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Treatment of landfill leachate and municipal wastewater in subsurface flow filters using mineralized peat and hydrated oil shale ash

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Author's contribution

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ABSTRACT

In this PhD dissertation the performance and efficiency of well-mineralized *Sphagnum* peat and hydrated oil shale ash, used as media in vertical and horizontal subsurface flow filters in the removal of the main contaminants – phosphorus (P), nitrogen (N) and organic matter from landfill leachate and municipal wastewater, are assessed. In addition, to summarize the existing information on different filter materials used for phosphorus removal from wastewater, a review of the literature (Publication V) was performed.

In 2003 onsite pilot scale experiments (Publication I) were conducted at Väätsa landfill (in Estonia) to determine the performance of well mineralized peat in vertical subsurface flow filters in the removal of different contaminants from raw and pre-treated landfill leachate. In 2005 a subsequent experimental study (Publications I, II) was performed with the goal of comparing the efficiency of mineralized peat, hydrated oil shale ash and the combination of these materials in vertical subsurface flow filters in the treatment of leachate from different stages of the onsite treatment system. Both studies showed that peat filters were suitable for efficient nitrification – the removal efficiency of ammonium-nitrogen (NH_4-N) was as high as 93%. Good results were obtained in the reduction of total phosphorus (TP) concentration from both raw and pre-treated leachate (up to 81% and 70–99% respectively) whereas the aerobic conditions in the peat promoted the removal of organic matter (reduction of BOD_7 of up to 95%).

In 2006–2007 a third study (Publications III–IV) was conducted with pilot-scale vertical (VF) and horizontal flow (HF) filters to explore the P removal capacity of hydrated oil shale ash from municipal wastewater (Tapa treatment plant; duration of the experiment 6 months) and leachate (Väätsa landfill; duration of the experiment 6 months). Due to the limitations of hydrated oil shale ash filters towards contaminants other than P, the hydrated ash filters were combined with peat filter elements. The median TP removal capacity during the third study was >90% (for PO_4-P even 98–99%) in the HF hydrated ash filter (with hydraulic retention time 5–7 days), and greater than 50% in VF ash filters (probably because of the lower hydraulic retention time). The results of the pilot studies allow one to claim that in HF hydrated ash filters at hydraulic loading of 53 mm d^{-1} or less, and with average inflow P concentrations not exceeding 17 mg L^{-1}, high median TP removal efficiency is guaranteed.

Changes in the composition of the hydrated oil shale ash suggest a statistically significant increase in P in all filter systems, whereas almost all TP was removed from the inflow leachate, (R^2=0.99) and the efficiency was high throughout the test period. Average P accumulation in hydrated ash filters was 100–180 mg P kg^{-1}. The chemical composition of the filter materials after all studies shows that P content in both hydrated ash and in mineralized peat increased during the experiments and, more importantly, when peat lost its efficiency quite quickly, the phosphorus accumulation in all HF hydrated ash filters did not demonstrate any signs of saturation.

However, despite the good results (especially in P removal) in the after-treatment of landfill leachate and municipal wastewater in pilot-scale filters of different studies, research with full-scale systems should be carried out before we can recommend hydrated oil shale ash and mineralized peat be extensively used in constructed wetland systems and soil filters as-alternative and promising filter media.

1. INTRODUCTION

All member states of the European Union (EU) are committed to ensure a good chemical and biological status for all water bodies in the EU by 2015 (e.g. inland surface waters, transitional waters, coastal waters and groundwater; Council of the European Communities, 2000). This means that all member states have to treat contaminated water before releasing it into receiving waters. Typical municipal wastewater has biochemical oxygen demand (BOD_7) of from 115 to 460 mg O_2 L^{-1}, and chemical oxygen demand (COD) from 250 to 1000 mg O_2 L^{-1}, and total nitrogen (TN) and TP concentrations are on average 20–85 mg L^{-1} and 4–20 mg L^{-1} respectively. In order to comply with European Union regulations, wastewater sewerage and wastewater treatment plants must operate correctly and should also include a nitrogen and phosphorus reduction step by the end of 2010 in all settlements with 2000–10,000 individuals. In accordance with European Union requirements, by the end of 2013 wastewater treatment should also be guaranteed in settlements where the loading rate is 50 PE (person equivalent), which means that urban areas and densely populated villages should also be involved. These measures originating from EU requirements should bring Estonian water bodies up to a good ecological condition by the year 2015 (National Audit Office of Estonia, 2007). However, several types of contaminated waters, e.g. urban runoff and landfill leachate, are not connected to the wastewater treatment system and are often not treated and the treatment efficiency in most conventional systems does not meet the established requirements.

The majority of Estonia's 800 municipal wastewater treatment plants are small conventional biological treatment plants that are not operating as required, and the greatest problems occur in the removal of nutrients. Most of the systems can only remove about 30% of phosphorus. These systems are not designed for intensive nutrient removal, and hence the acceptable degree of purification is difficult to achieve. Phosphorus removal in conventional small-scale wastewater treatment systems is a critical issue that has not yet been adequately solved. Moreover, continuing eutrophication, especially in freshwater ecosystems, has led to increasing governmental regulatory pressure for the lowering of P concentrations through enhanced P removal from wastewater (Kadlec & Wallace, 2008). Combined wastewater treatment plants with biological and chemical treatment steps can mostly achieve the required purification efficiency for phosphorus, but the whole system, with its high installation and maintenance costs, is not often available to small enterprises. Phosphorus removal from wastewater at large population or industrial sites can be solved through coagulation with Al- and Fe-sulphates. For technical and economical reasons, however, this technology is not applicable at a smaller scale. Therefore alternative means for phosphorus removal from wastewater have been studied.

In 1999 a Council Directive (99/31/EC) on the landfilling of the waste entered into force in the EU. The aim of the Directive is to prevent or reduce as far as possible the negative effects on the environment arising from the land-

filling of waste, by introducing stringent technical requirements for waste and landfills (European Union Council Directive, 1999). The Directive is intended to prevent or reduce the adverse effects of the landfilling of waste on the environment, in particular on surface water, groundwater, soil, air and human health. In Estonia there is a lack of long-term experience in the treatment of landfill leachate. From the year 2000 there are five sanitary landfills with the collection and treatment of leachate that meet the requirements of the EU Council Directive and Estonian regulations (RTL 2004, 56, 938). From 2009 all of the 350 old landfills that did not meet the standards were closed (Ministry of the Environment, 2007). The composition of municipal solid waste landfill leachate generally differs significantly from municipal wastewater and varies greatly depending on the waste quantity and quality of the waste – the age of the waste and also its decomposition rate and landfilling technologies. Leachate is considered difficult to treat due to its typically high concentration of phosphorus (up to 100 mg L^{-1}; Tchobanoglous et al., 1993), ammonia nitrogen (up to 300 mg L^{-1}; Kadlec, 2003; Lo, 1996; Kargi and Pamukoglu, 2003; Kurniawan et al., 2006), high COD value (up to 60,000 mg L^{-1}; Tchobanoglous et al., 1993), heavy metals (McLellan and Rock, 1988), hazardous organic substances, e.g. aromatic compounds, chlorinated aliphatic compounds, phenols, phthalates and pesticides (Paxéus, 2000; Schwarzbauer et al., 2002; Baun et al., 2004).

1.1. Subsurface flow constructed wetlands

On a worldwide scale, constructed wetlands (CWs) for wastewater treatment are becoming increasingly popular (Kadlec & Knight, 1996). This is mainly thanks to their cost-efficiency and multi-functionality: in addition to water purification efficiency, they also provide various landscape functions (diversification of habitats, biodiversity support, aesthetic aspects) and socio-economic services (e.g., biomass for building material and energy production; Mander et al., 2003). Even in cold climate regions, especially in the sparsely populated countryside, CWs are prior to conventional wastewater treatment systems (Mander & Jenssen, 2002).

The technical solution investigated in this dissertation consist of the use of unplanted vertical (VSSF) and horizontal subsurface flow (HSSF) constructed wetlands (i.e. soil filters) – sustainable and environmentally-friendly systems that require minimal energy and maintenance for the treatment of a variety of wastewaters – e.g. domestic, agricultural, industrial wastewater, stormwater, wastewater from aquacultures, landfill leachate etc. (Maehlum, 1995; Maehlum, 1999; Comeau et al., 2001; Kadlec & Wallace, 2008). Point sources at large population and/or industrial sites can be effectively treated using conventional purification systems. These are, however, technologically and economically unsuitable at a smaller scale, where constructed wetlands can be used instead (Vymazal et al., 1998; Kadlec & Wallace, 2008). Wastewater treatment in SSF CWs and soil filters have only a few limiting factors – one of these is that they

require a large area, and hence are more suitable in sparsely populated areas. However, because of their great volume and slow purification processes, VSSF and HSSF filters are more tolerant to changing nutrient loads and variable flow rates than conventional treatment plants.

