate and the residence time of the water in the filter, as well as the properties of the influent and the ambient temperature. These variables vary considerably across the many laboratory studies that have been conducted on different filter materials (Johansson Westholm, 2006; Cucarella and Renman, 2009; Vohla et al., 2011), making meaningful comparison of their results impossible. Deviations in P retention have been found between laboratory test filter units and full-scale filters (Renman and Renman, 2010). To be able to estimate and forecast P retention in the filters, the variables’ influences need to be understood. A better understanding of P retention under varying conditions can also facilitate the conversion of short-term laboratory results into reliable estimations of full-scale filter performance.

This study investigates the effects of a range of factors possibly influencing P retention, identifies mineral phases in filter materials and discusses the underlying processes of P retention. In addition, it takes a first step towards estimating filter performance using hydro-geochemical transport modelling.
1.1 Aims and objectives

The overall aim of this thesis was to increase the reliability of forecasting P retention in full-scale filters by increasing the understanding of P retention in P filters under varying conditions and by identifying measures that could lead to more reliable methods of testing filter materials at laboratory scale.

Thus, the thesis has three objectives:

The first objective was to investigate – under controlled laboratory conditions – the effect of several variables on P retention and estimations of P retention by
- studying the effect of influent properties (type of influent, P concentration) on P retention,
- studying the effect of filter characteristics such as flow regime and material properties on P retention,
- studying the effect of temperature on P retention,
- assessing how the effluent parameters should be selected and interpreted, and
- determining the required number of experimental replicates.

The second objective was to achieve a better understanding of the mechanisms of P retention in the filter
- by identifying mineral phases in the filter materials that contribute to P retention,
- by identifying P-containing phases formed in the filter materials, and
- by determining the time needed for the P to react in the filters.

The third objective was to take some first steps towards estimating P retention in filters by means of hydro-geochemical transport modelling.
1.2 Structure of the thesis

This is a compilation thesis and synthesises the results of the six appended papers that will hereafter be referred to as Papers I to VI. The studies presented in these papers cover the aspects shown in Fig. 1. In papers I – IV, several factors potentially influencing the performance of the filters were investigated. These factors included properties of the influent and the filter as well as the ambient temperature. The time the P needed to react in the material was determined in Papers I and III, whereas mineral phase investigations were undertaken in Paper II, IV and V (Fig. 1). Furthermore, the way of selecting and interpreting effluent parameters was assessed (Paper II).

In the thesis, the design of laboratory filter experiments is discussed and measures that could lead to more reliable investigations of filter materials in the laboratory are suggested. In addition, hydro-geochemical transport models were developed and discussed as a tool for estimating filter longevity.

![Figure 1](Outline of the papers that this thesis is based on.)
2 BACKGROUND

2.1 Filter materials

A large number of different filter materials used for P removal in on-site wastewater treatment systems have been investigated to date. The results of these studies have been summarised in two literature reviews (Johansson Westholm, 2006; Vohla et al., 2011). In both reviews, the investigated materials were divided into natural materials, industrial by-products and man-made materials. Natural products include e.g. sand, gravel, shell sand, peat and limestone. Industrial by-products from the steel industry such as blast furnace slag, electric arc furnace slag and basic oxygen furnace slag have been investigated to a large extent e.g. in the USA (Drizo et al., 2006; Lee et al., 2010), Australia (Sakadevan and Bavor, 1998; Shilton et al., 2006; Pratt et al., 2007), New Zealand (Shilton et al., 2006; Pratt and Shilton, 2010; Shilton et al., 2013), France (Barca et al., 2012; Barca et al., 2013) and Sweden (Johansson, 1999; Hedström and Rastas, 2006). Man-made products include Filtra P (Gustafsson et al., 2008), Polonite (Renman and Renman, 2010), and lightweight aggregates such as LECA (light expanded clay aggregates (Johansson, 1997)) and Filtralite P (Ádám et al., 2005; Heistad et al., 2006). These products have mainly been studied in Scandinavian countries.

2.2 Mechanisms of phosphorus retention in the filter

The main P retention mechanisms in filter materials have been observed to be precipitation with calcium (Ca) and sorption to metal oxides. Examples include P adsorption onto metal oxides/oxyhydroxides, observed in New Zealand melter slag (Pratt et al., 2007). In Filtralite P, P has been found to be bound to aluminium but also to Ca and magnesium (Ádám et al., 2006). Vohla et al. (2011) reviewed over 80 subtypes of both natural and man-made materials plus industrial by-products and reported that the majority of them had a high pH value >7 and high Ca and/or CaO content, suggesting precipitation to be the main process of P retention (Vohla et al., 2011). Precipitation with Ca has been shown to be important in e.g. Polonite and its parent material opoka (Johansson and Gustafsson, 2000; Eveborn et al., 2009), in Filtra P, Filtralite P, wollastonite, and Absol (Eveborn et al., 2009), in natural palygorskite (Gan et al., 2009), in coal ash (Yan et al., 2007), and in steel slags produced in Europe (Barca et al., 2012) such as blast furnace slag (Johansson and Gustafsson, 2000; Eveborn et al., 2009), electric arc furnace slag and basic oxygen furnace slag (Barca et al., 2013). Dissolved P is retained due to its reaction with Ca ions that are released from the filter material into the water phase, where they form Ca-phosphates and precipitate. The occurrence of P phases in the wastewater and the Ca ions supplied by the filter material are important for these reactions. Furthermore, it is important to understand Ca-phosphate formation and the conditions that promote it. Thus, this section focuses on the P phases occurring in wastewater, the mineral phases in the filter materials that supply Ca ions and the Ca-phosphates formed.
2.2.1 Phosphorus in wastewater

P occurs in wastewater almost solely as phosphates which occur in solution, in particles or detritus, or in the bodies of aquatic organisms (Clesceri et al., 1989). The phosphates are present in three forms: orthophosphate, polyphosphate and organically-bound phosphate (Tchobanoglous and Burton, 1991). The biggest part of the total dissolved P is present as orthophosphate (Houhou et al., 2009). Polyphosphates are present in fresh wastewaters but are converted into orthophosphates in sewers and by biological treatment processes (Droste, 1997). With the pH of wastewater being around 7, the dominant forms of orthophosphate are $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ (Droste, 1997) as $\text{PO}_4^{3-}$ ions occur only above pH 9.5 (Scheffer and Schachtschabel, 1998).

The total P content of a wastewater sample can be divided into two operationally-defined fractions, the particulate and the total dissolved fraction. The latter is obtained by 0.45 $\mu$m filtration and is composed of dissolved inorganic and organic P and colloidal-sized phosphorus species (McKelvie et al., 1995). The particulate P fraction in the wastewater, as retained by a 0.45 $\mu$m filter, might be removed from the wastewater by mechanical retention in the filter. However, the main part of the P in the influent to a filter unit can be assumed to be dissolved, especially if preceded by a well-functioning mechanical and biological pre-treatment.

2.2.2 Dissolving mineral phases

Different mineral phases that may be responsible for the supply of Ca$^{2+}$ and OH$^-$ ions required for the precipitation of Ca-phosphates have been detected in a number of filter materials. Lime (CaO) has been observed as being contained in the majority of available filter materials (Vohla et al., 2005). Many materials also contain calcite e.g. limestone, shell-sand and Filtralite P (Lyngsie et al., 2014), natural sepiolite (Yin et al., 2011), and oil shale ash (Liira et al., 2009). Dolomite (CaMgCO$_3$) was detected in natural sepiolites (Yin et al., 2011) and shell-sand (Lyngsie et al., 2014). Amorphous CaO-Al$_2$O$_3$-SiO$_2$ (CAS) was observed to be the mineral responsible for P removal in paper sludge that had been calcined at 800°C (Wajima and Rakovan, 2013). Dissolution of the minerals bredigite (Ca$_{14}$Mg$_2$(SiO$_4$)$_8$) and gehlenite (Ca$_2$Al$_2$SiO$_7$) was suggested for blast furnace slag (Kostura et al., 2005). Filtralite P was reported to consist of calcite, mixtures of poorly ordered Al, Ca, Fe and Mg silicates, Ca and Mg oxides and clay silicates (Lyngsie et al., 2014). The presence of wollastonite in Polonite was indicated using Fourier transform infrared (FTIR) spectroscopy (Gustafsson et al., 2008).

A sufficient and uniform dissolution of Ca from the material is desirable for maintaining a concentration of Ca ions in the solution that is favorable for the precipitation of Ca-phosphates. Therefore, it is important to understand what the dissolution of the mineral phases is dependent on. Claveau-Mallet et al. (2012) suggested some factors influencing the dissolution rate of Ca in electric arc furnace slag i.e. the size of the slag particles, accumulation of precipitates and CaO and FeO content.
2.2.3 Calcium phosphate formation

Precipitation of Ca-phosphates occurs as crystalline minerals or their amorphous precursors. Ca-phosphates that form in aqueous solution are dicalcium phosphate dihydrate (DCPD or brushite, CaHPO$_4$·2H$_2$O), dicalcium phosphate anhydrous (monetite, Ca(HPO$_4$)$_2$), tricalcium phosphate (TCP, Ca$_3$(PO$_4$)$_2$), octacalcium phosphate (OCP, Ca$_7$(PO$_4$)$_6$·5H$_2$O), defect apatite (DA, Ca$_9.4$(HPO$_4$)$_{0.6}$(PO$_4$)$_{5.4}$(OH)$_{1.4}$), and hydroxyapatite (HAP, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) (Koutsoukos and Valsami-Jones, 2004). In addition, amorphous Ca-phosphate (ACP), being an unstable precursor phase, is formed in supersaturated solutions at pH >7.0. In the experiments of Freeman and Rowell (1981), dicalcium phosphate (DCP) formed on calcite, with OCP sometimes occurring as a thin surface coating on the DCP. All three different species of calcium phosphate (DCPD, dicalcium phosphate anhydrous and OCP) can precipitate if the total P concentration is higher than 4 mg L$^{-1}$ and the Ca$^{2+}$ activity is at least 200 mg L$^{-1}$ (Stuanes, 1984). Ca concentrations observed in the effluent of electric arc furnace filter columns were 200 mg L$^{-1}$ when the pH was 11 (Claveau-Mallet et al., 2012). Ca-phosphate precipitation is generally encouraged by alkaline conditions (Feenstra and De Bruyn, 1979; Mann, 1997; Baker et al., 1998; Cheung and Venkitachalam, 2000). HAP precipitation may require a pH>10.5 (Claveau-Mallet et al., 2012).

HAP, the most thermodynamically stable Ca-phosphate phase (Koutsoukos and Valsami-Jones, 2004), has been found to be the precipitating compound in many materials e.g. opoka (Johansson and Gustafsson, 2000), Filtralite P, Filtra P, Polonite, wollastonite and Absol (Eveborn et al., 2009) and a variety of slags (Johansson and Gustafsson, 2000; Kim et al., 2006; Bowden et al., 2009; Claveau-Mallet et al., 2012). OCP was found in basic oxygen furnace slag (Bowden et al., 2009) and DCPD was the main mineral formed in calcined paper sludge (Wajima and Rakovan, 2013).

In used samples of Filtra P, no crystalline HAP, DCP or OCP were found in a study by Gustafsson et al. (2008); the phosphate phase that had formed during their experiment seemed to be poorly crystalline in nature. In their FTIR analyses, they found a peak that could be attributed to amorphous tricalcium phosphate (ATCP), but also to the presence of other poorly crystalline phosphate minerals (e.g. Al and Fe phosphates) or to adsorbed phosphate (Gustafsson et al., 2008). However, in a later study on used filter materials by Eveborn et al. (2009), in addition to ACP (>25%), crystalline Ca-phosphates (OCP or HAP) were also observed in Filtra P using X-ray absorption near edge structure (XANES) spectroscopy. In the same study, HAP was detected in Filtralite P and Polonite. In Filtralite P, a substantial part of the bound phosphorus (>35%) was also associated with Al and Fe phases (Eveborn et al., 2009). The authors found no systematic differences between P phases in samples loaded with real wastewater versus synthetic wastewater.

The above describes how HAP formation is important for P retention in filters. The growth of HAP crystals is affected by several parameters such as the pH (Kim et al., 2006; Claveau-Mallet et al., 2012; Mañas et al., 2012), residence time / flow velocity and composition of the water (Claveau-Mallet et al., 2012), and alkalinity (Johansson and Gustafsson, 2000). The optimum pH range for HAP crystallisation in powdered converter slag was 6.6 - 7.0 and 8.0 - 9.5 at P concentrations of 73 mg L$^{-1}$ and <5mg L$^{-1}$, respectively (Kim et al., 2006). Flow velocity was not observed to affect the growth rate.
of HAP crystal in electric arc furnace slag but a high velocity prevented settling and thus the organisation of crystals in a dense network; instead, it led to a loose accumulation of crystals in a dispersed space in the filter creating more confined voids (Claveau-Mallet et al., 2012). Alkalinity may also be important in limiting the extent of HAP precipitation; Ca-containing materials may be less efficient P retainers if the alkalinity is high because CO$_3^{2-}$ ions may remove Ca ions through calcite precipitation (Johansson & Gustafsson 2000). However, Kostura et al. (2005) found a strong positive correlation between acid neutralization capacity and P binding capacity in blast furnace slag where higher P binding capacity was observed in samples with high alkalinity.

2.2.4 Reaction time

In experimental and full-scale filters, the residence time of the wastewater in the filter is an important design parameter. The residence time should be long enough to allow for the P to react with Ca. For some materials, P sorption kinetics have been studied in batch experiments e.g. for blast furnace slags (Kostura et al., 2005) and boehmite (Li et al., 2012). In a batch test by Kostura et al. (2005), equilibrium began to establish after 8 hours. A more rapid reaction of Ca and P is reported by Li et al. (2012) who showed that HAP can form within minutes at pH 9 in the presence of boehmite.

The P-Ca-reaction time in different filter materials under conditions prevailing in P treatment filters has not been comprehensively investigated. Two studies suggested that this time might be relatively long. Drizo et al. (2002) reported that a residence time of at least 12 hours was needed for deposits of Ca-phosphate precipitates to occur on the surface of electric arc furnace slags. Amorphous Ca-phosphate, the precursor phase of HAP, needed <7 days to transform into HAP in granular sludge (Mañas et al., 2012).

2.3 Methods to investigate the phosphorus retention capacity of filter materials

Several methods have been used to determine the amount of P that can be retained by a potential filter material. Laboratory batch and filter (column or box) experiments have frequently been used (Johansson Westholm, 2006; Vohla et al., 2011), but also pilot and field studies of Polonite (Renman and Renman, 2010) and Filtralite P (Browne and Jenssen, 2005; Heistad et al., 2006; Ádám et al., 2006; Jenssen et al., 2010) exist.

2.3.1 Batch experiments

In batch tests that aim to determine the P binding capacity of a material, the reactive filter material is brought into contact with the solution until equilibrium is reached; the P binding capacity of the material is then determined from the difference between the initial and final P concentrations. It is also common practice to fit adsorption isotherms, such as Langmuir or Freundlich isotherms, to the laboratory data and to calculate the binding capacity from their slope. Batch tests are widely used to make an initial assessment of a material, as they are comparatively easy and cost-effective to carry out.
Among the commercial materials, Filtralite P and Polonite have been studied in batch tests. The P binding capacity of Filtralite P was determined to be 3.3 g P kg\(^{-1}\) (Ádám et al., 2005) and as high as 8 and 12 g P kg\(^{-1}\), at initial concentrations of 320 and 480 ppm, respectively (Jenssen and Krogstad, 2003). The P binding capacity of Polonite has been determined to be 119.6 g P kg\(^{-1}\) (Brogowski and Renman, 2004). Filtra P and Top16 have not been investigated using batch experiments.

The disadvantage of batch experiments is that they are carried out under conditions that differ substantively from those relevant to real-scale filters e.g. extensive contact between P and the material under aerobic conditions, excess P availability, and at room temperature. In addition, the amount of material tested is very small, jeopardising representativeness, and equilibrium is often only assumed but not actually reached (Ádám et al., 2005). Furthermore, the determined P binding capacity strongly depends on the experimental settings (Cucarella and Renman, 2009). For example, depending on the initial P concentrations used, the binding capacity determined in electric arc furnace slag varied by a factor of 13 (Drizo et al., 2002). The initial P concentrations vary substantially across the different studies. For these reasons, the P binding capacity determined for the material is not accurate and can be both higher and lower than that determined in filter experiments. An overestimation of the P binding capacity using batch experiments was observed for e.g. steel slag (Drizo et al., 2002) and Filtralite P (Jenssen et al., 2005). Underestimations were observed in sands (Arias et al., 2001), steel slags (Pratt and Shilton, 2009) and Filtralite P (Ádám et al., 2005).

### 2.3.2 Filter experiments on a laboratory and pilot scale

Due to the disadvantages of batch experiments discussed above, the use of long-term filter tests, in which the material is saturated, has been recommended (Drizo et al., 2002) and is more appropriate because the conditions better resemble those found in the field. Filter experiments have been carried out in laboratory filter columns on a variety of materials (Johansson Westholm, 2006; Vohla et al., 2011), among them Polonite and Filtra P (Gustafsson et al., 2008). Filtralite P has been studied in laboratory-scale boxes (Ádám et al., 2005). Similar to batch experiments but less pronounced, the conditions prevailing in filter experiments also differ from those relevant to the field and have differed considerably across the studies conducted to date. Therefore, the P binding capacities determined in filter experiments also vary. The P binding capacities of Filtra P, Filtralite P and Polonite determined at different scales and under varying conditions in previous studies are discussed further in section 2.4.

### 2.3.3 Field trials

Full-scale field experiments are the most reliable method to estimate the performance of a filter material. However, they are cost-intensive and time-consuming and, apart from Filtralite P, only a few studies on commercial alkaline filter materials exist. Filtra P and Top16 have not yet been studied at full-scale. Polonite was tested in a compact filter treating the primary wastewater of one household (Renman and Renman, 2010). Filtralite P was tested extensively in full-scale treatment of secondary wastewater.
filter treating wastewater from a school (Ádám et al., 2006), in a compact filter treating wastewater from three households (Heistad et al., 2006), in a Scandinavian study where three full-scale plants were tested in Norway, and two plants each in Denmark, Sweden and Finland (Jenssen et al., 2010), as well as in several other studies (Browne and Jenssen, 2005; Mateus and Pinho, 2010; Karabelnik et al., 2012). Results from the full-scale trials show that facilities using Filtralite P filters effectively remove P from wastewater over several years (Table 2).

2.4 Phosphorus retention in filter materials under varying conditions

The amount of P that can be bound to a material has been termed ‘adsorption capacity’ or ‘sorption capacity’ in previous studies (Ádám et al., 2005; Cucarella and Renman, 2009) (Ádám et al., 2007). The more neutral terms ‘binding capacity’ and ‘retention capacity’ have also been used (Brix et al., 2001; Arias, 2005; Drizo et al., 2008; Liira et al., 2009; Pratt and Shilton, 2009; Kõiv et al., 2010). The term ‘sorption’ comprises both adsorption and absorption. Adsorption is the process in which molecules adhere to the surface of a solid by London forces (physical adsorption), or by new chemical bonds (chemisorption) (Mortimer, 1986). Adsorptive processes have been observed in some filter materials such as steel slags (Pratt et al., 2007). However, in alkaline materials, the main retention mechanism is not adsorption but precipitation of Ca-phosphates as discussed in section 2.2. Therefore, the terms ‘binding capacity’ and ‘retention capacity’ appear to be more justified because they do not reference the retention mechanism.

2.4.1 Phosphorus retention in the filter materials determined in filter experiments at different scales

The retention of P in Filtra P, Filtralite P and Polonite has been studied in laboratory filter experiments, and Filtralite P and Polonite have also been studied at full-scale and in pilot scale studies. As results from batch tests have been shown to be inappropriate to be used for lifetime estimations (see section 2.3), this section focuses on the P retention behavior of the materials investigated in filter experiments. The operational conditions used and the P removal rates and / or P binding capacities determined from these investigations are shown for laboratory filters (Table 1) as well as for pilot-scale and full-scale filters (Table 2). The conditions during the tests varied and the results differ considerably across the studies. Generally, the loading rates applied were lower and the residence times higher in the field than in the laboratory (Tables 1 and 2). Across the laboratory studies, the filter bed sizes used range from 0.42 to 653 L and the residence times from 0.54 to 86 hours (Table 1). The bed sizes of the full-scale filters also varied; they ranged from 6 to 180 m³ with associated residence times of 4 to 33 days (Table 2).
Table 1  Filter design and operational conditions used in laboratory and pilot scale filters for testing P retention in Filtra P, Filtralite P and Polonite, n: number of investigated filters. d: days, w: weeks, yr: years, n.d.: not determined, PS: P solution, WWp and WWs: primary and secondary wastewater.

<table>
<thead>
<tr>
<th>Material</th>
<th>Filter bed size</th>
<th>Influent type</th>
<th>Loading rate L m⁻² d⁻¹</th>
<th>Residence time hours</th>
<th>Influent total P mg L⁻¹</th>
<th>Influent BOD mg L⁻¹</th>
<th>Run time</th>
<th>Saturation</th>
<th>P binding capacity g kg⁻¹</th>
<th>P removal rate %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtra P</td>
<td>3.9 L</td>
<td>PS</td>
<td>710</td>
<td>6</td>
<td>4.5</td>
<td>-</td>
<td>35w</td>
<td>no</td>
<td>n.d.</td>
<td>98.2</td>
<td>(Gustafsson et al., 2008)</td>
</tr>
<tr>
<td>Filtralite P</td>
<td>20 L</td>
<td>PS</td>
<td>357</td>
<td>3.5d</td>
<td>10</td>
<td>-</td>
<td>43w</td>
<td>yes</td>
<td>0.497</td>
<td>n.d.</td>
<td>(Ádám et al., 2007)</td>
</tr>
<tr>
<td>Filtralite P</td>
<td>20 L</td>
<td>WWs</td>
<td>318</td>
<td>3.8d</td>
<td>4.9</td>
<td>3.5</td>
<td>32w</td>
<td>no</td>
<td>0.473</td>
<td>n.d.</td>
<td>(Ádám et al., 2007)</td>
</tr>
<tr>
<td>Filtralite P</td>
<td>1.3 L</td>
<td>PS</td>
<td>255</td>
<td>10</td>
<td>2</td>
<td>-</td>
<td>1.5yr</td>
<td>(yes)</td>
<td>1.10</td>
<td>n.d.</td>
<td>(Ádám et al., 2005)</td>
</tr>
<tr>
<td>Filtralite P</td>
<td>1.3 L</td>
<td>PS</td>
<td>510</td>
<td>5</td>
<td>15</td>
<td>-</td>
<td>21w</td>
<td>yes</td>
<td>4.86</td>
<td>n.d.</td>
<td>(Ádám et al., 2005)</td>
</tr>
<tr>
<td>Filtralite P</td>
<td>3.9 L</td>
<td>PS</td>
<td>1020</td>
<td>2.5</td>
<td>15</td>
<td>-</td>
<td>1.5yr</td>
<td>no</td>
<td>10.14</td>
<td>99</td>
<td>(Ádám et al., 2006)</td>
</tr>
<tr>
<td>Polonite</td>
<td>3.9 L</td>
<td>PS</td>
<td>530</td>
<td>8</td>
<td>4.5</td>
<td>-</td>
<td>68w</td>
<td>no</td>
<td>n.d.</td>
<td>96.7</td>
<td>(Gustafsson et al., 2008)</td>
</tr>
<tr>
<td>Polonite</td>
<td>0.42 L</td>
<td>WWp</td>
<td>3031c</td>
<td>0.54</td>
<td>9</td>
<td>30.6</td>
<td>13w</td>
<td>no</td>
<td>1.14</td>
<td>81</td>
<td>(Nilsson et al., 2013a)</td>
</tr>
</tbody>
</table>

*only dissolved P measured in the influent and effluent  †laboratory box experiment  ‡recirculating batch mode
Table 2  Filter design and operational conditions used in full-scale filters and on-site pilot-scale filter columns with Filtra P, Filtralite P and Polonite treating secondary wastewater. d: days, h: hours, n: number of investigated filters, n.d.: not determined, n.p.: not presented.

<table>
<thead>
<tr>
<th>Material (scale)</th>
<th>Filter bed size</th>
<th>n</th>
<th>Loading rate</th>
<th>Residence time</th>
<th>Influent BOD</th>
<th>Influent total P</th>
<th>Effluent total P</th>
<th>P removal rate</th>
<th>Run time</th>
<th>Saturation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtralite P (full)</td>
<td>6</td>
<td>1</td>
<td>90-173 m³</td>
<td>4-8d</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;0.2</td>
<td>99.4</td>
<td>3</td>
<td>no</td>
<td>(Heistad et al., 2006)</td>
</tr>
<tr>
<td>Filtralite P (full)</td>
<td>5-25</td>
<td>4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>15</td>
<td>6.9</td>
<td>0.2</td>
<td>98</td>
<td>2-3</td>
<td>no</td>
<td>(Jenssen et al., 2010)</td>
</tr>
<tr>
<td>Filtralite P (full)</td>
<td>35-40</td>
<td>5</td>
<td>n.d.</td>
<td>n.d.</td>
<td>49</td>
<td>11</td>
<td>0.3</td>
<td>99</td>
<td>2-3</td>
<td>no</td>
<td>(Jenssen et al., 2010)</td>
</tr>
<tr>
<td>Filtralite P (full)</td>
<td>180</td>
<td>1</td>
<td>222</td>
<td>33d</td>
<td>n.d.</td>
<td>2.9</td>
<td>0.08</td>
<td>97</td>
<td>3</td>
<td>no</td>
<td>(Ádám et al., 2006)</td>
</tr>
<tr>
<td>Filtralite P (full)</td>
<td>90b</td>
<td>2b</td>
<td>1667b m³</td>
<td>6000b</td>
<td>1.8db</td>
<td>2db</td>
<td>5c</td>
<td>0.52</td>
<td>0.25</td>
<td>ca. 48</td>
<td>no</td>
</tr>
<tr>
<td>Polonite (pilot)</td>
<td>0.004</td>
<td>3</td>
<td>924</td>
<td>5.5h</td>
<td>120d</td>
<td>8</td>
<td>n.p.</td>
<td>76</td>
<td>0.3c</td>
<td>no</td>
<td>(Nilsson et al., 2013b)</td>
</tr>
<tr>
<td>Polonite (full)</td>
<td>0.035</td>
<td>2</td>
<td>76</td>
<td>n.d.</td>
<td>20</td>
<td>5.3</td>
<td>93</td>
<td>0.5</td>
<td>no</td>
<td>(Renman and Renman, 2010)</td>
<td></td>
</tr>
<tr>
<td>Polonite (pilot)</td>
<td>0.8</td>
<td>1</td>
<td>60</td>
<td>1-72h</td>
<td>n.d.</td>
<td>5f</td>
<td>0.7f</td>
<td>88</td>
<td>1.8</td>
<td>no</td>
<td>(Renman and Renman, 2010)</td>
</tr>
</tbody>
</table>

*average over the investigated filters  btwo filters in series  concentration of TOC  dprimary wastewater (septic tank effluent)

*excluding resting period  fdissolved P
2.4.2 Parameters influencing phosphorus retention in the filters

Several parameters, such as the filter design parameters and the operational conditions, influence P retention in the filters and the determined P binding capacity. These include the influent type, the influent P concentration, the hydraulic loading rate, the residence time, the scale of the filter and the ambient temperature. Some of these parameters have previously been studied to some extent.

Influent properties. In laboratory experiments, the type of influent used is important. Depending on whether wastewater or synthetic P solution is used, the P binding capacity determined can vary. It has been observed in batch experiments with blast furnace slag (Hedström and Rastas, 2006) and a column experiment with Filtralite P (Ádám et al., 2007) that the use of wastewater, rather than P solution, decreases P binding. However, the conditions in which the batch experiments by Hedström and Rastas (2006) were carried out did not resemble field conditions at all and the experiment by Ádám et al. (2007) was conducted with only two filter columns, fed with different influent P concentrations which may have confounded the effect of the influent source. Therefore, the effect of influent source on P binding capacity still needs to be evidenced. Additionally, the effect has not yet been quantified.

Properties of the influent that possibly influence P retention include the organic content and the P concentration. Recently, the effect of organic load on P removal of Polonite was studied (Nilsson et al., 2013b). In their on-site column experiment, the authors used primary (132 mg TOC L⁻¹) and secondary (43 mg TOC L⁻¹) wastewater and observed that an increased organic load decreased the P removal capacity of the material. The effect of varying the influent P concentration was studied by Ádám et al. (2005). The authors increased the P concentration of the P solution from 2 to 15 mg L⁻¹ and found an increase in P retention in a box experiment using Filtralite P.

Loading rate and residence time. The effect of residence time has been discussed in several studies (Brooks et al., 2000; Shilton et al., 2005; Barca et al., 2013) whereas the effects of loading rate on P retention and wash-out of particulate P have not been extensively studied. Generally, longer retention times were observed to promote P retention. Shilton et al. (2005) observed that increasing the residence time (3, 12, 48 and 96 hours) increased (ca. 10-fold) the P removal by an iron slag filter. The authors pointed out that the relationship was non-linear; at low residence times, the increase in P removal rate was bigger. Also, in electric arc and basic oxygen furnace slag, the P removal efficiencies improved with increasing residence time, probably due to a higher pH regime (Barca et al., 2013). The authors observed a pH of >9 at residence times >3 days whereas at shorter residence times (1−2 days), pH values were elevated only during the first five weeks and then stabilized below a pH of 9. Brooks et al. (2000) decreased the retention time in a filter column (filled with wollastonite powder and tailings at a ratio of 1:3) from 26 to 15 hours and observed a decrease of 11% in the percentage of P removed. In another column (with a ratio powder to tailings of 1:1), an increase in residence time from 54 to 143 hours did not affect the P removal (Brooks et al., 2000).
The loading rate governs the velocity of the solution in the pores of the filter material and can therefore be expected to affect the retention or wash-out of particulate P from the filter. Particulate P comprises P-containing (organic) particles in the wastewater and newly formed small Ca-phosphate particles. These aspects were discussed in a recent study by Claveau-Mallet et al. (2012) who observed particle leaching from their experimental columns, with residence times of 1.5 and 3.8 h, due to a high pore water velocity of 49 and 152 mm h⁻¹. In their column with a residence time of 16.3 h (pore water velocity 14 mm h⁻¹), they observed the water velocity to be low enough to allow particle settlement. At the higher velocities, the authors also observed that more new HAP seeds were formed and distributed over a wider area, creating confined voids and thus short-circuits, which was given as a reason for the lower retention capacity observed at higher velocities.