In Estonia, constructed wetlands have mainly been used for the purification of domestic wastewater, but also as after-treatment of the effluents from conventional treatment plants. As of 2010, about 30 CW systems have been installed in Estonia. Several different natural and man-made materials and industrial by-products have been tested and used as filter media in subsurface flow CWs and soil filters in Estonia, e.g. local sands (Mander and Mauring, 1997; Mander et al., 2001; Mander et al., 2003), gravels (Vohla et al., 2005), lightweight clay aggregates (Noorvee et al., 2007; Öövel et al., 2007; Põldvere et al., 2009; Nurk et al., 2009), different types of peat (Öövel et al., 2005; Kõiv et al., 2006 (Publication I); Kängsepp et al., 2008; Kõiv et al., 2009a (Publication II); Kõiv et al., 2009b (Publication III)) and hydrated oil shale ash (Vohla et al., 2005; Kaasik et al., 2008; Kõiv et al., 2009a; Kõiv et al., 2009b; Liira et al., 2009; Kõiv et al., 20XX (Publication IV)).

Subsurface flow (SSF) CWs function very effectively in the treatment of the wastewater of small settlements and rural areas where pollution loading is 50 – 500 PE (maximum 2000 – 5000 PE), and they can be also suitable for the after-treatment of effluents from conventional treatment plants.

For 40 years, elevated phosphorus and nitrogen have been recognized as the main nutrients responsible for eutrophication (Vollenweider, 1968; Schindler, 1977; Tiessen, 1995). Excess N and P are mostly delivered from anthropogenic sources such as domestic and industrial sewage, agricultural runoff, and industrial wastewater (Soranno et al., 1996; Bennett et al., 2001). Therefore effluents from human activities must be treated to remove the surplus phosphorus and nitrogen, in order to maintain the ecological balance of natural systems (Conley et al., 2009).

1.2. Removal of nitrogen using subsurface flow constructed wetlands

There is a growing interest in achieving effluents that are low in nitrogen (Cooper, 1999). The removal of inorganic nitrogen is of major concern because of its toxicity to infants, fish, and other aquatic animals (USEPA, 1993).The nitrogen removal performance of subsurface-flow (SSF) CWs treating ammonium-rich wastewaters is often relatively poor and has proven difficult to predict with accuracy (Brix & Schierup, 1990; Knight et al., 1993; Hammer & Knight, 1994; Reed & Brown, 1995). Nitrogen removal in wetlands is achieved through N cycling and storage (Knight et al., 1993). The extent of nitrogen removal is more determined by the availability of dissolved oxygen in the treatment system. Whereas nitrification requires sufficient oxygen, denitrification occurs in the absence of oxygen. One means to assure sufficient aeration is to use a vertical

subsurface flow (VSSF) CW/filter, which has a much greater oxygen transfer capacity than horizontal subsurface flow (HSSF) wetland systems (Cooper, 1999). Hence VSSF CWs can achieve very good results in the removal of organic substances and enhance nitrification remarkably. Since the conditions in HSSF CWs are usually anoxic or anaerobic, combined HSSF and VSSF CWs can balance out each other's weaknesses, and it is possible to design a system that successfully removes organic matter and nitrogen (Radoux et al., 2000; Gòmez Cerezo et al., 2001; Cooper et al., 1999).

1.3. Removal of phosphorus using subsurface flow constructed wetlands

The removal of P in constructed treatment wetlands is a complicated process that is difficult to sustain. The potential of SSF systems to remove phosphorus is limited and highly dependent on the nature of the materials used for their construction (Grüneberg & Kern, 2001; Sakadevan & Bavor, 1998; Johansson Westholm, 2006). The main advantage of SSF filter systems over conventional treatment plants is the favourable characteristics of the filter media (Grüneberg & Kern, 2001) – its large adsorbing surface area, typically long retention time, flexibility in alternating aerobic-anaerobic zones, and diverse microbiological populations (Mæhlum, 1999). Different contaminants are removed from water through various chemical, physical and biological processes, and particularly through sorption. The search for efficient and long-lasting filter media has been a key issue for more than a decade (Arias et al., 2001). Phosphorus removal in subsurface flow CWs is closely associated with the physico–chemical (e.g. pH, EC, dissolved ions) and hydrological properties (e.g. loading rate, retention time) of the filter material, because P is mainly sorbed by or precipitated in filter media (Faulkner & Richardson, 1989; Kadlec & Knight, 1996; Sakadevan & Bavor, 1998; Vymazal et al., 2000).

In addition to good hydraulic conductivity, the chemical composition of the adsorption media is a critical factor in CW design, and therefore the content of reactive Ca-, Fe- and Al-minerals is important in efficient P removal. Thus filter media must be selected very carefully. Even if a medium with high P binding capacity has been selected, it may become saturated after a few years (Arias et al., 2001). An obvious and sustainable solution would also be a separate filter unit containing replaceable material with a high P binding capacity (Brix et al., 2001). In such systems, appropriate pre-treatment will also allow for a longer lifetime of the filter media, by decreasing the risk of clogging (Platzer & Mauch, 1997; Blazejewski & Murat-Blazejewska, 1997; Langergraber et al., 2002) and permitting the use of finer reactive filter media with higher sorption capacity (Hedström, 2006).

A great variety of different types of materials for P retention in CWs have been described (Vohla et al. 2010 (Publication V)). Traditionally, locally available sands and soils have been used as filter media in subsurface flow wetlands

for retaining P, even without any data about P-removal efficiency (Johansson Westholm, 2006), for example sand filters or gravel (Rustige et al., 2003). Studies performed during the last decade have demonstrated the importance of finding locally available materials with high P retention capacity. Johansson Westholm (2006) has also emphasized the fact that regardless of the great amount of existing scientific data, the potential and efficiencies of many different materials and studies are very difficult to compare and generalize directly.

The removal of P by filtration through reactive media has been demonstrated in recent years (Forbes et al., 2004; Gustafsson et al., 2008; Arias et al., 2003; Kaasik et al. 2008) especially with alkaline media (Publication V). The active filtration technique uses the direct immobilization of phosphates into low soluble forms by the dissolution of Ca-phases into pore water and the precipitation of Ca-phosphates. Potential materials for the active filtration of P include Ca-rich natural materials, such as shell sand (Mæhlum & Stålnacke, 1999; Adam et al., 2007), natural wollastonite (Brooks et al., 2000) and the mineral apatite (Bellier et al., 2006); industrial by-products, such as metallurgical slags (e.g. steel slag, Drizo et al., 2008; and blast furnace slag, Sakadevan & Bavor, 1998; Johansson & Gustafsson, 2000) and ash, e.g. hydrated oil shale ash (Vohla et al., 2005; Kaasik et al., 2008); and also man-made products, such as Filtralite®-P (Adam et al., 2007). Phosphorus removal using these materials (that usually have a pH greater than 9) is governed by the dissolution of Ca and hydroxide phases into pore water and the precipitation of Ca-phosphates as hydroxyl apatite or other phases (Publication V). Active filtration relies on simple chemical reactions, the effectiveness of which depends on the ionic strength of the solution, the activity of Ca and other competing ions, and the forms and activity of the phosphorus. Earlier studies (e.g. Chen et al. 2002, Adam et al. 2007) have shown that P removal is inhibited in the presence of competitive anions such as Cl^-, SO_4^{2-}, CO_3^{2-} and also organic compounds (e.g. humic acid), whereas extensive super-saturation of pore-water with respect to Ca and phosphate is required for the precipitation of stable Ca-phosphate phases (Arias et al., 2003; House, 1999; Liira et al 2009).

1.4. The potential of hydrated oil shale ash as a filter media in the treatment of municipal wastewater and landfill leachate

The hydrated oil shale ash sediment used in the studies of this dissertation (Publications II–IV) is a Ca-rich industrial by-product that results from the burning of kerogenous oil shale (also known as kukersite) used in Estonian thermal power plants. The ash content of the shale after burning is ~45% in the dry state, and ~6–8 million tonnes of waste is annually produced at the two largest plants. The oil shale is highly calcareous (with a calcite/dolomite content of 40–60%), and the ash remaining after combustion is rich in free lime (CaO)

and anhydrite ($CaSO_4$), with an Al-Si glass-like phase and secondary Ca(Mg)-silicate minerals (Kuusik et al., 2005). The ash is water-deposited to the large open plateaus, and due to hydration reactions forms a variety of secondary Ca-minerals – ettringite, Ca-aluminates and calcite. The composition and properties of the hydrated oil shale ash is discussed in detail by Kuusik et al. (2005), Vohla et al. (2005), Kaasik et al. (2008), Kõiv et al. (2009a; Publication II) and Liira et al. (2009).