**Temperature.** The effect of temperature has not yet been comprehensively investigated. However, Barca et al. (2013) observed increased removal efficiencies when the temperature increased during their field experiment with steel slags, and Agyei et al. (2002) found that increases in temperature enhanced P binding to fly ash, slag and Portland cement. Furthermore, dissolved P is precipitated by Ca ions released by dissolving minerals e.g. wollastonite, which has temperature-dependent dissolution rates (Sverdrup, 1990). The precipitation of Ca-phosphates such as hydroxylapatite (HAP) is also affected by temperature because their solubility products (K) are temperature-dependent (Appelo and Postma, 1993). In addition, temperature controls crystal growth (Wang and Nancollas, 2008) and is thus important for the formation of HAP and other types of Ca-phosphate crystals. Temperature could also affect the performance of P filters indirectly by influencing growth rates of microbes in them.

### 2.5 Longevity estimations

One approach to estimate the approximate longevity of a filter unit is to extrapolate results from laboratory filters to the field. For example, the P binding capacity of a filter material determined from long-term laboratory column experiments (run until the material is saturated) can be used to calculate the time until the filter material would be saturated at full-scale (Drizio et al., 2002). Making predictions on the basis of adsorption isotherms derived from batch experiments has been shown to be inappropriate (Pratt and Shilton, 2009). Another suggested approach is the estimation of the expected P binding capacity of a material from its acid neutralisation capacity (Kostura et al., 2005; Yan et al., 2007), which might be used to predict the amount of available Ca in a material. Then, based on the Ca/PO₄ molar ratio for a given Ca-phosphate mineral, P retention capacity can be predicted (Yan et al., 2007).

Modelling has been suggested as another approach to estimate P retention (Claveau-Mallet et al., 2012; Barca et al., 2013). Barca et al. (2012) employed a reaction rate model derived by Kadlec and Wallace (2009) from the first-order kinetic removal rate equation to calculate the necessary filter volume as a function of the expected effluent total P concentration. The authors used a removal rate constant in the equation that equalled the P removal rate calculated from cold-season data of their full-scale filter. Claveau-Mallet et al. (2012) developed a conceptual model that they expressed for the
effluent pH over time as a function of three variables: the kinetic constant of dissolution of slag, the theoretical initial void volume and the crystal accumulation factor (introduced in the mathematical expression to consider the volume occupied by crystals and confined voids). The authors stated that knowing the expressions for these variables would allow a determination of how long the effluent pH would remain above a critical value such as 10.5 and thus allow an estimation of the longevity of the filter (Claveau-Mallet et al., 2012).

These reviewed approaches for estimating P retention neglect several important aspects, such as the influences of varying conditions. The model proposed by Claveau-Mallet et al. (2012) is just a conceptual one and contains variables that are difficult to estimate because they are dependent on several other (partly unknown) variables. Furthermore, it presumes a correlation of the P removal rate and the pH, which is uncertain; as well as the formation of HAP as the only retention mechanism (Claveau-Mallet et al., 2012) which is probably not the case in many filter materials. A more comprehensive approach to model P retention is most likely necessary, being one that takes into account the chemical reactions of the P in the filter and their dependence on varying conditions.
3.1 Materials

3.1.1 Filter materials

The filter materials used in the experiments (Fig. 2) were Filtra P, Filtralite P, Top16 and Polonite, all being commercial products. The properties of the materials are given in Table 3.

![Filter materials](image)

**Figure 2** Filter materials used in the experiments: clockwise from upper left, Filtra P, Filtralite P, Polonite and Top16.

Filtra P was manufactured from iron-containing gypsum and lime and was supplied by Nordkalk, Finland. The material is no longer available as the company stopped the production of the material ca. 2010. Filtralite P is derived from Norwegian lightweight aggregate and supplied by Weber Sain-Gobain Byggevarer, Norway. The Top16 material is manufactured by Envitop Ltd in Finland. Polonite is manufactured from Opoka rock in Poland that is heated to 900°C (Gustafsson et al., 2008) and is distributed by Bioptech AB, Sweden.
Table 3  Total element content in g kg\(^{-1}\) total solids (TS) and physical properties of the investigated filter materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Filtra P</th>
<th>Filtralite P</th>
<th>Top16</th>
<th>Polonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td></td>
<td>11.3</td>
<td>269</td>
<td>4.4</td>
<td>272</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td>355</td>
<td>35.7</td>
<td>203</td>
<td>167</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>4.57</td>
<td>86.1</td>
<td>4.82</td>
<td>31.2</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>3.24</td>
<td>56.5</td>
<td>78.6</td>
<td>17.5</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>1.44</td>
<td>29.2</td>
<td>0.992</td>
<td>7.84</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td>2.22</td>
<td>28.3</td>
<td>12.5</td>
<td>4.46</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td>0.1</td>
<td>n.d.</td>
<td>3.7</td>
<td>0.103</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>0.26</td>
<td>0.24</td>
<td>118</td>
<td>0.424</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td>n.d.</td>
<td>0.24</td>
<td>3.09</td>
<td>2.14</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td>0.69</td>
<td>n.d.</td>
<td>4.23</td>
<td>1.07</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>0.25</td>
<td>n.d.</td>
<td>0.046</td>
<td>0.28</td>
</tr>
<tr>
<td>TS [%]</td>
<td></td>
<td>87.7</td>
<td>n.d.</td>
<td>82.6 ± 0.3</td>
<td>96.1 ± 0.7</td>
</tr>
<tr>
<td>LOI [%TS]</td>
<td></td>
<td>9.9</td>
<td>n.d.</td>
<td>8.1</td>
<td>9.8</td>
</tr>
<tr>
<td>Bulk density [g cm(^{-3})]</td>
<td>1.079 ± 0.022</td>
<td>0.370(^a)</td>
<td>0.745 ± 0.023</td>
<td>0.781 ± 0.006</td>
<td></td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>0.446 ± 0.005</td>
<td>ca. 0.6(^a)</td>
<td>0.573 ± 0.008</td>
<td>0.560 ± 0.022</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)according to the product data sheet

3.1.2 Influent solutions

Two influent solutions were used in the experiments (Fig. 3): P solution prepared in the laboratory and secondary wastewater collected from two wastewater treatment plants in Luleå.

![Wastewater with stirring device and P solution](image)

Figure 3  Wastewater with stirring device (left) and P solution (right) used for the experiments.

The P solution was prepared by dissolving KH\(_2\)PO\(_4\) in distilled water. The secondary wastewater was collected from the municipal wastewater treatment plants in Sundom (downstream of a tower trickling filter, Paper III) and Ångesbyn (from the surface of the activated sludge basin, Paper IV). To obtain the target P concentrations, human urine was added to the wastewater from Sundom and a P solution based on KH\(_2\)PO\(_4\) added to the wastewater from Ångesbyn.
3.2 Methods

3.2.1 Batch experiments

The time needed for the P to react (reaction time) was determined in two sets (A and B) of batch experiments (Fig. 4). Set A (Paper I) was a high liquid-to-solid ratio (LS = 20 L kg\(^{-1}\)) batch shaking experiment with Filtra P. Set B (Paper III) was a non-shaking experiment with Filtralite P at a low LS ratio of 1.77 L kg\(^{-1}\) resembling that of full-scale filters.

**Figure 4** Set A (left) and set B (right) of batch experiments to determine the time needed for the P to react.

**Reaction time, set A.** For set A (Paper I), six series of batch experiments were carried out at initial concentrations of \(c_i = 3, 12, 25, 50, 100\) and 1000 mg P L\(^{-1}\). Samples of Filtra P were placed into Erlenmeyer flasks and equilibrated with P solutions at LS 20. The flasks were shaken on a shaking plate at 100 rpm for 0.5, 1, 2, 4 and 48 hours and additionally for the concentrations \(c_i = 100\) and 1000 mg P L\(^{-1}\), for 8 and 24 hours. The liquid phase was then filtered through a 0.45 mm filter and analysed with respect to dissolved P. The pH of the unfiltered samples was measured.

**Reaction time, set B.** For set B (Paper III), two series of batch experiments were carried out in duplicate (\(n = 2\)): one was conducted using P solution and the other one using wastewater. The concentration of dissolved P was 12 mg L\(^{-1}\) in the P solution and 11 mg L\(^{-1}\) in the wastewater (collected from Sundom’s treatment plant). Samples of 201.9 g of Filtralite P (corresponding to ca. 200 g of dry material) were weighed into 1 L glass beakers. Then, \(353.5 \pm 9.0\) g of phosphate solution was added to one set of beakers and \(356.7 \pm 7.9\) g of wastewater was added to the other set of beakers until the material was almost covered but did not start floating upwards. The beakers were covered with plastic sheets and left standing at room temperature for 5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h and 16 h. The liquid phase was then filtered through a 0.45 mm filter and analysed with respect to dissolved P. The pH of the unfiltered samples was measured.
3.2.2 Filter column experiments

**Experimental design.** To investigate the effects of influent P concentration, influent type, loading rate and temperature on P retention in filters, three filter column experiments (experiment A (Paper II), B (Paper III) and C (Paper IV)) were carried out using $2^2$ full factorial designs (Montgomery, 2009) with replicates ($n = 2$). In experiment B, three centre points were added while in experiments A and C, no centre points were included. The investigated factors and their settings are shown in Table 4. The low level of P concentration (12 mg L$^{-1}$) reflected the typical concentrations in untreated on-site wastewater (Swedish EPA, 2006) and also resembled the P concentrations of secondary effluent in on-site facilities that have been found to be between 5 and 14 mg L$^{-1}$ (Arias et al., 2003). The low level for loading rate (varying between 96 and 419 L m$^{-2}$ d$^{-1}$ across the three experiments) resembled the loading rates commonly present in compact full-scale filters i.e. in small filter units, typically filter wells. The high levels of P concentration (50 mg L$^{-1}$) and loading rate (1023 (experiment A) and 1122 L m$^{-2}$ d$^{-1}$ (experiment B) reflected extreme conditions aimed at accelerating the laboratory testing. The low level for temperature (4.3°C) resembled the operational conditions that are likely to prevail in full-scale filters for a substantial part of the year, particularly in areas with cool climates, while the high level for temperature (16.5°C) reflected conditions that are usually present during laboratory testing.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Investigated factors and experimental settings in the three filter column experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Variable</strong></td>
<td><strong>A</strong> (Paper II)</td>
</tr>
<tr>
<td>Investigated factors</td>
<td>influent P concentration</td>
</tr>
<tr>
<td>loading rate</td>
<td>loading rate</td>
</tr>
<tr>
<td>Influent solution</td>
<td>P solution 12 mg P L$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>P solution 50 mg P L$^{-1}$</td>
</tr>
<tr>
<td>Loading rate [Lm$^{-2}$d$^{-1}$]</td>
<td>419; 1023</td>
</tr>
<tr>
<td>Temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials</td>
<td>Filtra P</td>
</tr>
</tbody>
</table>

$^a$spiked with urine $^b$spiked with K$_2$HPO$_4$

**Experimental set-up.** Using peristaltic pumps, the influent solution was passed in up-flow mode through the filter columns and the effluent was collected in 20L- plastic containers (Fig. 5). The columns were made of acrylic glass and had an inner diameter of 74 mm. A layer of glass beads was placed on the bottom of the columns to ensure an even flow distribution. The outlet of the columns was funnel-shaped and also filled with glass beads to ensure a smooth outflow (Fig. 5).
**Figure 5** Experimental set-up used for the three filter column experiments.

**Effluent sampling.** Twice weekly, the weight of the effluent was recorded and samples were taken for the analyses of total and dissolved P, total and dissolved organic carbon (TOC and DOC, only in experiments B and C), total suspended solids (TSS), and for measuring the turbidity (only in experiment A). The pH and redox potential were measured from grab samples taken at the same time as the effluent samples. During sampling, the flow through the filters was interrupted for some hours.

**Data evaluation.** To determine the points of breakthrough and filter saturation, threshold values were defined for the ratio of effluent dissolved P to influent dissolved P (Table 5). The point of breakthrough was defined based on an effluent P concentration of 1 mg L⁻¹, a figure normally used as the discharge limit for small-scale wastewater facilities in Norway (Heistad et al., 2006) and also given as a guidance value by the Swedish Environmental Protection Agency (Swedish EPA, 2006). Breakthrough and saturation points were identified using simple moving averages. P binding capacities were calculated according to eq. 1.

\[
P \text{ binding capacity} \ [\text{g kg}^{-1}] = \frac{\sum_{i=1}^{n} (c_{i\text{in}} - c_{i\text{out}}) \cdot V_{i}}{m}
\]  

(1)

where:

- \(n\) number of samples taken until saturation,
- \(c_{i\text{in, out}}\) concentration of total, dissolved or particulate P in the influent and effluent [mg L⁻¹],
- \(V_{i}\) volume of P solution or wastewater that has passed through the filter between sample \(i-1\) and \(i\) [L], and
- \(m\) mass of the filter material [g].
Data were further evaluated using analysis of variance (ANOVA) and multiple linear regression and the MODDE software package (Umetrics AB, 2006). The significance level was set to $\alpha = 0.05$.

### Table 5

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Threshold for breakthrough</th>
<th>Threshold for saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$\geq 0.08$; $\geq 0.02$</td>
<td>$\geq 0.85$</td>
</tr>
<tr>
<td>B</td>
<td>$\geq 0.08$</td>
<td>$\geq 0.92$</td>
</tr>
<tr>
<td>C</td>
<td>$\geq 0.08^a$</td>
<td>$&gt; 0.8$</td>
</tr>
</tbody>
</table>

*a* ratio of effluent total P concentration to the influent total P concentration was used.

**Power analysis.** Statistical power (the probability of rejecting a false statistical null hypothesis, eq. 2) was calculated retrospectively for the three column experiments to evaluate whether the effects of the factors on the total P binding capacities (calculated considering data from the entire breakthrough curves) of the investigated materials were reliably determined. The total P binding capacity comprises both the retained dissolved P and the retained or washed out particulate P i.e. the whole quantity of retained P for the wastewater columns and the whole quantity of reacted P for the P solution columns. The null hypotheses in the factorial experiments were that there was no effect caused by the investigated factors and their interactions on P binding capacity.

$$
\text{power} = 1 - F(f_{\alpha}; 1, v, \lambda)
$$

where:
- **power** = probability of rejecting a false null hypothesis,
- **F** = probability of the F distribution,
- **f_{\alpha}** = critical value (upper point of the F distribution with 1 and $v$ degrees of freedom) with $\alpha = 0.05$,
- **v** = degrees of freedom for error, and
- **$\lambda$** = noncentrality parameter, $\lambda = n * r * \delta^2 / (4\sigma^2)$, where $n$ is the number of replicates, $r$ the number of corner points, $\delta$ the effect and $\sigma$ the estimated standard deviation.

For the calculations, the number of factors (two), the number of corner points (four) and the number of replicates (two) were predetermined by the experimental designs and were the same for all three experiments. The number of centre points was zero in experiments A and C, and three in experiment B. The significance level was set to $\alpha = 0.05$. The standard deviation ($\sigma$) was the square root of the mean square error (MS error) which was estimated based on the collected data. MS error equals the error sum of squares divided by the error degrees of freedom (MS error = $SS_{\text{error}}/df_{\text{error}}$). MS error was calculated using non-transformed data and omitting insignificant model terms. The minimum detected effect that was of interest was specified as 25% of the average total P binding capacity of the respective experiment. This effect is the difference between the low and high factor level means of total P binding capacity. The Minitab software package (Minitab Inc., 2010) was used for the calculations.
3.2.3 Phase identification with X-ray diffraction and infrared spectroscopy

To identify the mineral phases present in the filter material both before and after use, X-ray powder diffraction (XRPD, Papers II, IV, V) and Fourier transform infrared (FTIR) spectroscopy (Paper V) were used. XRPD gives information about the crystalline phases while the presence of specific molecular configurations can be obtained from FTIR (Hillier et al., 2003).

In the outflow hose of the Filtra P columns (experiment A), a white precipitate had formed which was analysed using XRPD. Both fresh and used samples of Filtralite P (used sample from a filter loaded with P solution), Top16 and Polonite were analysed using XRPD. Fresh and used samples (from columns fed with P solution) of Filtralite P (Paper V) were also analysed using FTIR.

**XRDPD.** The precipitate that had formed in the outflow hose of the Filtra P columns (experiment A) was sampled and dried with XRPD analyses being carried out using a SIEMENS D5000 X-ray diffractometer with a KRISTALLOFLEX 760 X-ray generator. Used and fresh samples of Filtralite P, Top16 and Polonite for XRPD analyses (Papers IV, V) were wet ground and spray-dried to produce random powders, then their XRPD patterns were recorded from 2 to 75° 2θ using Cobalt Kα radiation. The obtained XRPD patterns were compared to reference patterns from the International Centre for Diffraction Database.

**FTIR.** Filtralite P samples were ground in a mortar, mixed with potassium bromide and pressed into pellets that were analysed using a Bruker IFS66v/S FTIR spectrometer.

3.2.4 Hydro-geochemical transport modelling

The hydro-geochemical transport code PHREEQC (Parkhurst and Appelo, 2012) was used to model the transport and reaction of P observed in experimental filter columns filled with Filtralite P that were fed with P solution (experiment B, described in detail in section 3.2.2 and in Paper III). PHREEQC uses the one-dimensional advection-reaction-dispersion equation (eq. 3):

\[
\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D_L \frac{\partial^2 c}{\partial x^2} - \frac{\partial q}{\partial t}
\]

where:
- \(t\) is time (s),
- \(C\) is the concentration in water (mol/kgw),
- \(v\) is flow velocity (m s\(^{-1}\)),
- \(x\) is distance in the main flow direction (m),
- \(D_L\) is the longitudinal dispersion coefficient (m\(^2\) s\(^{-1}\)), and
- \(q\) is the concentration in the solid phase (mol/kgw).

Two models were developed (model 1 and model 2, Paper V). Effluent data from replicated (n = 2) filters run at a loading rate of 97 ± 3 L m\(^{-2}\) d\(^{-1}\) were used to calibrate the models.
**Hydro-geochemical model parameters.** The influent properties used in the models resembled those in the experiment: the influent temperature was set to 20°C, pH was 5, redox potential (pe) was 5.1, and the concentrations of PO$_4^{3-}$ and K were 39.9 and 16.136 mg L$^{-1}$, respectively. The influent solution was brought to equilibrium with atmospheric CO$_2$. The dissolving minerals in both models were wollastonite and Ca oxide (both kinetically dissolved, see Paper V for details) and, additionally in model 2, calcite which was assumed to be at equilibrium and was allowed to precipitate and dissolve. To fit the models to the experimentally-derived breakthrough curves (model calibration), three parameters were adjusted for wollastonite and Ca oxide: the initial molar concentration of the mineral, the specific dissolution rate and the initial surface area of the solid. For calcite in model 2, only the initial molar concentration was varied.

**Transport model parameters.** The transport parameters used were the molecular diffusion coefficient ($D_m$) and the dispersivity. $D_m$ was determined as $1.295 \times 10^{-9}$ m$^2$ s$^{-1}$ using the Wilke and Chang equation (Wilke and Chang, 1955). The longitudinal dispersion ($D_L$), and thus the dispersivity, was studied by simulating a tracer column experiment using packed-bed models of spherical particles with a ratio of maximum to minimum particle diameter in the range of 1 - 4 (Paper VI). Based on the simulations, a $D_L/D_m$ versus Péclet number plot was produced.

### 3.2.5 Analyses

To determine the concentrations of dissolved P and DOC, samples were filtered immediately through 0.45μm filters, and subsequently analysed for total P and TOC. Total P and TOC were determined for unfiltered samples. Samples (both filtered and unfiltered) used for determining the concentrations of P and organic carbon were acidified and stored at 5°C until analysis. Samples for BOD$_7$ analysis were stored frozen at -18°C.

For set A of the reaction time experiment (Paper I), concentrations of dissolved P were analysed using an inductively coupled plasma (ICP) technique, without prior digestion, as the sample was assumed to be totally dissolved during the procedure. In all other experiments (Papers II – IV), concentrations of total P in unfiltered and filtered samples were determined using the ammonium molybdate spectrometric method, also known as the ascorbic acid method (Swedish Standards Institute, 2005b).

Concentrations of TOC in unfiltered and filtered samples (Papers III, IV) were determined using Hach Lange cuvette tests as defined by the method EN 1484. BOD$_7$ (Paper IV) was determined according to the standard methods SS-EN 1899-1 and SS-EN 25814. TSS (Papers II - IV) was determined following the European standard EN 872: 2005 (Swedish Standards Institute, 2005a). The pH (Papers I - IV) was measured using a WTW pH330 pH meter with a WTW SenTix41 pH electrode. The redox potential (Papers II-IV) was measured using a pHM95 pH/ion meter (Radiometer, Copenhagen).
4 RESULTS

4.1 Properties of the materials used in the experiments

4.1.1 Phase identifications

**XRPD (Papers II, IV, V).** The phases detected in fresh and used samples of Filtralite P, Top16 and Polonite using XRPD are shown in Table 6. Calcite and quartz were detected in all three materials. The fresh samples of Top16 contained gypsum (CaSO$_4$·2(H$_2$O)) and bassanite (CaSO$_4$·0.5(H$_2$O)) and those of Polonite contained wollastonite (CaSiO$_3$) and portlandite (the naturally occurring form of Ca(OH)$_2$, Table 6). For Filtralite P, there was a large proportion of amorphous material in both fresh and used samples, but no obvious Ca-bearing silicates were identified. Some minerals disappeared from the materials during the experiments as they were present in the fresh samples but were not detected in the used ones: gypsum and bassanite disappeared from Top16 and portlandite from Polonite. No crystalline Ca-phosphate phases were found in the used samples of Filtralite P, Top16 and Polonite; however, the white precipitate that had formed in the outflow hose of the Filtra P columns was found to be hydroxyapatite (HAP, Table 6).

**Table 6** Phases detected in the materials before and after use in the filter experiments using XRPD (n.d.: not determined).

<table>
<thead>
<tr>
<th>Material</th>
<th>Phases identified</th>
<th>Phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtra P</td>
<td>n.d.*</td>
<td>HAP*</td>
</tr>
<tr>
<td>Filtralite P</td>
<td>amorphous phases,</td>
<td>amorphous phases,</td>
</tr>
<tr>
<td></td>
<td>quartz, feldspars,</td>
<td>quartz, feldspars,</td>
</tr>
<tr>
<td></td>
<td>calcite,</td>
<td>calcite,</td>
</tr>
<tr>
<td></td>
<td>periclase,</td>
<td>periclase,</td>
</tr>
<tr>
<td></td>
<td>possibly spinel phases</td>
<td>possibly spinel phases</td>
</tr>
<tr>
<td>Top16</td>
<td>quartz, gypsum,</td>
<td>quartz, calcite,</td>
</tr>
<tr>
<td></td>
<td>bassanite</td>
<td>no gypsum, no bassanite,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>no crystalline calcium phosphates</td>
</tr>
<tr>
<td>Polonite</td>
<td>quartz, calcite,</td>
<td>quartz, calcite,</td>
</tr>
<tr>
<td></td>
<td>wollastonite, portlandite</td>
<td>wollastonite, no portlandite,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>no crystalline calcium phosphates</td>
</tr>
</tbody>
</table>

*hydroxyapatite, detected in the white precipitate that had formed in the outflow hose of the Filtra P columns

**FTIR (Paper V).** The FTIR spectra of both fresh and used Filtralite P indicated the presence of calcite, silicate and possibly clay minerals. Other peaks (only in the spectrum of the fresh sample) were possibly due to the presence of Mg-rich biotite and Ca(OH)$_2$. A further peak at 446 cm$^{-1}$ is indicative of the presence of hematite in Filtralite P.
spectrum of the used sample indicated the presence of a phosphate mineral. The peak was not sufficiently well resolved to allow identification, but its general position was consistent with expectations of amorphous tricalcium phosphate (ATCP) (Gustafsson et al., 2008).

4.1.2 Phosphorus retention

The P binding capacities of the studied materials that were determined under similar conditions (Papers II - IV) are overlaid in Fig. 6 for comparison. The prevailing conditions during these filter experiments were as follows:

- The experiments were carried out at room temperature (not monitored).
- The influent P concentration reflected the typical concentrations in untreated wastewater at full-scale on-site facilities, ca. 12 mg L⁻¹ (Swedish EPA, 2006).
- The loading rates (varying between 96 and 419 L m⁻² d⁻¹ across the three experiments) complied with the loading rates commonly present in compact full-scale filter units. These loading rates range from 177 to 943 L m⁻² d⁻¹ in filter wells with a diameter of 900 to 1200 mm used by two to four people with a daily water consumption of 100 to 150 L d⁻¹. Loading rates ranging from 90 to 173 L m⁻² d⁻¹ have been reported in a filter tank filled with Filtralite P (Heistad et al., 2006).

Figure 6 P binding capacities of the four materials (n = 2), calculated considering data from the entire breakthrough curves, investigated at room temperature. The figure shows the amounts of retained dissolved P, as well as the amount of washed-out particulate P from the P solution-fed filters, and the amount of retained particulate P in the wastewater-fed filters.
Figure 7  (a) Ratio of total P concentrations in the effluent and influent with level of breakthrough shown as dashed line, (b) ratio of dissolved P concentrations in the effluent and influent, and (c) pH of the effluent of the filter columns filled with the four investigated materials.
Fig. 6 shows that the P binding capacities determined differed substantially between the investigated materials. The amount of washed-out particulate P from the filter columns loaded with P solution differs considerably between Filtra P and Filtralite P, while the amount of retained particulate P in the filters loaded with wastewater (Filtralite P, Top16 and Polonite) is rather constant.

The P binding capacities were calculated according to eq. 1 using the effluent data that are visualized in the breakthrough curves (Fig. 7). Both the total (Fig. 7a) and dissolved P (Fig. 7b) concentrations of the effluents, proportional to the influent total and dissolved P concentrations, are shown. The shape of the determined breakthrough curves differed between the materials (Fig. 7a, b) e.g. the breakthrough of dissolved P occurred much earlier in Filtralite P and Top16 compared to Polonite and Filtra P (Fig. 7b). Also, the pH of the effluents varied across the materials studied (Fig. 7c). The pH in the effluent of the Top16 columns was consistently around 8, whereas the pH of the other materials was initially high and decreased during the experimental runtime.

![Figure 8](image)

*Figure 8*  Filtra P (left), Top16 (centre) and Polonite (right) in the experimental columns after saturation.

Filtra P and Top16 disintegrated during the filter column experiments while Polonite and Filtralite P did not show any signs of disintegration (Fig. 8). Despite the disintegritive behaviour of Filtra P and Top16, clogging was not observed.

### 4.1.3 Time needed for the phosphorus to react

**Set A (Paper I).** In the experiments with Filtra P, the shortest chosen contact time (0.5 hours) was sufficient to completely remove dissolved P from the solution, when an initial P concentration of 12 mg L\(^{-1}\) was used (Fig. 9a). The same was valid for the initial concentrations of 3 and 25 mg L\(^{-1}\) (Paper I). At an initial P concentration of 100 mg L\(^{-1}\), the concentration of dissolved P decreased by only 20% within 0.5 hours and it took 8 hours for the entire amount of dissolved P to react. A complete removal of dissolved P coincided with a high pH (Fig. 9b): at the initial concentration of 12 mg L\(^{-1}\) the pH was already high (11.9) after 0.5 hours, whereas at the initial concentration of 100 mg L\(^{-1}\), the high pH (11.7) was reached after 8 hours (Fig. 9b).
Set B (Paper III). In the experiments with Filtralite P, the concentration of dissolved P could be reduced to below the detection limit within 5 minutes reaction time when P solution was used (Fig. 9c). The pH after 5 minutes was measured at 11.8 (Fig. 9d). Using wastewater, more time (15 minutes) was required to decrease the concentration of dissolved P and it did not decrease as much (it had decreased by 99%, Fig. 9c). The pH established after 15 minutes was 11.4 (Fig. 9d).

4.2 Phosphorus binding capacity under varying conditions

4.2.1 Effect of influent properties

The effect of two influent characteristics on the P binding capacity was investigated. First, the P concentration was varied using P solution (experiment A, Paper II). Second, two influent types were tested in experiment B; P solution and secondary wastewater (Paper III). Both parameters affected the P binding capacity (Fig. 10) as discussed in the following.

Influent P concentration (Paper II). The total P binding capacity of Filtra P calculated using data from the entire breakthrough curve (until saturation) decreased when the influent P concentration was increased from 12 to 50 mg L\(^{-1}\) (Fig. 10);
however, this difference in P binding capacity was not significant ($\alpha = 0.05$). When the higher influent concentration was used, breakthrough occurred at a significantly lower number of treated bed volumes (56 compared to 327 average bed volumes for low-concentration filters). Also, the average pH in the effluent was significantly decreased in the high concentration filters and the pH drop occurred earlier. Furthermore, when P binding capacities were calculated considering only pre-breakthrough data, there was a significant effect of influent P concentration: the total P binding capacity was, on average, twice as low in filters treated with the high concentration than in low concentration filters, which can be explained by the early breakthrough and lower pH regime in the high concentration filters.

**Influent type (Paper III).** Using secondary wastewater as an influent instead of P solution significantly decreased the P binding in Filtralite P (Fig. 10). Both the total P binding capacity and the amount of dissolved P retained in the filters were affected. The total P binding capacity comprises the retained dissolved P and the washed-out (P solution filters) or retained (wastewater filters) particulate P. Using secondary wastewater as an influent instead of P solution also significantly decreased the start pH and mean pH in the filters. The start pH was, on average, 9.2 in the wastewater filters as opposed to 10.5 in the P solution filters.

![Figure 10](image_url)

**Figure 10** P binding capacities of Filtra P determined at different influent P concentrations using P solution and an average loading rate of 419 L m$^{-2}$ d$^{-1}$ and P binding capacities of Filtralite P determined using P solution and wastewater and an average loading rate of 96 L m$^{-2}$ d$^{-1}$, $n = 2$. P binding capacities were calculated using data from the entire breakthrough curves.
Table 7  Properties of the influent wastewater used in experiment B and C (as measured at the higher temperature) shown as mean ± standard deviation (n.d.: not determined).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td>Total P</td>
<td>mg L⁻¹</td>
<td>13 ± 3.6</td>
</tr>
<tr>
<td>Dissolved P</td>
<td>mg L⁻¹</td>
<td>11 ± 1.7</td>
</tr>
<tr>
<td>TOC</td>
<td>mg L⁻¹</td>
<td>126 ± 34</td>
</tr>
<tr>
<td>DOC</td>
<td>mg L⁻¹</td>
<td>108 ± 8</td>
</tr>
<tr>
<td>BOD₇</td>
<td>mg L⁻¹</td>
<td>n.d.</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.1 ± 0.1</td>
</tr>
<tr>
<td>Redox potential</td>
<td>mV</td>
<td>127 ± 31</td>
</tr>
<tr>
<td>TSS</td>
<td>mg L⁻¹</td>
<td>87 ± 104</td>
</tr>
</tbody>
</table>

The properties of the wastewater used in experiment B are shown in Table 7. This wastewater was collected from the activated sludge basin and was spiked with urine. Its properties were compared to the properties of the wastewater collected after the trickling tower and spiked with KH₂PO₄, which was used in experiment C. The concentrations of DOC, TOC and TSS differed considerably between the two wastewaters (Table 7).