Vohla et al. (2005), Kaasik et al. (2008) and Liira et al. (2009) have recently shown the effectiveness of Ca-rich hydrated oil shale ash as a possible material for P removal in constructed wetland systems. These experiments have shown the P removal effectiveness of fly ash and hydrated oil shale ash in the batch experiment to be >95% at phosphorus loadings as high as 700–1000 mg P·L^{-1} (Vohla et al., 2005) and up to 99.9%, with maximum binding capacity as high as 65 mg P g^{-1} (Kaasik et al., 2008). Laboratory-scale experiments show removal of up to 91% with loading of 8–15 mg P L^{-1} at 12 h retention time, but the binding capacity was rapidly lost due to chemical clogging of the filter by Ca-carbonate precipitates (Liira et al., 2009). Nevertheless, the actual efficiencies are usually considerably lower in real or large-scale systems, where retention time limits the filter-water reactions (e.g. Adam et al., 2007).

Hydrated oil shale ash (for detailed description see Materials and Methods) and other described reactive materials are not equally efficient for the removal of nitrogen and organic matter, and the outflow of these materials frequently has high pH due to equilibrium with Ca-mineral phases present in the filter material (Publication IV). Therefore we should look for other filter media to be used in combination with filters designed for P-removal to obtain a complex effect and overall improvement of water quality.

1.5. The potential of mineralized peat as a filter media in the treatment of wastewater and landfill leachate

One possibility is to use environmentally-friendly, sustainable and locally available natural materials, e.g. peat – partially fossilized decomposed plant matter that develops in wet areas in the absence of oxygen. Several studies (Rock et al., 1984; Viraraghavan & Ayyaswami, 1987; Couillard, 1994; Talbot et al., 1996; Lyons & Reidy, 1997; Kennedy & Van Geel, 2000; Heavey, 2003; Kinsley et al., 2003; Champagne & Khalekuzzaman, 2006) have identified peat as an alternative low-cost filter medium for on-site wastewater treatment, and it also has high sorption capacity relative to commercial sorbents (Allen et al., 1997; Bailey et al., 1999; McKay et al., 1999). Most peat filters are designed for the treatment of municipal wastewater (Brooks et al., 1984; Talbot et al., 1996; Geerts et al., 2001), and several systems have also shown very good performance in the treatment of landfill leachate (Cameron, 1978; McLellan & Rock,

1988; Kadlec, 2003, Kinsley et al., 2004), septic tank effluent (Brooks et al., 1984; Couillard, 1994; Kennedy & Van Geel, 2000), acid mine drainage (Champagne et al., 1999), stormwater (Zhou et al., 2003) and liquid swine manures (Rizzuti et al., 2002) etc. Likewise, the results of experiments on floodplain fens in Estonia have shown the high potential of peatlands in the after-treatment of wastewater (Öövel et al., 2005). Previous research on peat as a filter material focused on the mechanisms of sorption and the sorption capacity of the peat (Allen et al., 1997; Ho & McKay, 1999; Ringqvist et al., 2002; Kalmykova et al., 2008a; Kalmykova et al., 2008b). The influence of the actual running and maintenance conditions for peat filters is, however, rarely addressed. Although peat is an inexpensive and attractive material, such advantages must be balanced against the importance of peatland conservation and the maintenance of habitat diversity (Ma & Tobin, 2004).

Several laboratory and field experiments have demonstrated that peat as a filter material for SSF CWs and soil filters and other treatment systems can effectively reduce nitrogen concentration (Champagne et al., 2006) and remove suspended solids (Lens et al., 1994; White et al., 1995; Gunes et al., 1998), pathogenic bacteria (Nichols and Boelter, 1982; McLellan and Rock, 1988; White et al., 1995), mineralize organic material (Brooks et al., 1984; Viraraghavan, 1993) and retain phosphorus (James et al., 1992; Roberge et al., 1999) and also heavy metals (Davila et al., 1992; Brown et al., 2000; Ringqvist & Öborn, 2002). Earlier studies (Rock et al., 1982) already showed the good performance of peat filters in the removal of organic matter and nitrogen. Brooks et al. (1984) reported that a filter filled with fibrous *Sphagnum* peat removed 91% of BOD_5, 84% of COD and 83% of TN from domestic wastewater. The published literature indicates that peat filters are quite variable in removing phosphorus, and efficiency can range between 10% and 80% (Brooks et al., 1984; Viraraghaven & Rana, 1991).

Peat possesses several characteristics that make it a favourable filter medium for contaminant removal, such as high water holding capacity, low density, large surface area (>200 m^2 g^{-1}), high porosity (80–90%) and excellent ion exchange properties (Bergeron, 1987; McLellan & Rock, 1988; Mitsch & Gosselink, 1993; Sharma & Forster, 1993; Buttler et al., 1994; McKay, 1996; Brown et al., 2000). A peat filter may be subject to changing environmental conditions, including temperature, redox potential, water load and water quality. Operating periods may be interrupted and filters left dry, stagnated in water or frozen (Kalmykova et al., 2009).

The properties of peat depend on several factors, including the ambient conditions during its formation, the extent of its decomposition and the method of harvesting (Couillard, 1994). Nevertheless, only limited information regarding the behaviour of peat filter systems under varying contaminant, as well as hydraulic loading rates when operated in a filter configuration is available. In addition, the treatment efficiency and the total operational life of the peat filter systems are vulnerable to varying contaminant loads, particularly

organic (COD, BOD$_7$), NH$_4$-N, and TSS concentrations, as well as hydraulic loading rates (Champagne & Khalekuzzaman, 2006).

In Estonia, peatlands cover 22% of the country's total land area. Estonian peat resources are estimated at 2.4 billion tones, of which 0.2 billion tones are less decomposed and 1.4 billion tones are well decomposed (Statistical Office of Estonia, 2006). The potentially large availability of peat and its unique combination of biological, physical and chemical properties make it suitable for a wide variety of uses, including environmental protection (McLellan & Rock, 1988).

The majority of the research into the performance of peat in different types of treatment systems has been performed using fibrous poorly mineralized/ humified (e.g. *Sphagnum, Carex*) peat (Brooks et al. 1994; Ringqvist et al., 2002; Ringqvist & Öborn, 2002; Van Geel & Parker, 2003), and almost no data about the efficiency of well mineralized Sphagnum peat can be found. Therefore the capacity of the well-mineralized *Sphagnum* peat (saprist peat, H$_7$– H$_8$ according to the von Post scale; Puustjarvi & Robertson, 1975) to remove contaminants from landfill leachate and municipal wastewater was studied and the results are presented in this dissertation (Publications I–IV). The well-mineralized *Sphagnum* peat (for a detailed description see Materials and Methods) was obtained from the lower deposits of a depleted industrial peatland, as described by Kõiv et al. (2006; Publication I).

Objectives

The main objective of this dissertation is to determine the treatment capacity of well mineralized *Sphagnum* peat (henceforth referred to as peat) and hydrated oil shale ash (henceforth referred to as hydrated ash) in order to reduce nutrient (especially phosphorus) concentrations and BOD and COD values in landfill leachate from different stages of the leachate treatment system and in pre-treated municipal wastewater. The specific tasks of the study are as follows:

- To analyse the efficiency of vertical subsurface flow (VSSF) peat filters in treating effluents from a conventional leachate treatment system (Publication I). In addition, changes in the composition of the peat were studied.
- To determine the treatment capacity of well mineralized peat and hydrated ash and combination of these materials in VSSF filters, and to analyse the relationship between the initial loading and mass removal values for both filter materials and to study the effect of the duration of the experiment on purification efficiency (Publication I and II).
- To determine the treatment capacity of hydrated oil shale ash in pilot-scale vertical and horizontal subsurface flow filters designed to reduce phosphorus in pre-treated municipal wastewater from the town of Tapa and pre-treated landfill leachate in Väätsa, Estonia (Publication III and IV). This part of the investigation aimed to estimate the phosphorus (P) binding capacity of hydrated ash, as well as combinations of hydrated ash with mineralized peat. The specific aims were: (a) to understand the influence of different P loadings and wastewater compositions (different concentrations and forms of contaminants) on P removal, and (b) to acquire data on the removal mechanism of P and the performance of hydrated ash filters and mineralized peat filters.

The objectives of the literature review (Publication V) are: (a) to summarize existing information on different filter media used for P removal from wastewater that could be applied to one database, with the advantages and disadvantages of each amendment, and (b) to clarify the relationship between P retention capacity, pH level, Ca (CaO) content, and the hydraulic parameters of the filter media.

2. MATERIALS AND METHODS

The results of three experimental studies and one literature review are presented in this dissertation. All experiments were conducted with leachate (raw leachate and leachate from different stages of the treatment plant) from Väätsa landfill (Publications I–IV) and in the last study (Publications III and IV) pre-treated municipal wastewater from the treatment plant of the town of Tapa, were also used. Two filter materials were used in these experiments: well mineralized peat (in all experiments; Publications I–IV) and hydrated oil shale ash (Publications II–IV).

In the literature review (Publication V), data about various filter materials has been collected to give an overview of the advantages, but also to emphasize the critical conditions and possible limiting factors for the usage of different materials for phosphorus removal.