4.2.2 Effect of loading rate

The effect of increasing the loading rate on the total P binding capacity and the amount of P retained in Filtra P (Paper II) and Filtralite P (Paper III) was investigated. Here, the total P binding capacity comprises both the amount of P retained in the filters and the

Figure 11  P binding capacities of Filtra P and Filtralite P determined at the different loading rates using P solution as an influent with total P concentrations of 12 mg L⁻¹ (Filtra P) and 13 mg L⁻¹ (Filtralite P).
amount of particulate washed-out P i.e. it is the sum of the amount of dissolved P that reacted with the filter material. The amount of P retained is the part of the reacted dissolved P that was retained in the filter columns. The total P binding capacities and amounts of retained P determined at the different loading rates but under similar conditions (using P solution as an influent source with concentrations of total P comparable to those at full-scale, and the P binding capacities calculated using data from the entire breakthrough curves) are shown in Fig. 11.

In experiment A with Filtra P, the total P binding capacity was higher at the higher loading rate (Fig. 11) but this increase was not statistically significant. Increasing the loading rate did not affect the amount of retained P in Filtra P but it significantly increased the amount of washed-out particulate P. In experiment B with Filtralite P, increasing the loading rate significantly decreased both the total P binding capacity and the amount of retained P (Fig. 11). The amount of washed-out particulate P from Filtralite P was very low at the low loading rate and increased at the higher loading rates (Fig. 11).

4.2.3 Effect of ambient temperature

Increasing the temperature from 4.3 to 16.5°C significantly increased the total and dissolved P binding capacity of Top16 and Polonite (Fig. 12). It also increased the average redox potential and the reduction of TSS, TOC and particulate organic carbon determined for both materials (Paper IV). The pH was not affected by temperature in either material.

![Figure 12](image-url)  
**Figure 12** Total P binding capacities of Top16 and Polonite determined at 4.3 and 16.5°C.
4.3  Power analysis

Statistical power (the probability of rejecting a false statistical null hypothesis, eq. 2) was calculated retrospectively for the three column experiments (Table 8) to evaluate whether the effects of the factors on the total P binding capacities of the investigated materials were reliably determined. A high value of power (1) was determined for experiment C (Table 8) which means that there was a 100% probability of rejecting a false null hypothesis and thus detecting an effect if it really existed. Power was lower in experiment A (22%) and B (43%, Table 8). The number of replicates that would have been necessary to obtain a power of 80% was 9 and 5 for experiment A and B, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment A (Filtra P)</th>
<th>Experiment B (Filtralite P)</th>
<th>Experiment C (Top16, Polonite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>power</td>
<td>0.22</td>
<td>0.43</td>
<td>1</td>
</tr>
<tr>
<td>factors with significant effect</td>
<td>none</td>
<td>loading rate, influent type</td>
<td>temperature, material</td>
</tr>
<tr>
<td>terms omitted from the regression model in the power calculation</td>
<td>concentration, loading rate</td>
<td>interaction: loading rate $\times$ influent type</td>
<td>none</td>
</tr>
<tr>
<td>$\sigma = \sqrt{MS\ error}$</td>
<td>1.60</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>minimum effect [g P kg$^{-1}$]</td>
<td>1.6</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>number of replicates needed to obtain a power of 0.8$^a$</td>
<td>9</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>(actual power = 0.82)</td>
<td>(actual power = 0.87)</td>
<td>(actual power = 1)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ no terms omitted from model

4.4  Models describing phosphorus retention

Two hydro-geochemical transport models were developed using the PHREEQC software, model 1 and model 2 (Paper V). Model 1 satisfactorily described the experimentally observed concentrations of dissolved P in the effluent (Fig. 13a) but did not match the observed pH well. The modelled pH matched the observed pH up to ca. 40 bed volumes, but deviated from it at $> 40$ bed volumes (Fig. 13b). Therefore, a second model was developed which described the measured pH well (Fig. 13b) but strongly underestimated the concentrations of dissolved P in the effluent (Fig. 13a).
In both models, the phases that were subject to kinetically constrained dissolution were wollastonite and calcium oxide (CaO). The possible precipitating Ca-P phases chosen for inclusion in both models were amorphous tricalcium phosphate (ATCP), dibasic calcium phosphate dehydrate (DCPD), octacalcium phosphate (OCP), calcite (CaCO₃) and amorphous silica (SiO₂(a)). Model 2 additionally included an initial amount of calcite so that both dissolution and precipitation of calcite were possible.

The developed $D_L/D_m$ versus Pécelt number plot (Paper VI) was used to estimate the dispersivity. First, the $D_L$ present in the experimental columns was estimated from the plot. Assuming a tortuosity of ca. 0.7, the dispersivity was calculated to be 0.00033 m.

![Diagram](image.png)

**Figure 13** Modelled and measured ($n = 2$) concentrations of dissolved P with modelled Ca concentrations (a) and modelled and measured pH (b) in the effluent of the Filtralite P columns.
5 DISCUSSION

5.1 Phosphorus retention mechanisms in the materials

The dissolution of Ca ions from the filter material to the water phase, their reaction with dissolved P and subsequent precipitation of Ca-phosphates can be assumed to be the major P retention mechanism in alkaline filter materials (Gustafsson et al., 2008; Eveborn et al., 2009). Thus, this retention mechanism was important in the filter materials investigated in this study, as they were characterised by a high Ca content (Table 3) and were alkaline, as reflected in the high pH in the effluents of the column experiments (Fig. 7) and supernatants of the batch experiments (Fig. 9 b, d). The P-containing precipitates formed showed a tendency to be washed out of the filter columns (e.g. Fig. 11) which decreased P retention. In the following, both the mineral phases responsible for the release of Ca ions and the Ca-phosphate phases forming in the filters are discussed based on the results from the XRPD and FTIR investigations and the geochemical simulations. In addition, the retention / wash-out of the formed precipitates are discussed.

5.1.1 Dissolving phases

The mineral phases releasing the Ca ions required for the reaction with the dissolved P differed between the investigated materials. Filtra P was manufactured from iron-containing gypsum and limestone and thus these phases, or their conversion products formed during manufacture, were probably the main dissolving phases. The dissolution of lime (calcium oxide, CaO, and/or calcium hydroxide, Ca(OH)₂) in Filtra P was confirmed by the initially very high pH of above 12 (Fig. 7c). The Ca-releasing phases in Filtralite P could not be detected using XRPD, possibly because they were amorphous (there were large proportions of amorphous material in both fresh and used Filtralite P, Table 6). Filtralite P was derived from Norwegian lightweight aggregate which is based on clay (Jenssen and Krogstad, 2003). Probably, lime (CaO) and a Ca-silicate were the phases supplying Ca ions, which was shown by the hydro-geochemical transport models developed. However, lime was not detected using XRPD (Table 6), probably due to its low concentration. In Top16, gypsum (CaSO₄·2(H₂O)) and bassanite (CaSO₄·0.5(H₂O)) appeared to be responsible for the supply of Ca ions, as these phases disappeared from the materials during the column experiments (Table 6). Both Top16 and Filtra P disintegrated during the experiments while Filtralite P and Polonite were stable (Fig. 8). The gypsum content was a characteristic that Top16 and Filtra P had in common and that probably caused the disintegration, something observed in a previous study on Filtra P (Gustafsson et al., 2008). In Polonite, the phases, detected using XRPD (Table 6), that probably dissolved and released Ca ions to the solution were wollastonite and portlandite (the naturally occurring form of Ca(OH)₂), the latter having disappeared from the material during the column experiments. Polonite was manufactured from siliceous sedimentary opoka rock which consists mainly of SiO₂ and CaCO₃ (Brogowski and Renman, 2004) and was found to contain wollastonite in a previous study (Kietlinska...
and Renman, 2005). Calcite may have also dissolved; it was detected in the fresh Polonite samples but not in the used ones. However, in Filtralite P, calcite was detected in both fresh and used samples and the geochemical simulations suggested that calcite did not dissolve but precipitated.

If lime (CaO or Ca(OH)₂) is present in the filter material, both the concentration of available Ca ions in the solution and the pH are increased in the solution, and thus the reaction of Ca and dissolved P is promoted. Readily dissolving lime in Polonite (Table 6) and Filtralite P associated with the initially high pH (Fig. 7c) caused the dissolved P to initially react completely and rapidly as reflected by the low concentrations of dissolved P in the effluents (low values of \( \frac{C_{\text{dissolved}}}{C_0} \) in the breakthrough curves, Fig. 7b). However, these readily formed Ca-phosphates tended to escape from the filters as reflected by the large amount of washed-out particulate P from the Filtra P columns (Fig. 10), the difference between dissolved P and total P concentrations in the effluents of the Polonite columns (first few samplings) and also Filtralite P columns (first sampling only, Fig. 7a, b). In addition, lime was rapidly dissolved and then depleted as reflected in the initially very high and then decreasing pH (Fig. 7c). The depletion of lime was also observed in the hydro-geochemical transport models. Hence, high lime content supports P retention only initially and also appears to cause a wash-out of particulate P.

5.1.2 Precipitating phases

There was evidence for the formation of hydroxylapatite (HAP) in Filtra P which was detected in the white precipitate that was sampled from the outflow hose of one of the filter columns (Table 6). This finding is consistent with other studies. Crystalline Ca-phosphates (HAP and OCP) were detected in Filtralite P, Filtra P, Polonite, Absol, water-cooled blast furnace slag and wollastonite using X-ray absorption near edge structure (XANES) spectroscopy (Eveborn et al., 2009) and in basic oxygen steel slag (Bowden et al., 2009). HAP was also detected in electric arc furnace slag (Drizo et al., 2006) and on the surface of a porous Ca-based sorbent (Khadhraoui et al., 2002). However, in the used samples of Filtralite P, Top16 and Polonite evaluated in this thesis, crystalline Ca-phosphate phases were not detected using XRPD, possibly because the concentrations were too low. The same was observed by Eveborn et al. (2009) who studied used Filtralite P, Filtra P, Polonite, Absol, water-cooled blast furnace slag and wollastonite and stated that P species were undetectable in most XRPD patterns except for the Polonite sample, in which the authors detected poorly crystallized HAP. However, the Polonite sample studied (Eveborn et al., 2009) originated from a column experiment where P solution was used as an influent and not wastewater as in this study. It can be assumed that a higher pH regime prevailed in their experiment, enhancing precipitation and thus the concentration of Ca-phosphates in the used material.

The FTIR spectrum of the used Filtralite P sample indicated the presence of amorphous tricalcium phosphate (ATCP). The precipitation of ATCP was also suggested by the hydro-geochemical transport models developed in this thesis. This is consistent with the findings of Eveborn et al. (2009) who identified ATCP in used Filtralite P and Polonite samples. As ATCP is an amorphous phase, it cannot be detected using XRPD.
Amorphous Ca-phosphate has been found to be a precursor phase of HAP (Mañas et al., 2012), therefore it is possible that the ATCP formed in the filters converts to HAP over time.

5.1.3  Retention and wash-out of particulate phosphorus

The P retention mechanism in the filters comprises not only the formation of Ca-phosphates but also their retention in the filter. In the column experiments with Filtra P, Filtralite P and Polonite, some of the Ca-phosphates precipitates formed were not retained but washed out of the filters which is reflected in the difference between the concentrations of total and dissolved P in the effluents of the filter columns (Figs. 7a, b) and the amount of washed-out particulate P shown in Figs. 10, 11. In the experiment with Filtra P, this occurred to a large extent; the amount of washed-out particulate P was about the same as the retained dissolved P (e.g. Fig. 11). As discussed above, the wash-out of particulate P appeared to happen in materials that contained lime. In order to be mechanically retained, the P-particles formed need to be given time to grow big enough and/or the filter material particles need to be shaped in order to support mechanical retention. It is also possible that P-containing crystals grow on the surface of the filter particles e.g. on calcite: Ca-phosphate crystals precipitate from solution and grow on relatively few spots on the surface of calcite, those spots possibly holding adsorbed P (Freeman and Rowell, 1981). Ca-phosphate coatings on the surface of filter particles have been observed in previous studies e.g. on the surface of basic oxygen steel slag (Bowden et al., 2009). P accumulating on the surface of basic oxygen furnace (BOF) iron oxide was found to be concentrated in regions where calcite grains were coated with a fine-grained iron oxide material but not on non-coated calcite (Baker et al., 1998). The growth of P-containing crystals on calcite might be a process that occurred in the investigated materials; calcite was detected in Filtralite P and Polonite and was shown to precipitate in the developed hydro-geochemical transport models.

5.2  Phosphorus retention by different materials

The differences in P binding capacity determined for the investigated materials (Fig. 6) can be attributed to their different properties. These properties include the materials’ chemical composition, their particle size distribution, their particle porosity and shape, and surface area. Of particular importance is the material composition because it governs the P retention mechanism in terms of the dissolving phases, establishing pH and thus precipitating mineral phases.

Among the investigated materials, the largest amount of P was retained in Polonite, followed by Top16, Filtra P and Filtralite P (Fig. 6). The materials are distinguished by the mineral phases supplying the Ca ions for the reaction with dissolved P and governing the pH, as discussed in section 5.1. These differences in mineral composition are one reason for the different P binding capacities observed. Lime and wollastonite dissolving from Polonite seem to supply sufficient Ca ions and also maintain an adequate pH for the precipitation of Ca-phosphates which is reflected in the high P binding capacity of Polonite (ca. 5.4 g kg⁻¹, Fig. 6). High levels of P removal by Polonite were also observed.
in previous studies (Gustafsson et al., 2008; Renman and Renman, 2010; Nilsson et al., 2013b). Also, in Top16 (with gypsum as the dissolving phase), a high P binding capacity was determined, although the pH was comparatively low (ca. 8, Fig. 7c). The binding capacity determined for Filtralite P (1.35 and 1.18 g P kg\(^{-1}\) for P solution and wastewater filters, respectively) was lower than for the other materials (Fig. 6) and it was saturated at a considerably lower number of bed volumes (Fig. 7a, b). One reason for this could be the lower pH in Filtralite P compared to the other materials (Fig. 7c) which might have caused the Ca and phosphate ions to react less readily. However, this cannot be the only explanation because the pH in Top16 was even lower while the material exhibited a higher P binding capacity (Fig. 6). Maybe the kinetically constrained dissolution of Ca ions from the Ca-silicate contained in the material was slow in relation to the given residence time of the solution in the columns, so that the concentration of Ca ions remained low, impeding the formation of Ca-phosphates. It is also possible that the high influent concentrations of organic matter caused the low determined P binding capacities (discussed in section 5.3.2). However, the P binding capacities determined for Filtralite P are consistent with previous studies on the material (Table 1): binding capacities between 1.1 and 10.14 g kg\(^{-1}\) (at different loading rates and influent P concentrations) have been determined in a box experiment with Filtralite P (Ádám et al., 2005), where the boxes that were run in similar conditions to those of experiment B (a loading rate of 255 L m\(^{-2}\) d\(^{-1}\) and an influent P concentration of 10 mg L\(^{-1}\)) reached a capacity of 5.62 g kg\(^{-1}\). A binding capacity of 0.497 g kg\(^{-1}\) was determined in a big (20 L) column with Filtralite P that was loaded with P solution (10 mg L\(^{-1}\)) at a loading rate of 357 L m\(^{-2}\) d\(^{-1}\) (Ádám et al., 2007).