2.1. Site description and pre-treatment of landfill leachate and municipal wastewater

The Väätsa landfill has been in operation since the year 2000. It is the first sanitary landfill in Estonia that meets the requirements of the EU Council Directive 1999/31/EC (European Union Council Directive, 1999).

Approximately 10–20 m^3 of leachate is produced per day and treated in a conventional biological treatment system, consisting of an activated sludge treatment plant and an aerobic-anoxic pond. The purification efficiency of the system is quite high; nevertheless, the treatment efficiency does not meet the limit values (RT I 2001.69.424) for most of the contaminants, e.g. for chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP), with median outflow values of 825, 180 and 3.4 mg L^{-1} respectively (Table 1).

The Tapa conventional biological wastewater treatment plant (activated sludge treatment) established in 1996 processes the municipal wastewater from the town of Tapa and the nearby distillery (approximately 500 m^3 of wastewater is produced per day). The purification efficiency of the Tapa system has been quite sufficient for all of the required (RT I 2001.69.424) parameters (Table 1), except for TP, which had a very unstable outflow value, from 0.13–17.0 mg L^{-1} (median 5.0 mg L^{-1}).

The composition of raw landfill leachate and leachate from different stages of the conventional treatment plant and also the composition of pre-treated municipal wastewater from the conventional treatment systems differ significantly (Table 1). In Väätsa landfill the raw leachate is describable by the genuinely high concentration of nutrients and organic matter, and such composition makes it truly difficult to purify. Therefore the pre-treated leachate from the conventional treatment system is also characterized by high Cl$^-$, SO$_4^{2-}$, Mg^{2+}, K$^-$, COD and TN – in median 530, 340, 170, 890, 825 and 180 mg L^{-1} respectively (Table 1).

Table 1. Median outflow values of the variables (mg L^{-1}) from the onsite Väätsa and Tapa treatment plants and limit values from the Estonian regulations (RT I 2001.69.424).

	Type	Period	BOD$_7$	COD	TP	TN	TSS	pH
Estonian regulations	landfill leachate		25.0	125.0	2.0	75.0	25.0	6–9
Väätsa landfill	raw leachate	2003	1953	3811	1.31	446	152	8.2
	leachate from activated sludge treatment plant	2004–2005	286	1352	5.4	392	129	8.5
	leachate from pond*	2004–2005	78	848	3.6	144	65	8.8
		September 2006 – March 2007	8.3	450.0	2.9	150.0	52.0	8.8
		March 2007 – September 2007	26.0	1040.0	4.1	210.0	80.0	8.7
Estonian regulations	municipal wastewater		15.0	125.0	1.0	15.0	15.0	6–9
Tapa wastewater	pre-treated wastewater*	September 2006 to March 2007	1.6	<50.0	5.0	12.0	6.0	7.7

* effluent of the treatment system

Interestingly, the total phosphorus (TP) concentration in pre-treated leachate at Väätsa landfill is quite stable, varying from 2.5 to 5.2 mg L^{-1} (median 3.5 mg L^{-1}).

In contrast, the Cl^-, SO_4^{2-}, Mg^{2+}, K^-, COD and TN concentrations in pre-treated wastewater from the Tapa municipal treatment system are much lower - on average 98, 67, 19, 17.5 and <50, 12 mg L^{-1} respectively (Table 1). The TP content in Tapa wastewater is, however, higher (median 5.25 mg L^{-1}), and is also highly variable (0.14–17.0 mg L^{-1}). The phosphorus at both sites is mostly in the form of PO_4-P (median 80% and 94% of TP in Väätsa and Tapa respectively). The BOD_7 value of the influents is quite low, showing a median of 14.0 mg L^{-1} in Väätsa and 1.6 mg L^{-1} in the Tapa experiment.

2.2. Filter materials

2.2.1. Well mineralized peat

In all experiments, well-mineralized *Sphagnum* peat collected from Lokuta peat bog (Fig. 1), which is located near Väätsa landfill in Estonia, was used. The well mineralized peat (H_7-H_8 according to von Post scale) was obtained from the lower deposits of the depleted industrial peatland.

Because of the high variability in the biological and chemical composition of the peat, it is almost impossible to present the average composition of this material. The properties of peat depend on several factors, including the ambient conditions during its formation, the extent of its decomposition and the method of harvesting (Couillard, 1994). Therefore, the range of chemical characteristics of well mineralized peat used in the experiments of this dissertation is presented in Table 2.

Table 2. The chemical composition (wt %) of well-mineralized peat before its use in the experiments of this dissertation; first study – Publication I, second study – Publication II, third study – Publications III and IV.

Parameter	pH	P	Ca	K	Mg	N	Organic matter
First study (2003[c])	6.70	0.002[a]	8.294	0.093	1.416	0.500	37.20[b]
Second study (2005[c])	6.93	0.031	3.070	0.050	1.150	0.670	63.46
Third study (2006[c])	7.23	0.033	5.095	0.080	1.200	0.680	57.28

[a] In the first study, only the content of plant-available phosphorus (the AL method) in peat was analysed
[b] Some mineral particles most likely affected the analysis, and the measured value is doubtful
[c] Indicated the year when the peat was obtained from Lokuta peat bog

In the first study and second study (Publications I and II), the peat was sieved through a 26 mm sieve to remove stones and roots, and in subsequent experiments (Publications III and IV) mineralized peat without any pre-treatment was used (Fig. 1).

Figure 1. Well mineralized peat: on the depleted peat land (on the left) and in filter systems (on the right).

2.2.2. Hydrated oil shale ash

Kerogenous oil-shale used at Estonian thermal power plants is a solid fuel of low energetic value, which after combustion leaves large amounts (45–48% of shale dry mass) of ash. Estonian oil shale is highly calcareous (average calcite and dolomite content is 40–60% of the mineral matter), and the ash remaining after combustion is due to thermal decomposition (at temperatures of 1300–1500 °C) of carbonate minerals and subsequent reactions with flue gases rich in free lime (CaO) and anhydrite ($CaSO_4$).

The mineral composition of fresh ash from power plants is dominated by free lime (CaO), anhydrite ($CaSO_4$), quartz (SiO_2), C_2S belite (b-Ca_2SiO_4), merwinite ($Ca_3Mg(SiO_4)_2$), orthoclase ($KAlSi_3O_8$), melilite (($Ca,Na)_2(Al,Mg,Fe)$ $(Si,Al)_2O_7$) and periclase (MgO). The ash also contains minor amounts of calcite ($CaCO_3$) and tricalcium-silicate C_3S, tricalcium-aluminate C_3A and pseudo-wollastonite (CaO – SiO_2). About 20–30% of the ash consists of amorphous glass-like materials of (alumino-)silicate composition (Kuusik et al., 2005), which form after the partial melting and thermal decomposition of silicate minerals (K-feldspar, clay minerals).

The bottom and fly ash (caught in the dust chambers, i.e. cyclones) is transported to waste heaps (i.e. plateaus; Fig. 2) through a pipe system in water slurry at an ash–water ratio of 1:20. During the deposition, but also in plateaus, the formation of hydration and carbonation products will take place in the case of interaction between ash and water. The lime and anhydrite already begin to react with water in the ash removal system, and the hydration processes continue in open plateaus, resulting in the rapid formation of hydrated oil shale ash that contains different secondary Ca-minerals: ettringite [$Ca_6 Al_2 (SO_4)_3 (OH)_{12} \cdot 26H_2O$], hydrocalumite [$Ca_2Al(OH)_7 \cdot 3H_2O$], portlandite [$Ca(OH)_2$], and Ca-carbonates [$CaCO_3$] (Kaasik et al. 2008).

Figure 2. Hydrated oil shale ash: on the ash plateau (on the left) and crushed and sieved hydrated ash (fraction 5–20 mm; on the right).

The average mineral and chemical composition of hydrated oil shale ash is described in Table 3. The composition of the hydrated oil shale ashes (i.e. ash plateau sediments) can vary considerably depending on the advancement of diagenetic processes, specifically the carbonization of the surface layers of the plateau sediments (Kuusik et al., 2004). In these studies the hydrated oil shale ash excavated from the plateau was crushed and sieved to a fraction of 5–20 mm (Fig. 2).

Table 3. Chemical and mineral composition (wt %) of the hydrated oil shale ash (Kaasik et al., 2008; Liira et al., 2009).