5.3 Improving the design and interpretation of laboratory filter experiments

5.3.1 Design of filter column experiments

In this section, the design of the laboratory filter columns used to investigate P retention in the materials is discussed with regard to the method of collecting and sampling the effluent, the columns’ size and form and the flow mode.

Method of collecting and sampling the effluent. During filter column experiments, either the entire volume of effluent can be collected and sampled or grab samples of the effluent can be taken. These two options have considerable influence on the experimental set-up. In the filter column studies presented (experiments A to C, Papers II - IV) the entire volume of effluent was collected, weighed and sampled to ensure accuracy, control and reliability of the experiments. Collecting the entire volume of effluent ensured the accurate monitoring of the P mass flow through the filters and facilitated the creation of a mass balance. However, the practical restrictions on both the volume of effluent that could be handled and the number of samples that could be taken limited the size of the filter columns and thus the residence time (discussed in 5.3.3). Grab sampling, on the other hand, would allow for bigger columns and thus longer residence time, because the effluent does not need to be collected. As grab sampling is less work and time-intensive, it would also allow for longer experiments. Although
accuracy would decrease, grab sampling might be advantageous when testing filter materials because the flow regime in the filter columns could be designed to be more similar to that found in the field. This would certainly be important for the obtained results as the loading rate and/or residence time affected the P binding capacities of Filtra P and Filtralite P (Fig. 11).

Size, diameter and length of the experimental filter. The design of laboratory filter columns used in this thesis was a balancing act between an attempt to simulate full-scale conditions and the necessity of down-scaling for practical reasons. The size of the filter columns used in the experiments was rather small. The benefits of a small filter size are a shorter testing time, because the filter material becomes saturated faster, and a high controllability of the experiments because the entire volume of influent and effluent can be captured and sampled instead of taking grab samples (see above). Better controllability leads to more accurate results. However, the properties of small columns differ considerably from full-scale conditions, especially in terms of their shorter residence time, also implying that the performance of small laboratory filters differ from their performance in the field, making laboratory results less reliable.

The width (diameter) of the filter column is also important with regard to wall effects and preferential flow (channelling). Along the walls of a filter column, there may be reduced friction leading to water traveling faster along the walls (wall effect). A maldistribution of porosity in the column causes channelling. Both wall and channelling effects increase with decreasing column-to-particle diameter ratios (Winterberg and Tsotsas, 2000). Thus, the diameter of the filter column should be chosen to be large enough to minimise these effects. Filter beds with a column-to-particle diameter ratio of >40 can be regarded as infinitely extended and pressure drops can be satisfactorily calculated by simple models such as the Ergun equation (Winterberg and Tsotsas, 2000). At column-to-particle diameter ratios between 4 and 10, deviations up to 20% from the pressure drop calculated with the Ergun equation are possible due to maldistribution and wall friction (Winterberg and Tsotsas, 2000). The diameter of the filter columns used for the experiments presented in this thesis was 74 mm. The column-to-particle diameter ratios of the filter columns with the four tested materials (calculated with the diameter of the biggest particle (second biggest sieve size) of the respective material) were ca. 5.9 (Top16), 6.5 (Filtra P), 14.8 (Polonite) and 18.5 (Filtralite P). As the column-to-particle diameter ratio of some columns was <10, the flow in them might have been adversely affected by maldistribution and wall friction.

Dispersion is the irreversible spreading process of a volume of a solute in a fluid flowing through a porous medium and is caused by several mechanisms such as variations in local fluid velocity, molecular diffusion, chemical reactions and fluid properties variations (Jourak, 2013). A good spread of P in the filter columns is important to achieve optimum conditions for the reaction and thus retention of P. There are two kinds of dispersion in filter columns: lateral and longitudinal dispersion. While lateral dispersivities have been found to be independent of the location in the filter bed, longitudinal dispersivities need a certain bed length to reach constant values (Han et al., 1985). In addition, the bed length required to reach constant longitudinal dispersivities is longer for filter material with a wider particle size distribution compared to uniform particles and also increases with increasing Pécelt number (increasing ratio of advective to diffusive
transport) (Han et al., 1985). If the filter column is not long enough to comply with specific criteria (which include the bed length-to-particle diameter ratio and the Péclet number), dispersion coefficients can be low and depend on the location in the filter bed (Han et al., 1985). To achieve a dispersion in experimental columns that is similar to that found in the field, the bed length-to-particle diameter ratio should be chosen to be high enough. Dispersivities of Filtralite P have been determined using tracer tests and ranged from 0.02 to 0.3 m depending on the flow rate and the solute concentration (Suliman et al., 2005).

The effects of wall friction, maldistribution of porosity and unstable dispersion coefficients can generally be assumed to be of minor concern because they can be minimised if the column diameter and length are large enough in relation to the diameter of the particles of the packed bed. The effect of a short residence time, however, is very important to carefully factor in when designing laboratory filters, as residence time directly affects the formation of Ca-phosphates in the filter and thus directly contributes to P retention (see section 5.3.3). Therefore, the residence time in the filters should be as similar as possible to that of a full-scale filter, as far as practical restrictions allow.

**Flow mode.** Up-flow mode was used in the column experiments because the water flow against gravity was assumed to distribute small Ca-phosphate particles more evenly in the filter material by carrying them upwards. Further, the filter columns were continuously loaded to decrease the time needed for saturation of the materials. In full-scale applications, intermittent loading is applied which increases the residence time of the wastewater in the filter during loading breaks. An increased residence time might favour the precipitation of Ca-phosphates e.g. HAP. HAP needs time to form; Drizo et al. (2002) detected HAP on the surface of electric arc furnace slag used in a column experiment with a residence time of 0.5 days as opposed to an experiment with a residence time of 0.34 days, where no HAP was found. Thus, with continuous loading as applied this study, lower P binding capacities might be determined compared to intermittent loading.

**Number of replicates.** The number of replicates in experiment C was sufficient which is reflected in the high value of statistical power calculated (100%, Table 8). A high power is desirable because it is coupled with a low probability of a type II error. A type II error is the probability for the failure to reject a false null hypothesis. The null hypotheses in the factorial experiments were that there was no effect of the investigated factors and their interaction on P binding capacity. The high power in experiment C was a result of the low standard variation \( \sigma \) compared to the minimum effect (1.1 g P kg\(^{-1}\), Table 8). In addition, all investigated factors were included in the regression model of experiment C. Omitting terms from the regression model, however, decreases power.

The powers calculated for experiments A and B were only 22 and 43% respectively, due to the high standard deviation of these experiments in comparison to the minimum effect (Table 8). The probability of detecting an effect if it really existed was, therefore, rather low. In experiment B, both loading rate and influent type were found to be significant factors i.e. the null hypothesis was rejected. Therefore, a type II error (failure to reject a false null hypothesis) did not occur and the number of replicates was sufficient
despite the rather low power. However, in experiment A, the null hypothesis could not be rejected on the basis of the collected data as none of the investigated factors significantly affected the total P binding capacity (determined by considering data of the entire breakthrough curve). The probability for a type two error (1 minus power) was very high (78%, Table 8) which means that there was a 78% probability that there actually was an effect but it was not detected. Thus, the result of experiment A (no effect of influent P concentration and loading rate on the total P binding capacity) cannot be regarded as reliable. The number of replicates necessary to increase the power of this specific experiment to 80% was 9 (Table 8). It should be noted that this number of replicates applies to a $2^2$ factorial experiment i.e. the number of experimental runs would be 36. An experiment with this many replicates would therefore be almost impossible to undertake practically.

5.3.2 Influent properties

**P concentration.** Increasing influent P concentrations is a way of accelerating laboratory filter tests which has been practiced by several researchers (Drizo et al., 1999; Johansson, 1999; Drizo et al., 2002; Drizo et al., 2006). However, in this study, an increased influent P concentration had a negative impact on the performance of the filters. It changed the shape of the breakthrough curve towards earlier breakthrough and lowered the pH regime in the filters, thus establishing conditions in the filter that differed from field conditions. The pH is crucial for the precipitation of Ca-phosphates which is favoured at high pH (Feenstra and De Bruyn, 1979) and thus for the P retention in the filter. The pH measured in the influent solutions with a P concentration of 12 and 50 mg L$^{-1}$ was 6.0 ± 0.3 and 5.4 ± 0.1, respectively. Decreasing the acid behaviour of the phosphate salt used in the solutions (KH$_2$PO$_4$) by adding a buffer to the influent might be a way of avoiding a low pH regime despite high P concentrations. Furthermore, increasing the influent P concentration from 12 to 50 mg L$^{-1}$ significantly affected the P binding capacity determined with pre-breakthrough data which, on average, decreased twofold. In tracer experiments with Filtralite P, Suliman et al. (2005) observed that the average retention time of a solute in the filters decreased when the concentration increased at constant hydraulic loading. This might be an explanation for the deterioration in performance of the filters at higher influent P concentrations.

**Influent source.** The influent sources used for the filter experiments in this thesis were P solution and secondary wastewater. Using different influent sources affected the P binding capacity of Filtralite P (Fig. 10) which was significantly lower when wastewater was used as an influent. Three possible explanations for this were discussed in Paper III: a different pH regime, inhibition of Ca-phosphate formation by humic substances and clogging of the filter by accumulation of particles with the formation of a biofilm. The pH was significantly lower in the wastewater filters, possibly due to the soluble organics in wastewater, a great part of them being acetic acids (Narkis et al., 1980). However, low pH is detrimental for the precipitation of Ca-phosphates (Feenstra and De Bruyn, 1979). Furthermore, the humic substances contained in the wastewater may have inhibited the precipitation of Ca-phosphates, the inhibitory effect being pronounced at pH 8, small at pH 9 and non-existent at pH 10 (Song et al., 2006). In addition, a TOC reduction of 71% (Paper III) indicated an accumulation of organic matter in the filters which may
have hampered the dissolution of Ca from the filter material. It is also possible that Ca was consumed by organic matter (other than humic substances) and not precipitated but washed out of the filter as suggested by Song et al. (2006), making the Ca ions unavailable for the reaction with P.

Using wastewater for filter tests would yield more reliable results compared to using synthetic P solution because the conditions established in the filters would be more similar to field conditions. However, this approach has several drawbacks. Collecting wastewater and transporting it to the laboratory is laborious and also requires hygiene safety measures. As the wastewater in the experiments presented in this thesis was gradually fed to the filter columns, a part of it was stored for ≤ 4 days. The properties of the wastewater were determined directly after it was collected but during the storage time, changes of the properties might have occurred. For instance, parts of the dissolved P and DOC might have been consumed by microorganisms, thus decreasing their respective concentrations and increasing the concentrations of particulate P and particulate organic carbon. This process is a potentially serious source of error.

In laboratory studies, using synthetic P solution instead of wastewater would be more convenient but it would overestimate the P binding capacity determined because of the negative effect of wastewater. Adjusting the achieved P binding capacity with a correction factor would be a way of compensating for this effect. Based on the results of the Filtralite P experiments with the low loading rate, the correction factor would have to be 0.8.

Concentration of organic matter and suspended solids. Organic matter and suspended solids contained in the influent can potentially cause problems in the filter. Humic substances can combine with Ca ions (Song et al., 2006), making them no longer available for the reaction with P. In addition, they can induce a clogging of the filter and a biofilm coating of the filter particles which would hamper the dissolution of Ca ions. The effects of these parameters were not tested in a controlled experiment within this work, but it has been shown that higher BOD concentrations decrease P removal (Nilsson et al., 2013b). The P binding capacities determined for Filtralite P in experiment B (using both P solution and wastewater) were much smaller than those for Top16 and Polonite determined in experiment C (Fig. 6). This difference was considered to be caused by a deviation in material properties (section 5.2), probably being the main reason for the lower determined P binding capacities. Another reason might be the different properties of the influent wastewater, as the two wastewaters used in experiment B and C differed substantially with regard to their contents of DOC, TOC and TSS, being ca. 8, 6 and 4 times higher in experiment B than in experiment C (Table 7). These differences were due to the different additives used for increasing the P concentrations i.e. urine, and P solution based on KH₂PO₄, in experiment B and C, respectively, but may also be due to the different origins of the wastewaters that were collected from beyond the output of a trickling tower (experiment B) and from an activated sludge basin (experiment C). The reduction of TOC was 71% in Filtralite P (experiment B, Paper III) as opposed to experiment C, where it was 49 % in both Top16 and Polonite (Paper IV). As both the reduction of TOC and the influent concentrations of TOC were much higher in experiment B, the amounts of TOC retained in the filter
were also higher. Therefore, the above stated problems might partly explain the lower determined P binding capacity in Filtralite P compared to Top16 and Polonite.

5.3.3 Loading rate and residence time

Effect of loading rate on P binding. In addition to an increased influent P concentration, loading rates higher than those in full-scale filters have been used to accelerate laboratory filter experiments (Brooks et al., 2000; Seo et al., 2005; Ádám et al., 2005). In this study, increasing the loading rate appeared to affect the total P binding capacity of Filtra P and Filtralite P in different ways (Fig. 11). In Filtralite P, the total P binding capacity significantly decreased when the loading rate increased (Fig. 11). The total P binding capacity of Filtra P increased with increasing loading rate, but this increase was not statistically significant. However, as the statistical power for the Filtra P-experiment (experiment A) was low (0.22, Table 8), there is a high probability (0.78) that there actually was an effect but it was not detected. Thus, there was at least an indication of a positive effect of the loading rate in the Filtra P data. The opposite effect of the loading rate might be explained by the different retention mechanisms of the materials. In Filtra P, the dissolution of Ca ions from lime was probably promoted by the higher loading rate as discussed in Paper II. A high concentration of Ca ions and a high pH probably caused the rapid formation of small Ca-phosphate particles that were carried away with the fluid flow as reflected in the large amounts of washed-out particulate P from Filtra P (Fig. 11). In Filtralite P, the kinetically constrained dissolution of Ca ions was probably slower and the pH was lower (Fig. 7c). Therefore, the formation of Ca-phosphates was slower and much less effective as reflected in the lower P binding capacity of Filtralite P (Figs. 6, 11). Probably, Ca-phosphates grew on the surfaces of the filter particles in this material e.g. on calcite as suggested by Freeman and Rowell (1981). At the higher loading rate, these processes were not given enough time to happen which led to a lower determined P binding capacity (Fig. 11). It is also possible that the higher loading rate caused irregular flow patterns deteriorating the conditions for P retention e.g. by higher dispersion and preferential flow. Another explanation for the lower P binding capacity of Filtralite P at high loading rates could be wash-out of reactive Ca ions which was observed in a study by Ádám et al. (2005).