Chemical composition		Mineral composition	
SiO_2	25.96	Quartz	9.6
Al_2O_3	6.25	Orthoclase	6.9
Fe_2O_3	3.56	Clay minerals	3.1
MgO	3.42	Ca/Mg-silicates	16.6
CaO	29.22	Periclase	2.1
Na_2O	0.11	Melilite	5.3
K_2O	2.97	Calcite/vaterite	28
TiO_2	0.36	Portlandite	6.8
P_2O_5	0.13	Ettringite	15.2
MnO	0.04	Hydrocalumite	4.1
Loss on ignition	27.98	Gypsum	2.3
Total C	2.22		
Total S	1.63		

The chemical composition of the hydrated oil shale ash corresponds to its mineral composition – the major oxides are CaO (on average 29.22%), SiO_2 (on average 25.96%) and Al_2O_3 (on average 6.25%) (Table 3; Kaasik et al., 2008). The trace element (including heavy metal) content in oil-shale ash is typically enriched compared with raw oil shale (e.g. Pets & Haldna, 1995; Saether et al., 2004), but the heavy metal concentrations (Kaasik et al., 2008) are below the critical limits, and the un-hydrated fly ash has been used for the liming of acidic soils in Estonia and north-western Russia (Pets et al., 1985).

2.3. Experimental design

In the first study (Publication I), with two onsite pilot-scale field experiments (lasting 36 days in summer 2003), the vertical subsurface flow filters filled with well mineralized peat were used for the treatment of Väätsa landfill leachate. The two metal filter bodies (filters F1, F2) had a volume of 1 m³, were rectangular in shape and had a permeable floor (Fig. 3).

Peat filter F1 of experiment 1 (E1) was loaded with the raw leachate and peat filter F2 of the experiment 2 (E2) with the pre-treated leachate from the aerobic-anoxic pond (i.e. effluent from the onsite treatment system). The even distribution of leachate into filters F1 and F2 was achieved using perforated elastic pipes placed above the filter bodies in a spiral pattern (Fig. 3). The filters were loaded using timer-adjusted pumping (with 290 mm d^{-1}, in total about 104.0 m³ per filter).
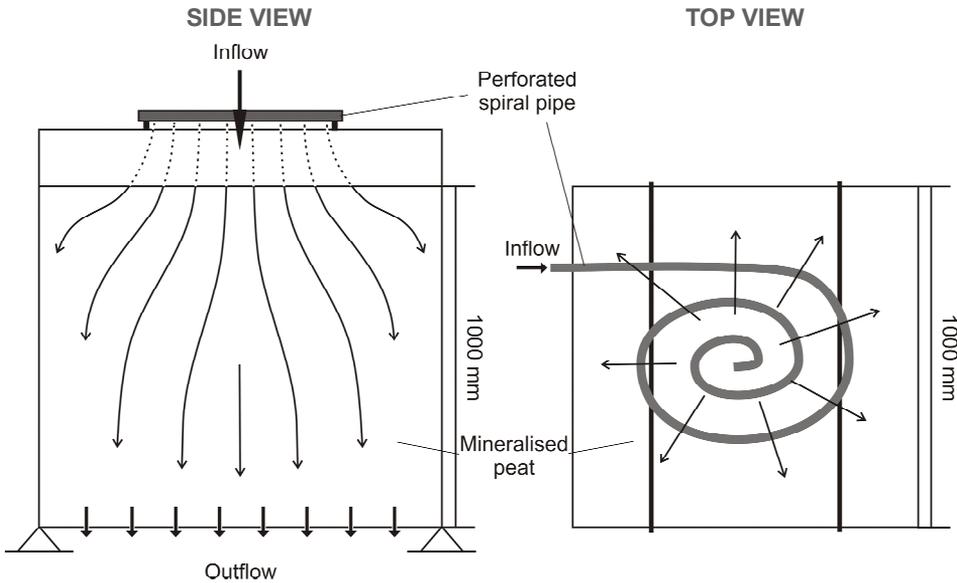
Figure 3. Experimental design of the first study: vertical flow filter bodies and leachate distribution to the peat filters in the experiment 1 (filter F1) and experiment 2 (filter F2).

The second study (Publications I, II) consisted of an indoor experiment (filters indicated with "S"; i.e. E1 in Publication II), which lasted from April to December 2005, and of an outdoor experiment (filters indicated with "V" i.e. E2 in Publication II) from May to October 2005, was also conducted at Väätsa landfill. In both experiments, three identical custom-designed vertical flow filters were used (total 6 filters; Fig. 4). The filters had a volume of 0.11 m³ and were made of PVC pipe (diameter 372 mm, h=1.2 m), and the filters were filled as followed:

- filters 1S and 1V were filled with peat (layer 1 m) (i.e. F3 and F4 in Publication I, respectively);
- filters 2S and 2V were filled with peat (top layer 0.5 m) and hydrated ash (bottom layer 0.5 m);
- filters 3S and 3V were filled with hydrated ash (layer 1 m).

In the indoor experiment three vertical flow filters 1S, 2S and 3S were loaded with leachate from an activated sludge treatment plant (the effluent of the first stage of the activated sludge treatment plant) and in the outdoor experiment, filters 1V, 2V and 3V were loaded with leachate from the outflow of the aerobic-anoxic pond (effluent of the onsite treatment system). All filters were loaded using timer-adjusted pumping. The even distribution of leachate into the filters was achieved using perforated pipe inside crushed granite (fraction 6–

8 mm) above the filter material (Fig. 4). During the first months the hydraulic loading rate (HLR) of the indoor experiment was too high (136 mm d^{-1}), and it was decreased to 41 mm d^{-1}. The outdoor experiment had a stable HLR of 82 mm d^{-1}.
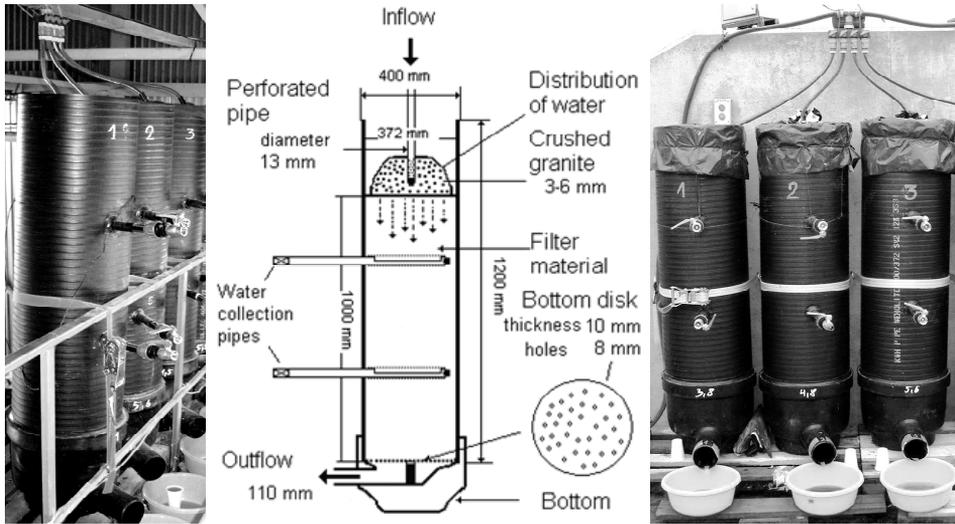
Figure 4. Experimental design of the second study: construction of filters (middle), indoor experiment (filters 1S, 2S, 3S; on the left), and outdoor experiment (filters 1V, 2V, 3V; on the right).

In the third study (Publications III and IV), pilot-scale experiments with identical experimental designs (Fig. 5) were conducted in parallel at two sites: at the municipal wastewater treatment plant in the small town of Tapa and at Väätsa landfill in Estonia. The Tapa experiment lasted from September 2006 to March 2007 (total 6 months), and Väätsa the experiment took place from September 2006 to September 2007 (total 12 months). Small insulated houses were built for both experiments in order to avoid the freezing of filters during the winter period. The vertical flow (VF) filters had a volume of 0.86 m^3, and the horizontal flow (HF) filters 1.24 m^3. The filters were filled with a 1.1 m thick layer of material. The identical experimental design of the Väätsa (V) and Tapa (T) experiments consisted of the following components (Fig. 5):

- vertical flow peat filters (VV1 in Väätsa and TV1 in Tapa) followed by horizontal flow hydrated oil shale ash filters (VH1 in Väätsa and TH1 in Tapa);
- vertical flow hydrated ash filters (VV2 and TV2) followed by horizontal flow hydrated oil shale ash filters (VH2 and TH2);

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- vertical flow filters filled with peat (top layer 0.55 m) and hydrated ash (bottom layer 0.55 m) filters (VV3 and TV3) followed by horizontal flow peat filters (VH3 and TH3).

In order to test the higher inflow P load on horizontal flow hydrated ash filters (VH2 and TH2), the vertical flow filters (VV2 and TV2) were removed from the system after nearly 5 months in operation, and the HF filters were directly loaded with raw inflow (effluent from the onsite treatment system).
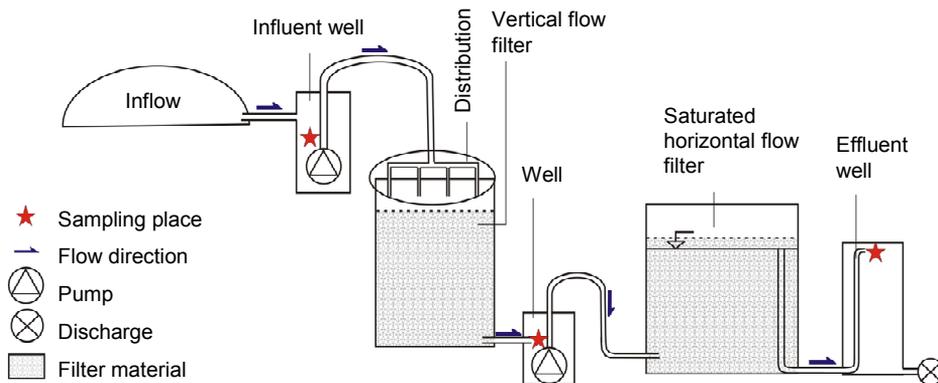
Figure 5. Experimental design of the third study: pilot systems in Tapa and Väätsa.

The loading rate was 76 mm d^{-1} for VF filters, and 53 mm d^{-1} for HF filters. The filter systems were periodically loaded using timer-adjusted pumping every 2 hours, i.e. 12 times per day. The amount of water in one dose was ~5 L. The average flow rate for all filters was 60 L d^{-1} during the entire period of operation. The even distribution of leachate and wastewater into the VF filters was achieved using perforated pipes inside crushed granite (fraction 6-8 mm) on top of the filter material. To provide maximal saturation and good contact between filter media and wastewater, the inflow water was pumped from the collecting well to the horizontal flow filter at the bottom, and an outflow pipe collected the water in the upper part of the HF filter (Fig. 5).

2.4. Sampling, analytical methods and statistical analyses

2.4.1. Water sampling and analyses

In all studies the water samples were taken during the experiments, according to standard procedures (ISO 5667–10:1992), and analyses were performed according to APHA et al. (1989) in certified laboratories (Tartu Veevärk Ltd and Tartu Environmental Research Ltd) using standard methods.

In the first study the leachate samples from the inflow and outflow of filters F1 and F2 were taken on days 2, 4, 6, 8, 15 and 22. In the experiments, pH, BOD_7 and COD values (mg O_2 L^{-1}), total nitrogen (TN), NH_4-N, NO_3-N, NO_2-N and total phosphorus (TP) concentrations (mg L^{-1}) were determined.

In the second study the leachate samples from the inflow and outflow of the filters were taken once a month as a daily average (12 samples in the indoor experiment and four samples in the outdoor experiment). In both experiments, also pH, BOD_7, COD values (mg O_2 L^{-1}) and concentration (mg L^{-1}) of TN, NH_4-N, NO_3-N, NO_2-N, TP, PO_4^{3-}, SO_4^{2-}, Ca^{2+}, Mg^{2+}, total suspended solids (TSS) and also conductivity (μS m^{-1}) were determined. Using portable Metler Toledo analyzers, the temperature (°C) and O_2 content (mg L^{-1} and %) in the samples were determined on site.

In the third study the water samples from the inflow and outflow of all filters of the pilot systems were taken once a week during the entire period of operation. In both experiments, BOD_7, COD values, total nitrogen (TN), NH_4-N, NO_3-N, NO_2-N, total phosphorus (TP), PO_4^{3-}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, K^-, Cu, Zn, Pb, Cd, Hg, As, Ni, Cr concentrations and pH were determined. Using the portable Metler Toledo analyzers, pH, O_2 (mg L^{-1} and %), conductivity (μS m^{-1}) and temperature (°C) were measured on site.

2.4.2. Soil sampling and analyses

The chemical composition of the mineralized peat (before and after the experiments) was analysed in a certified laboratory of the Estonian University of Life Sciences, and the content of organic matter (%), N (%), pH_{KCl} and P, K, Ca, Mg (mg kg^{-1}) was determined. The chemical composition of the initial hydrated oil shale ash and hydrated ash after the experiments was determined using standard ICP-ES and ICP-MS techniques at ACME Analytical Laboratories Ltd., Vancouver, Canada (Publications III and IV). The mineralogical composition of the initial hydrated ash and the hydrated oil shale ash after the experimental periods was studied using powder X-ray diffraction (XRD) with a Dron 3M difractometer. The micromorphology and spatial relationships of secondary mineralization were performed using a Zeiss DSM 940 scanning electron microscope (SEM) equipped with an Idfix Si-drift technology energy-dispersive analyzer (EDS). SEM preparations were coated with conductive gold or carbon coating during preparation.

2.4.2. Statistical analyses

In all studies the normality of variables was checked using the Lilliefors and Shapiro-Wilk tests; for normally distributed variables, the inflow and outflow values in different filters were compared via the pairwise t-test. When the distributions were skewed, the nonparametric Wilcoxon pairwise test was used.

When the assumptions of ANOVA were fulfilled, a Fisher LSD test was used for multiple comparisons of mean removal efficiencies in different filters. For the remaining variables, Kruskal-Wallis ANOVA and the multiple comparison of mean ranks for all filters was used. The STATISTICA 7.0 software was used and the level of significance of $\alpha=0.05$ was accepted in all cases.

2.5. Literature review

Preliminary screenings of available data for the literature review (Publication V) showed that the majority of investigated filter materials have high Ca and/or CaO content. Based on these data, an analysis of the influence of Ca and/or CaO content and pH on phosphorus retention capacity was performed. To provide a better overview of the different types of materials and their potential as a filter media, however, we have included in our analysis articles where only P-removal effectiveness or retention capacity were also presented. Some literature sources provided information on hydraulic loading rate (HLR) and hydraulic retention time (HRT). These data were taken into account and analyzed in combination with P retention values. A more detailed description of the literature analysis is given in Publication V (Vohla et al. 2010).

3. RESULTS AND DISCUSSION

In Estonia there are target values for municipal wastewater and landfill leachate treatment (Table 1; RT I 2001.69.424): i.e. contamination rates of 15 and 25 mg L^{-1} for BOD_7 in municipal wastewater and landfill leachate respectively (purification rate $\geq 90\%$); 125 mg L^{-1} for COD ($\geq 75\%$), 15 and 75 mg L^{-1} for TN ($\geq 75\%$), and 1.0 and 2.0 mg L^{-1} for TP respectively ($\geq 80\%$).

3.1. Landfill leachate and municipal wastewater treatment in experimental filters

The well mineralized peat filters (F1 and F2) had slightly better efficiency treating biologically pre-treated leachate from the second stage of the onsite treatment plant (Table 1) than the raw leachate (Publication I). However, when we compare the efficiency of the mineralized peat in the first study with the second (Publication II) and the third (Publication III), the treatment efficiency is better in the last two. One explanation for these results may be that the selected loading rate was too high for the filters in the first study (Kadlec, 2003). The overall results from the third study (Publication III) indicated that mineralized peat is more suitable for use in the vertical flow (VF) filters then in hydraulically saturated horizontal flow (HF) filters.

The hydrated oil shale ash showed better results in hydraulically saturated horizontal flow filters, where the hydraulic retention time is longer and therefore efficiency higher, especially in phosphorus removal (Publication IV).

3.1.1. Changes in pH value

The pH of the inflow leachate and wastewater to the experimental filters was quite constant at both sites. The median pH value in the effluent of the onsite leachate treatment system (pond effluent – F2 in, Outdoor in, V in; Fig. 6) was 8.8 and in the raw leachate (F1 in) 7.5, the effluent of the activated sludge treatment plant (i.e. inflow leachate to the indoor experiment – Indoor in) had a median pH value of 8.6. The pH value of the municipal wastewater (T in) was somewhat lower at median 7.7 (Fig. 6).

In all studies the pH variation at the outflow of each filter shows a clear dependence on filter material properties. The vertical flow (VF) mineralized peat (average pH_{KCl} 6.7) filter slightly increased the pH of the raw leachate to 7.8 (filter F1) and decreased the pH of the pond effluent and effluent from the activated sludge treatment plant (Fig. 6). In the Tapa wastewater treatment experiment the VF peat filter TV1 slightly lowered pH to a median value of 7.3. As stated by Patterson et al. (2001), the change in pH in the peat filters can be related to the organic acid components that were flushed out of the peat.