Increasing the loading rate had an opposite effect on P retention in Filtra P and Filtralite P, showing that its effects are dependent on the material. Thus, using this method to accelerate laboratory filter tests may give uncertain results because the effects of an increased loading rate are difficult to predict. The effects of the loading rate have not yet been comprehensively studied. However, a recent study shows that increased loading rates may negatively impact the retention of P in slags where the main retention mechanism is the formation of HAP crystals (Claveau-Mallet et al., 2012).

Loading rate versus residence time as a relevant design parameter. Loading rate expresses the volume of fluid passing through the filter per time unit. In this study, surface loading rate [in L m⁻² d⁻¹] is used, also taking into account the flow-active surface of the filter which is orthogonal to the flow direction. The loading rate is interconnected to the hydraulic residence time of the fluid in the filter column, which is calculated by dividing the pore volume of the filter column [L] by the flow [L d⁻¹]. At a constant size
of the filter column (i.e. constant pore volume), the residence time decreases with increasing loading rate. It can be debated as to whether loading rate or residence time is the more important parameter for P retention in the filters. Loading rate is the factor governing the pore velocity in the filter and can thus influence surface reactions on the material as well as the fixation of Ca-P precipitates on the surfaces of the filter particles and between particles. Residence time, on the other hand, determines the time available for Ca-P precipitates to form and to form bigger particles e.g. HAP crystals, that can be mechanically retained in the filter more easily.

Two aspects lend weight to the argument to use loading rate as the relevant design parameter. First, in the materials used in experiment A and B, the amount of washed-out particulate P significantly increased with increasing loading rate, probably because the higher pore water velocity increased the transport of small P-containing particles towards the outlet of the columns. Thus, the wash-out of the formed P-precipitates is an important issue which depends on the loading rate and this supports the choice of loading rate (and not residence time) as the investigated factor in the experiments. Second, it was shown that the time needed for the formation of Ca-P compounds is short (Fig. 9) and might therefore be of minor importance. The reaction time of P in Filtralite P as determined in the batch experiments was 5 and 15 minutes using P solution and wastewater, respectively (Fig. 9c), although the dissolved P in the wastewater did not react completely. In Filtra P, the reaction time was less than 30 minutes (which was the shortest time tested) for the batch with an initial P concentration of 12 mg L$^{-1}$ (Fig. 9a). A rapid reaction of Ca and P has also been reported in literature e.g. HAP has been shown to form within minutes at pH 9 in the presence of boehmite (Li et al., 2012). Therefore, the residence times in experiments A - C were chosen to be rather low; they ranged from 40 minutes (experiment A) to 9.6 hours (experiment B).

However, the results obtained in this thesis showed that residence time was also an important parameter. Some effects observed when increasing the loading rate might have been due to the decreased residence time e.g. the decreased amount of retained dissolved P in Filtralite P (Fig. 11). It has been shown in previous studies that the formation of Ca-phosphate needs time. Drizo et al. (2002) reported that a residence time of at least 12 hours was needed for deposits of Ca-phosphate precipitates to occur on the surface of electric arc furnace slags and Mañas et al. (2012) found amorphous Ca-phosphate to be the precursor phase of HAP in granular sludge transforming to HAP in less than 7 days. The residence times associated with the investigated loading rates in experiment B were 9.3 hours, 83 and 46 minutes (Paper III). Thus, possibly, a reduced precipitation of Ca-phosphates due to the decreased residence time might have caused the decrease in total P binding capacity and amount of retained P with increasing loading rate in experiment B. In addition, the escape of particulate P from the Polonite and Filtra P columns (e.g. Figs. 6, 11) could partly be due to the residence time which might have been too short for these Ca-P precipitates to agglomerate or crystallize to particles that were big enough to be retained mechanically in the filter. Furthermore, P breakthrough in the filters occurred quickly for all investigated materials (Fig. 7) although the loading rates were held at levels commonly used in full-scale filters (discussed in Paper III), which indicates that the residence time was not sufficient and appears to play a major role in P retention despite the short chemical reaction times (Fig. 9). Therefore, the shorter residence time
in laboratory columns compared to full-scale filters might implicate an underestimation of the determined P retention capacities.

A longer residence time could be obtained when increasing the filter size. However, the size of the experimental filter columns in this thesis was limited due to practical constraints e.g. the bed volume of the columns in experiment B was 0.27 L (Paper III). The maximum volume of effluent that was practically feasible to collect was 20 L and samples were taken at frequent intervals (twice weekly). The use of bigger filters would have made the collection of the entire volume of effluent very difficult, thus decreasing the controllability of the experiments (section 5.3.1); bigger filters would also have prolonged the experimental runtime unless the loading rates had been increased, creating several problems as discussed above.

5.3.4 Ambient temperature

The significant observed positive effect of increasing the temperature from 4.3 to 16.5°C on the P binding capacity of Top16 and Polonite (Fig. 12) has three possible explanations. Temperature may have affected the chemical reactions within the filter, the bacterial culture and also the mechanical retention of P. The reaction of Ca\(^{2+}\) and PO\(_4^{3-}\) is endothermic (Wajima and Rakovan, 2013) and therefore more likely to happen at higher temperatures. Thus, in the filters run at 16.5°C, enhanced precipitation of Ca-phosphates probably increased P retention. Further, it is possible that microorganisms contained in the wastewater collected from the activated sludge basin consumed some of the dissolved P. BOD and TSS removal in activated sludge basins has been shown to increase with temperature (Keefer, 1962), reflecting an increased activity of the bacteria contained in the sludge. Thus, bacterial activity might have been higher in the filters at the higher temperature leading to higher consumption and thus retention of dissolved P. In addition, it is possible that a strong formation of biofilm at the higher temperature narrowed the pores in the filters and thus enhanced the mechanical retention of particulate P which is reflected by e.g. the higher percentage of retained influent particle-bound P, being 41% (Top16) and 12% (Polonite) at 4.3°C and about 60% at 16.5°C in both materials. Narrower pores might have also enhanced the mechanical retention of small Ca-phosphate particles that had formed in the filters.

As the P binding capacities determined were lower at the lower temperature (Fig. 12), laboratory investigations carried out at room temperature might overestimate P retention. The temperature of on-site wastewater depends on the ground temperature. In particular, in treatment facilities with an upstream subsurface flow constructed wetland, which is common in Sweden, the wastewater can be assumed to cool down significantly before it reaches the filter. Wastewater temperatures in sewers were observed to be as low as 4 to 6°C during winter months (Sallanko and Pekkala, 2008). Therefore, the lower temperature tested in experiment C (4.3°C) resembled operational conditions that are likely to prevail in full-scale filters for a substantial part of the year, especially in areas with cool climates. To avoid errors connected to the higher temperature in the laboratory compared to the field, it might be advantageous to conduct filter experiments at lower temperature, something tried in a study by Ádám et al. (2006, 2007).
5.3.5 Analysis and interpretation of effluent parameters

Both dissolved and total P concentrations were measured in the effluents of the experimental filter columns in this study. This appeared to be crucial because the total P concentrations in the effluents differed from the dissolved P concentrations (Fig. 7), showing that part of the P in the effluent was bound to particles. However, many previous studies focused on the soluble phase exclusively (Johansson, 1997; Brooks et al., 2000; Cheung and Venkitachalam, 2000; Brix et al., 2001; Drizo et al., 2006; Gustafsson et al., 2008). In experiment A at both loading rates, and in experiment B at the high loading rate, the amount of P that was actually retained in the filters was of the same order of magnitude as the amount of washed-out particulate P (Fig. 11), thus stressing that the escape of particulate P merits critical attention.

In this thesis, P in the effluents and supernatants was analysed using ICP (set A of the reaction time experiment) and the ammonium molybdate spectrometric method (Swedish Standards Institute, 2005b). The latter is suited to concentrations between 0.01 and 6 mg L\(^{-1}\) (Clesceri et al., 1998) and, at concentrations between 0 and 1 mg L\(^{-1}\), it has an accuracy of \(\pm 8.4\%\) (Swedish Standards Institute, 2005b). The precision of the ICP analyses were between \(\pm 12\) and \(\pm 19\%\) (given by the testing laboratory). With ICP, all the P contained in the sample is measured (as the sample is completely dissolved during the procedure) while the ammonium molybdate method has been shown to underestimate the amount of dissolved organic P in undigested samples (Moorleghem et al., 2011). However, all samples in this study (filtered and unfiltered) were digested prior to analysis with the ammonium molybdate method so that the method can be assumed to have been sufficiently accurate.

Generally, filter effluent data can be evaluated with respect to either P breakthrough or material saturation (the points of breakthrough and saturation in experiments A to C were identified according to threshold values defined in Table 5). The two approaches yield different calculated P binding capacities as demonstrated using the effluent data of experiment A: on average, the P binding capacity calculated using the entirety of the outflow curve was 1.8 times greater than that obtained using only the pre-breakthrough section (Paper II). However, effluent concentrations of dissolved P were used for determining the point of breakthrough in this experiment because the amount of P that had reacted with the material was of interest. Using total P concentrations when determining the point of breakthrough might generally be more sensible, as effluent total P concentrations are considered when the function of full-scale filters is examined. Examining the concentrations of total P in the effluents of the filter columns, breakthrough occurred very early in all four materials (Fig. 7a) and, thus, the two approaches of evaluation could not be used for the effluent data. In full-scale facilities, filter materials should only be used until the discharge limit of 1 mg L\(^{-1}\) (Heistad et al., 2006; Swedish EPA, 2006) is exceeded and then replaced, suggesting that laboratory studies should focus on the filter performance before breakthrough and the factors that govern it. Conducting laboratory filter experiments until breakthrough only rather than until saturation would also be more time-effective, which might facilitate the adjustment of other laboratory parameters to better resemble field conditions. Bigger filter columns and thus longer residence times might be possible as well as loading rates and influent concentrations resembling those found in the field. Longevity estimations based on data collected in this way might be more accurate.
5.3.6 Design and settings in future filter experiments

Based on the results of this work, it can be stated that several parameters concerning the influent, the filter and the effluent are important to consider in laboratory filter experiments. Generally, the laboratory conditions should resemble field conditions as much as possible.

**Influent.** As the influent type was shown to affect the P binding capacity determined (Fig. 10), secondary wastewater (despite varying properties over time) might be more suitable to be used as an influent in laboratory filter experiments because the use of P solution can overestimate P retention. For convenience, it is conceivable to use P solution instead of wastewater and correct for the effect with a correction factor. Based on the results of experiment C with the low loading rate, this correction factor would have to be 0.8.

The organic matter content can negatively affect P binding as indicated by the results of this study and confirmed by e.g. Nilsson et al. (2013b). It should therefore be monitored and kept close to the figure expected in full-scale filters which is ca. 20 to 40 mg L\(^{-1}\) (Swedish EPA, 1991). The organic matter contents of wastewaters collected from treatment plants for experimental purposes can be different depending on the biological treatment step used (Table 7). In this thesis, both KH\(_2\)PO\(_4\) and urine were used as additives for increasing the wastewater’s P concentration. Despite the acid behaviour of KH\(_2\)PO\(_4\) and the connected adverse effect on P retention, it is preferable to urine because urine contains organic compounds.

When increasing the influent P concentration to accelerate laboratory testing, one has to be aware of the consequences. Data collected in experiment A indicated that the determined P binding capacity decreased with increasing concentration (Fig. 10). In addition, the shape of the breakthrough curves changed towards an earlier breakthrough, probably due to a lower pH regime. The addition of a buffer to adjust the pH might be a way to compensate for these effects.

An increased loading rate was observed to affect P retention in Filtra P and Filtralite P, with the amount of washed-out particulate P being especially increased (Fig. 11). This effect should be considered when experimental loading rates are increased in the laboratory.

**Filter.** Laboratory filter columns will always be smaller than full-scale filters and thus the residence time is shorter. However, the size of the experimental columns should be maximised as much as is practical to avoid the adverse effects of a short residence time (discussed in section 5.3.3). Although constant longitudinal dispersion can only be reached in longer columns (Han et al., 1985), maximisation of the filter size should not be done at the expense of the column width, in order to avoid adverse effects of flow maldistribution and wall friction at column-to-particle diameters >10 (Winterberg and Tsotsas, 2000).

The required number of filter replicates in experiments depends on the material investigated and the type of experiment carried out. The number of replicates required to obtain a power of 80% in the 2\(^2\) factorial experiments A, B and C were 9, 5 and 2,
respectively. These numbers can be a guidance for future experiments, but need to be recalculated if the experiment is of another type. Naturally, an experiment with a material with varying properties must be replicated more often than an experiment with a more homogenous material producing low standard deviations.

It might be advantageous to place experimental filters in a wastewater treatment plant which would make the laborious collection and transport of wastewater to the laboratory unnecessary and would also avoid the storage of wastewater and the connected change of its properties. The placement of experimental filters in an ambient temperature resembling that expected in the field can be recommended.

**Effluent.** It is important to analyse the concentrations of both dissolved and total P in the effluent of filter columns as there might be a considerable amount of particulate P in the effluent. Instead of collecting the entire volume of effluent, only taking grab samples might be considered. However, this would be at the expense of mass balance calculations. As in full-scale filters, the performance before breakthrough is important, and this could be the focus of laboratory studies. Carrying out laboratory filter experiments until breakthrough only rather than until saturation as well as grab sampling would lead to less laborious and more time-effective experiments, which might allow other laboratory parameters to be adjusted to better resemble field conditions. It would be possible to use a greater number of filter columns at one time, use bigger filter columns and thus obtain longer residence times as well as apply loading rates and influent concentrations resembling those found in the field. Longevity estimations based on data collected in this way might be more accurate.

### 5.4 Improving estimations of phosphorus retention in full-scale filters

The most reliable approach to estimating the performance of a filter material, especially with regard to P retention, is a full-scale field trial. However, this approach is costly in terms of time, labour and construction costs and therefore not the first choice when new filter materials are to be tested. Laboratory methods for the investigation of filter materials include batch tests and filter (column) tests. Both methods have frequently been used to study a large number of filter materials (Johansson Westholm, 2006; Cucarella and Renman, 2009; Vohla et al., 2011). The P binding capacity determined based on data collected in the laboratory can then be used to estimate the longevity of a filter material in a full-scale filter. In this thesis, another approach was tested which included laboratory investigations coupled with hydro-geochemical transport modelling. Both approaches are discussed in the following.

#### 5.4.1 Longevity estimations based on laboratory batch and column tests

Batch experiments can be regarded as an unsuitable method to be used solely to estimate the lifetime of a filter in full-scale. They are carried out under conditions that are substantially different to those pertinent to real-scale filters and have been shown to overestimate (Jenssen et al., 2005) and, in some cases, underestimate (Arias et al., 2001) the P binding capacity. The use of long-term column tests, in which the material is
saturated, has been recommended (Drizo et al., 2002) and is more appropriate because the conditions better resemble those found in the field. However, several parameters are different in the laboratory compared to the field because laboratory investigations need to be accelerated. The results presented in this thesis show that these variables affect the determined P binding capacity. To minimise these effects, modifications to laboratory filter column experiments for the investigation of filter materials were suggested (section 5.3.6). However, as these effects cannot be completely eliminated, the use of correction factors, that would need to be developed, might be a way of compensating for them.

5.4.2 Hydro-geochemical transport modelling

There will always be a discrepancy between the performance of a filter material in the laboratory and at full-scale. In this section, hydro-geochemical transport modelling as a tool for bridging this discrepancy is discussed.