The alkaline hydrated oil shale ash (the pH of water in contact with ash material is >12.0) increased the pH value of the effluent in VF filter 3S at the beginning of the indoor experiment (the first four months) to a median of 9.3, and after one year of operation the average pH was only 8.6. In the shorter outdoor experiment (which lasted for a total of four months) the median pH of the outflow leachate from VF filter 3V was 9.9 (Fig. 6). Due to the presence of portlandite, $Ca(OH)_2$, water treatment with hydrated oil shale ash increased the pH value of the influents from a median of 8.7 in the leachate and from 7.7 in the wastewater to a median of 11.5, 10.5, 11.7 and 12.0 in HF filters VH1, VH2, TH1 and TH2 respectively (Fig. 6; Publication IV).
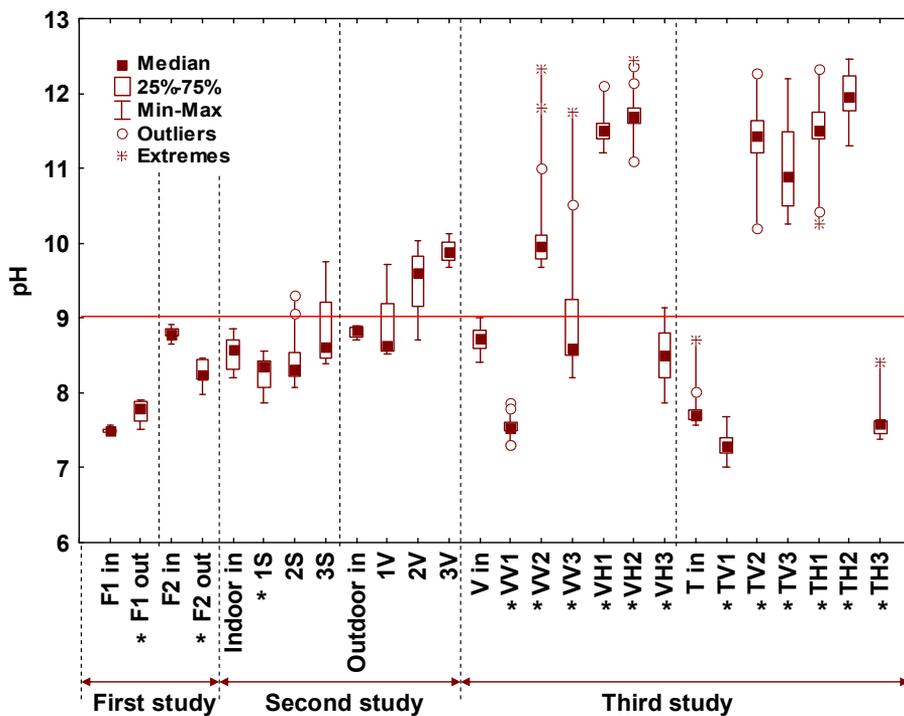
Figure 6. Changes in the pH value in all experimental studies. For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test). Target value according to Estonian regulations (RT I 2001.69.424) is marked with the red line.

In the combined VF peat/hydrated ash filters (2S, 2V, VV3, TV3), the effluent mostly showed a higher pH value then the influent (pH 8.3, 9.6, 8.6 and 10.9 respectively), probably because the alkaline hydrated ash was placed underneath the mineralized peat in VF filters. For example, the pH of the outflow water from combined peat/ash filters VV3 and TV3 increased the outflow of HF peat

filters VH3 and TH3 due to the dissolution of Ca-phases (portlandite and ettringite) present in the hydrated ash material. Compared to peat filters VV1 and TV1, however, which had stable outflow pH values during the experiments (Fig. 4 in Publication III), both combined VF filters (VV3 and TV3) showed a decrease in pH from an initial ~12 to 8.4 in Väätsa (longer experimental length), and to 10.8 in Tapa (shorter experimental period). The high pH from combined VF filters was significantly decreased to a tolerable pH 7–9 by subsequent HF peat filters (Fig. 6; Publication III).

3.1.2. Reduction of BOD_7 and COD values

A decrease in biochemical oxygen demand (BOD_7 value) was observed after treatment in almost all peat filters in all experiments, except for HF peat filters VH3 and TH3 (Fig. 7). In the Tapa experiment the median BOD value of the inflow wastewater was far below the limit value (median 1.6 mg O_2 L^{-1}; Table 1), and therefore no significant removal occurred in filters; only 17% removal of BOD_7 was found in TV1 and 29% removal in TV3 (Fig. 7).
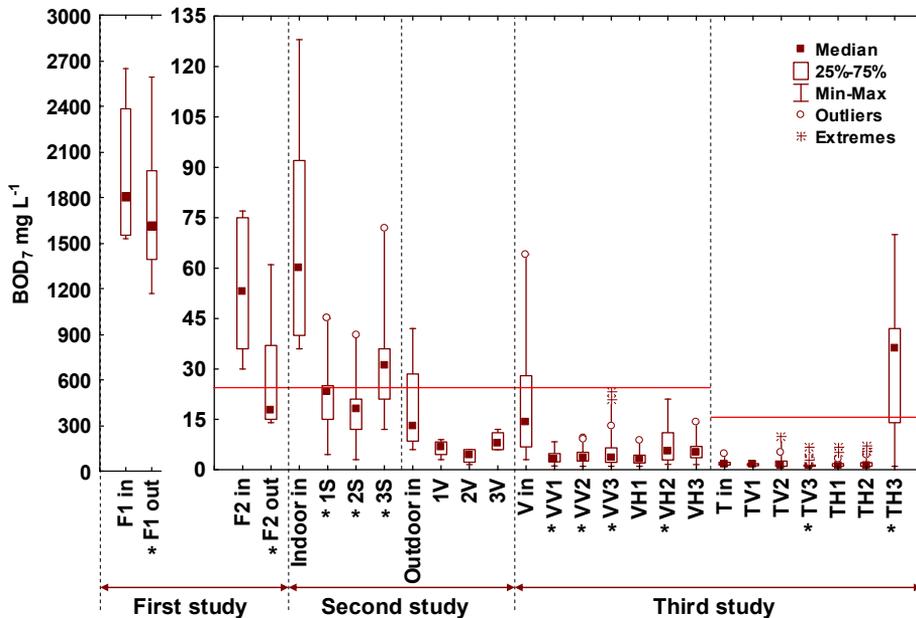
**Figure 7.** Reduction of BOD_7 value in experimental filters; median inflow and outflow values (mg O_2 L^{-1}). For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test). Target values according to Estonian regulations (RT I 2001.69.424) are marked with the red lines.

Similarly to Kinsley et al. (2004), most of the organic matter was removed from landfill leachate in VF peat filters, the median treatment efficiency in different VF peat filters was 13–75%, and the maximum reduction of BOD_7 was achieved in VV1 (75% on average). The outflow value that fulfils the prescribed limit for landfill leachate of 25.0 mg O_2 L^{-1} (RT I 2001.69.424) was achieved in all VF peat filters (median outflow 1.5–23 mg O_2 L^{-1}), except in the treatment of raw leachate in filter F1 (Fig. 7). The combined VF peat/hydrated ash filters showed relatively good results in the removal of organic matter from leachate, where the efficiency was 64–78%.

The results show that the VF peat filters had a good O_2 supply and favourable temperatures (e.g. in second study; Fig. 3 in Publication II) for the formation of necessary microbiological communities. The study by Talbot et al. (1996) demonstrated good results in the removal of organic matter from municipal wastewater (BOD_7 removal 96%), but in the Tapa experiment, however, the BOD_7 value in the inflow to the pilot experimental filters was already very low and no significant changes were observed. The VF hydrated oil shale ash filters (3S, 3V and VV2) removed about 43–54% of the inflow BOD_7 from the leachate, and the HF hydrated ash filters in the third study had only median reduction, namely 13% in VH1 and 52% in VH2.

The removal of heavily decomposable organic matter (high COD value) is one of the greatest problems in leachate purification (Table 1; Fig. 8). The COD value from leachate was most effectively reduced in VF peat/ash filters and hydrated ash filters – on average 40% in 2S and 20% in 2V and 22% in filter 3S, and 31% in filter 3V. The reduction of COD in the third study was on average below 10%, and only in the combined VF peat/ash filter at Väätsa (VV3) was the efficiency on the order of 17%. It should be noted that the COD value in the inflow at Väätsa landfill reached 1200 mg O_2 L^{-1}, which is an order of magnitude higher than that allowed by the regulations (Table 1). At Tapa wastewater treatment plant, the effluent COD value was <50 mg O_2 L^{-1}, which is well below the target value (125 mg L^{-1}; Table 1). At both sites, the conditions in HF peat filters VH3 and TH3 were not suitable for the removal of organics; and probably due to the hydraulically saturated and anaerobic conditions, we observed an increase in BOD_7 and COD values in the outflows (Fig. 7 and Fig. 8).