To successfully model the chemical reactions and the transport of the solute in the filter material using the advection-reaction-dispersion equation (eq. 3), information about the properties of both the filter material and the solution is required. To model the dispersive transport of the solute, the molecular diffusion coefficient (D_m) as a property of the solution and the longitudinal dispersion (D_L) as a property of the filter need to be determined. To model the chemical reactions in the filter, information about the mineralogical composition of the filter material is required. The D_m can be calculated using the Wilke and Chang equation (Wilke and Chang, 1955). To determine D_L and to gain information about the minerals dissolving from the material, laboratory investigations are necessary and are discussed in the following.

Laboratory investigations prior to modelling. Prior to modelling, the filter material was characterised in the laboratory and filter experiments were carried out. To facilitate the determination of the D_L needed for modelling the dispersive transport, the material needed to be characterised in terms of its particle size distribution. Using the effective particle diameter (d_{10}), the Péclet number (Péclet number = flow velocity×effective particle diameter/D_m) could be calculated. The D_L, and, thus, longitudinal dispersivity was then estimated from a D_L/D_m versus Péclet number plot (Paper VI).

To model the chemical reactions in the filters, it is important to acquire information about the mineral phases and their amounts. Thus, the material needs to be characterised in terms of its mineral composition. For the Filtralite P material studied, the minerals contained providing Ca^{2+} ions necessary for the precipitation of Ca-phosphates could not satisfactorily be identified using XRPD and FTIR. A more powerful approach to material characterisation would be the combination of scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) with XRPD as undertaken by Hillier et al. (2003). A petrographic study of the material, such as in polished thin sections with EDX, would give complimentary information on the composition and proportions of the various phases present, along with information on the composition of the X-ray amorphous material present (Stephen Hillier, personal communication, 10 December, 2012). These techniques are widely available and can also be applied quantitatively (Hillier et al., 2003) giving both qualitative and quantitative mineralogical information.
about filter material that is needed for geochemical modelling. However, the use of these techniques is not a standard procedure and requires expertise and, thus, an extensive mineralogical study of a material including quantification can be rather difficult to obtain. The approach used to develop the models presented in Fig. 13 included the identification of mineral phases with XRPD and FTIR, but also some guesses about mineral phases that could not be identified but were probably present. This method also used an adjustment of the initial amounts and dissolution rates of the different minerals until a satisfactory fit to experimentally derived breakthrough curves was obtained. Laboratory filter column experiments were thus required prior to modelling.

**Discussion of the developed models.** Two hydro-geochemical transport models were developed (Fig. 13). Model 1 described the experimentally-derived breakthrough curve well, and model 2 successfully simulated the effluent pH. However, a single model satisfactorily describing both the breakthrough curve and the effluent pH was not achieved, probably due to the fact that several processes influencing the reactions of P in the filter were neglected in the models developed. These processes were e.g. a possible passivation of the material due to the formation of a coating layer on the particles and / or the possible presence and weathering of an alumino-silicate which may have increased the pH observed in the experiments but neither were considered in the models. In addition, the ATCP precipitation might be kinetically constrained. Equilibrium with ATCP was assumed in the models but might not have been reached in the laboratory under the given flow regime. In addition, adsorption/absorption reactions, that were not accounted for in the models, might have occurred in the material at relatively low pH (BV>60, Fig. 13). In a previous study on Filtralite P, P was found to be associated also with Al and Fe (Eveborn et al., 2009).

The models were maintained in a comparatively simple mode, which may facilitate adaption of this methodology to assessments of other (new) alkaline filter materials. The models account for the main P retention mechanism that occurs in alkaline filter materials, that being the precipitation of Ca-P compounds which has been observed in several filter materials (Eveborn et al., 2009). The mineral phases in the developed models that were subject to kinetically constrained dissolution, wollastonite and CaO, are also probably contained in many other filter materials, as is calcite which was included in model 2. Therefore, the models are likely to be applicable to other filter materials. However, in order to use the models for robustly predicting the performance and longevity of full-scale filters, they need to be further developed and tested, as they neglect several potentially important variables and processes, such as adsorption processes that might occur in some filter materials such as slags (Pratt et al., 2007), the removal of particle-bound P from wastewater, and the effects of bacterial growth in the filters on P retention. Furthermore, the models would need to be validated using data from full-scale facilities.

### 5.5 Implications for full-scale filter design and monitoring

When designing full-scale filters, it is important to consider how P retention varies depending on the conditions. Although this thesis focuses on laboratory investigations of
the effects of several factors, the results also give indications for the filter materials’ behaviour in full-scale applications.

As an increased loading rate caused an increased wash-out of P-containing particles that had formed in the filters (Fig. 11), it might be sensible to keep loading rates in full-scale filters at low levels. This could be achieved by maximising the area used for active flow (wider filters) or by decreasing the overall flow to the filter by reducing the wastewater stream e.g. by separating grey-water and subjecting it to a separate treatment. A reduced flow rate through the filter might also reduce the wash-out of reactive Ca ions which was observed by Ádám et al. (2005) and thus prolong the lifetime of the filter. However, a reduced wastewater stream would also imply higher concentrations of P and organic compounds in the wastewater. Both these parameters were shown to negatively affect the P retention in this study (Fig. 10, section 5.3.2). As an increased influent P concentration caused the breakthrough of P to occur earlier, it can be assumed that P removal from lower concentration wastewater would be more complete than from an influent with high P concentrations. The high organic contents in the influent wastewater of the Filtralite P columns (Table 7) might have decreased the P binding capacity of the material and increasing BOD concentrations were also observed to decrease P removal by Polonite (Nilsson et al., 2013b). Therefore, the organic content of the influent wastewater should be minimised with pre-treatment.

Filters in warmer climates might generally remove P more efficiently than in cool climates because a higher temperature supports the precipitation of Ca-phosphates (section 5.3.4). The P concentrations of the effluents of the filter column experiments increased with time (Fig. 7), showing that proper monitoring of full-scale filters is important to be able to detect the point in time when effluent concentrations exceed regulative limits and the filter material needs to be changed. For effluent monitoring, it is important to consider not only dissolved but also particulate P which was shown to escape from the experimental columns (e.g. Fig. 7).

5.6 Usefulness of filter techniques for phosphorus retention in on-site wastewater treatment

When debating as to whether it is worthwhile to use filters for P retention in on-site wastewater treatment, it is important to consider the alternatives. One option is to retain the current on-site facilities that, in many cases, neither facilitate an efficient removal of P nor its recycling from the wastewater, but might still be a viable option at sites that discharge to insensitive catchments and/or where the introduction of advanced P treatment would be an unreasonable burden for the property owner. Alternative techniques for P removal in on-site facilities, other than filters, include the chemical precipitation of P with iron or aluminium salts and/or organic polymers, membrane bioreactors and separating systems (urine or black water separation). In the following, the current situation relating to P removal in on-site wastewater facilities is described and the use of filters is discussed as an option to enhance on-site P removal and recycling within the context of other available techniques.
5.6.1 On-site phosphorus treatment – the need for improvement of the current situation

Many on-site treatment facilities around the world consist of mechanical and/or biological treatment steps, and lack more advanced purification. In some countries, the discharge of P from on-site facilities is not regulated and thus advanced purification is not required. In Germany, for example, limits for P discharge are not specified for facilities up to a size of 10,000 pe (German Federal Government, 2013). Although not the primary goal, P removal occurs in the mechanical and biological treatment steps of on-site facilities to some extent; ca. 15 - 40% of P has been estimated to be retained in both steps together (Swedish EPA, 1991). However, the remains are discharged into ground waters (after some P has been retained in the soil), or into surface waters where they may cause eutrophication. These discharges have been identified as an important source for P input in the Baltic Sea and account for the majority of waterborne P inputs, along with agricultural inputs (HELCOM, 2005). A poor P removal in on-site facilities and thus high discharges also imply large losses from the P cycle and contribute to the acceleration of linear transport of P from mines to oceans as described by HELCOM (2005). The wastewater sector has been highlighted in previous studies as it is responsible for large losses from the global P cycle (Cordell et al., 2012). These losses are ineffective in terms of e.g. costs and energy. Therefore, an improvement in the current status of on-site wastewater P treatment is essential and, in some regions, performance requirements regarding the removal of P in on-site facilities have been prescribed e.g. in Sweden (Swedish EPA, 2006), Norway (Heistad et al., 2006) and Florida (U.S. EPA, 2002).

5.6.2 Options for on-site phosphorus treatment and recycling

Chemical precipitation of P with iron or aluminium salts and/or organic polymers is used in small compact on-site treatment units. The chemical can be dosed either after the biological treatment step, at which point the water is conveyed to a sedimentation tank, or added at an earlier stage (e.g. in the house) with subsequent precipitation of P in the septic tank. If maintained correctly, good P removal can be obtained. However, the precipitants used may contain contaminants such as heavy metals (Bavarian State Office for Water Management, 2005) which can decrease the quality of the produced sludge and thus its applicability as a fertilizer. Another disadvantage of this technique is that it requires continued maintenance; the regular restock of the chemical can be costly, time-consuming and tedious for the owner.

Membrane-based technologies such as membrane bioreactors (MBR) have been suggested being suitable for on-site wastewater treatment (Fane and Fane, 2005). They have been observed to remove P to 65% (Boehler et al., 2007) and 70 - 90% under certain conditions (Abegglen et al., 2008). However, they require intensive monitoring e.g. remote control over the internet and regular servicing to prevent malfunctioning (Abegglen et al., 2008).

As P contained in wastewater mainly originates from urine and faeces (Swedish EPA, 1995), separating these fractions from the wastewater can considerably reduce its nutrient content. Urine can be used as a fertilizer in agriculture after a certain storage period for
hygienisation (Jönsson et al., 1999). When blackwater is separated (e.g. using vacuum systems), it can be stored in a tank for subsequent collection and treatment. These techniques have a high potential to recover nutrients and have therefore been much discussed and tested (Balmér, 2004; Zeeman and Kujawa-Roeleveld, 2011; Tervahauta et al., 2013; Tjandraatmadja et al., 2013). However, they require an infrastructure for the collection and hygienisation of the separated fractions as well as substantial modifications to the sanitary facilities in the household which may reduce their convenience.

Filter beds, as investigated in this thesis, are a robust option for P removal in on-site facilities. Their maintenance is limited to the exchange of the filter material. Exchange intervals are dependent on the filter size and the material used. In a filter for one household, they range from a year or two for small filters to 15 years for bigger filter beds (Ádám et al., 2006). The technique facilitates the recycling of P to agriculture. The effect of Polonite as a soil conditioner has been shown to be comparable to that of liming (Cucarella et al., 2009). When applied as a fertilizer after use, filter materials have also been shown to improve barley yield in a pot experiment, although not as much as KH₂PO₄ (Cucarella et al., 2007). As P concentrations in the materials after use are low, additional P fertilization might be needed (Cucarella et al., 2012). However, a high efficacy of filter units might not always be achieved in practice. As the results of this thesis show, filter performance strongly depends on the design of the filter unit, the operating conditions and on the filter material used. A large number of potential filter materials are available but they must also be differentiated between in terms of their sustainability e.g. in terms of their energy use during manufacturing and transport (Weiss et al., 2008). In addition, the construction of filter units involves significant costs for the property owner. However, filter units have rather low maintenance requirements compared to other available options such as chemical precipitation and MBRs. They are also less invasive than separation systems and can possibly be retrofitted into existing facilities as a final step for P removal which can also reduce the bacterial contamination of the wastewater (Nilsson et al., 2013a). Thus, mainly due to their robustness, they may be viable options for many sites.
In this thesis, laboratory filter experiments were used to assess how the P retention in filters for on-site wastewater treatment is affected by various factors. To achieve a better understanding of the P retention mechanism, the mineral phases in the materials were examined and the P reaction time determined. Hydro-geochemical transport modelling was tested as a tool for estimating P retention in the filters.

The factors investigated significantly (\(\alpha = 0.05\)) affected the P retention in the filter materials, showing that they are important to consider when designing laboratory filter experiments and full-scale filters. Increasing the influent P concentration appeared to decrease (however, not significantly on a level of \(\alpha = 0.05\)) the P binding capacity determined for Filtra P and breakthrough occurred at a significantly lower number of treated bed volumes. Using wastewater rather than P solution decreased the P binding capacity of Filtralite P, probably due to organic compounds contained in the wastewater. Therefore, the influent concentrations of organic matter should be kept to a minimum.

The effect of an increased loading rate was tested using Filtra P and Filtralite P. Increasing the loading rates decreased the P binding capacity determined for Filtralite P and increased the amount of washed-out particulate P in both materials. Therefore, the loading rate is an important design parameter. However, the residence time was also shown to be important. The comparatively low P binding capacity determined in Filtralite P showed that the short residence time used was probably not sufficient despite the short P reaction times determined. Therefore, the use of small experimental filters and, thus, short residence times may underestimate the P binding capacity determined. However, the use of small filters facilitates the collection of the entire volume of effluent and, thus, the accurate calculation of a mass balance which cannot be achieved if only grab samples are taken.

Decreasing the ambient temperature from 16.5 to 4.3°C decreased the P binding capacity of Top16 and Polonite, probably because calcium phosphate formation as an endothermic process was decreased. Therefore, results obtained from experimental filters at room temperature might overestimate filter performance in the field where temperature can be lower. Full-scale filters might function better in warmer climates.

As P-containing particles were observed to escape from the experimental filter columns in this study, it is crucial to measure both the concentration of dissolved P and particulate P in the effluent of laboratory and full-scale filters. The particles can be overlooked when focusing exclusively on the dissolved phase which has happened in several previous studies.

To obtain reliable results, laboratory parameters should resemble field conditions as much as possible. Carrying out laboratory filter experiments until breakthrough rather than saturation would be considerably less time-consuming and work-intensive. This could facilitate the use of bigger filter columns and thus longer residence times, as well as loading rates and influent concentrations that better match those found in the field. Longevity estimations based on data collected in this way might be more accurate.
The mineral phases that contributed to P retention in the tested materials were investigated. Detected using X-ray powder diffraction, these phases were gypsum and bassanite in Top16, wollastonite, portlandite and calcite in Polonite and calcite in Filtralite P. The hydro-geochemical transport simulations suggested that in Filtralite P, the dissolving phases were calcium oxide, wollastonite and calcite. The phases formed in the filters during the experiments were also investigated. Using X-ray powder diffraction, hydroxylapatite was detected in the white precipitate that had formed in the outflow hose of the Filtra P columns. Both the Fourier transform infrared spectroscopic examination and the geochemical modelling indicated that amorphous tricalcium phosphate was the main phase that had formed in Filtralite P.

The time that the P needed to react with Filtra P and Filtralite P was determined to be less than 30 minutes and 5 minutes in Filtra P and Filtralite P, respectively, when P solution was used. Using wastewater, the reaction time of the P in Filtralite P increased to 15 minutes and the reaction was incomplete, probably due to the content of organic compounds in the wastewater that impeded the reaction.

The hydro-geochemical transport models developed in this thesis successfully simulated the removal of dissolved P by Filtralite P in the experimental filters and may therefore be a useful tool for estimating P retention in the filters. However, in order to use the models for robustly predicting the performance and longevity of full-scale filters, they need to be further developed and tested.
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Minitab Inc., 2010. Minitab®. 16.1.0


Suliman, F., Haugen, L., Jenssen, P. D., 2005. Salinity effect on the characteristics of saturated horizontal flow in small boxes containing Filtralite-P. Journal of Environmental Science and Health 40(6-7), 1403-1413.


Umetrics AB, 2006. MODDE. 8. 0. 0. 0, May 31 2006.