The reasons why BOD_7 and COD removal was sometimes not successful enough may be that factors were not favourable (pH range, the existence of inhibitors, the lack of substrate and phosphorus, temperature, contamination rate etc). For instance, the BOD_7 and COD values in raw leachate were too high (Table 1) for it to be treated only with a peat filter and in the hydrated ash the performance was probably low due to the high alkalinity of this material, which inhibits the biological treatment processes.
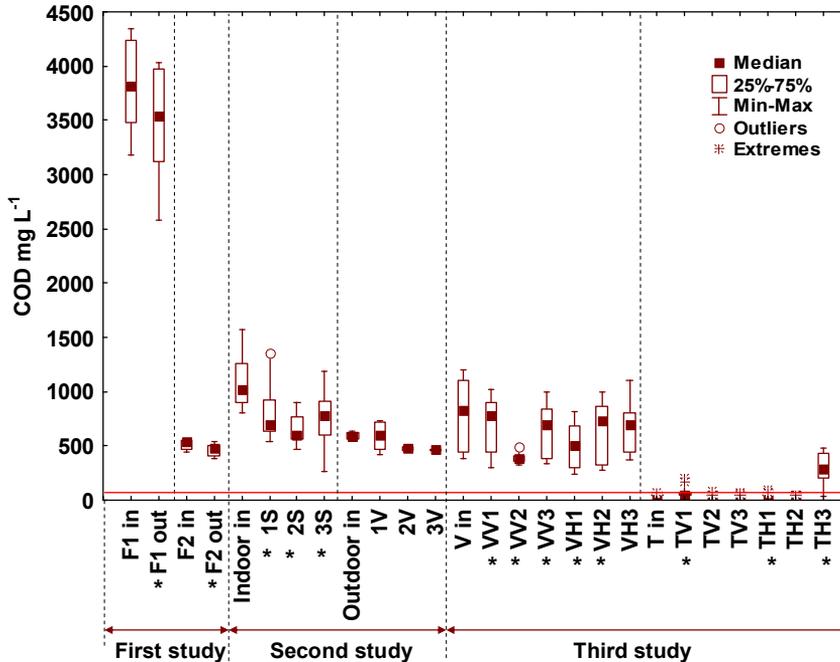
Figure 8. Reduction of the chemical oxygen demand (COD value) in experimental filters; median inflow and outflow values (mg O_2 L^{-1}). For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test). Target value according to Estonian regulations (RT I 2001.69.424) is marked with the red line.

3.1.3. Removal of total suspended solids

Similarly to BOD_7, the total suspended solids (TSS) concentration in the Tapa wastewater was also low (median 6.0 mg L^{-1}), and met the environmental requirements (15 mg L^{-1}; Fig. 9). Nevertheless, the VF peat filter TV1 was able to further decrease the inflow value by 33.3%. In peat/ash sediment filter TV3, however, the hydrated ash caused an increase in the TSS concentration in out-flow water during the first 4 months, probably because of the outwash of the small ash particles, which also caused higher pH values in the outflow from fil-ter TV3 (Fig. 6). When the outwash decreased and finally stopped, the ash filters also showed good removal of TSS (median 60%; Fig. 9).

In the effluent of the Väätsa landfill leachate treatment system the TSS concentration was considerably higher than in the wastewater (Fig. 9). Interes-tingly, the TSS concentration of the leachate from the activated sludge treatment plant was even lower than from the aerobic-anoxic pond (median 65 mg L^{-1}) during the second study. In the first study the TSS concentration was not detected.
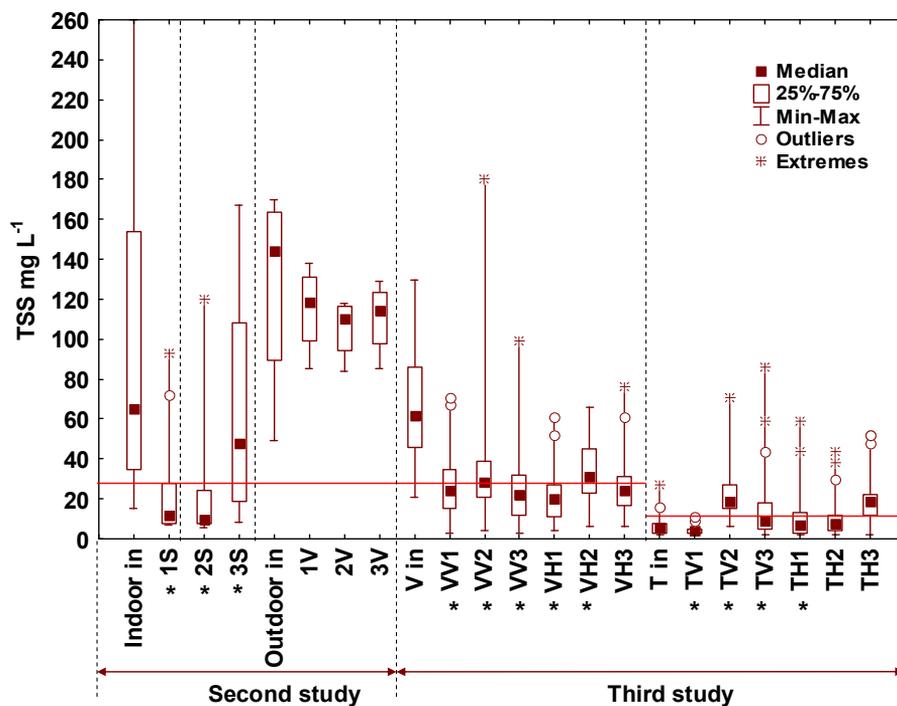
Figure 9. Removal of total suspended solids (TSS) in experimental filters; median inflow and outflow concentrations (mg L^{-1}). For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test). Target concentrations according to Estonian regulations (RT I 2001.69.424) are marked with the red lines.

The highest overall efficiency in the removal of TSS from leachate was achieved in the VF peat and combined peat/hydrated ash filters, where the median reduction was 60%, 60.4%, 72% and 76% in filters VV1, VV3, 1S and 2S, respectively, and the outflow values met the environmental requirements (25 mg L^{-1}, RT I 2001.69.424). Only in the outdoor experiment during the second study (Publication II), where the median inflow TSS concentration was considerably higher, the different VF filters (1V, 2V and 3V) did not show an average efficiency over 30%, and some outwash of TSS from VF filters during the first month in operation was visible. During the third study (Publication III) the HF peat filters had a negative effect on TSS concentration, similarly to the results in the removal of organic matter, e.g. in VH3 the outflow TSS was 19.0 mg L^{-1} when the inflow concentration from TV3 was only 10 mg L^{-1}.

The removal of TSS in our peat filters was considerably less efficient (e.g. 33% in TV1 and 60% in VV1; Publication III) than reported in other studies of similar peat filters (91–98% according to Talbot et al., 1996). The observed discrepancy is most probably due to differences in (a) the quality of inflowing

water and (b) the peat materials used in experiments – their botanical composition and most importantly the degree of humification, as far as well-humified (i.e. well-mineralized) peat filters (as used in our experiment) would release their fine partially decomposed particles and reduce the overall purification efficiency.

During the first weeks of the experiments we also saw an outwash of fine ash particles from VF hydrated ash filters in the third study, and therefore the concentration of total suspended solids (TSS) increased from 40 mg L^{-1} in leachate to 100 mg L^{-1} from VV2, and from 5 mg L^{-1} in wastewater to 70 mg L^{-1} from TV2. This intensive outwash lasted about two months, after which the outflow concentrations began to stabilize – median TSS in leachate 61.5 mg L^{-1} and 27 mg L^{-1} from VV2 and 23 mg L^{-1} from VV3, and 6 mg L^{-1} in wastewater, 19 mg L^{-1} from TV2 and 8.5 mg L^{-1} from TV3. The same behaviour was detected in the second study (Publication II), where VF hydrated ash filters 3S and 3V had higher outflow TSS concentration in the in the beginning of the experiments. This kind of outwash in the starting period is normal for the most of the filter materials. The median TSS removal efficiency in hydrated oil shale ash, however, was 17–25% in VF filters and 26–56% in the HF filters (Fig. 9).

3.1.4. Removal of different forms of nitrogen

In the raw leachate and in the effluent from the activated sludge treatment plant, most of the nitrogen was in the form of ammonia-nitrogen, the median NH_4-N concentration was 360 mg L^{-1} (Fig. 2 in Publication I) and 277 mg L^{-1} (Fig. 3 in Publication II), and TN concentration 440.5 and 406 mg L^{-1} in raw leachate (i.e. F1 in; Fig. 10) and leachate from the activated sludge plant (i.e. Indoor in) respectively. The nitrogen in pre-treated leachate in the first and second studies (i.e. aerobic-anoxic pond effluent: F2 in, Outdoor in; Fig. 10) was mostly in the form of nitrate-nitrogen (NO_3-N), and the concentration was 21–50 mg L^{-1} (median TN 105–144 mg L^{-1}).

In the first study the reduction of total N concentration was noticeably higher in F2, on average 35%. However, significant differences between inflow and outflow were only determined in F1 (efficiency 12%), and the reduction was not sufficient to fulfil the Estonian discharge limit (RT I 2001.69.424).

The results of the second study (Publication II) show that good conditions in filters for nitrification occurred after two months of performance, because microbiological processes usually need some start-up time, e.g. for the growth of biofilm on the filter material. The peat/hydrated ash filters 2S and 2V and ash filters 3S and 3V showed promising results in nitrification (Fig. 3 in Publication II), efficiency in the reduction of NH_4-N concentration of on average 50–80% (outflow concentration in 2S was 55 mg L^{-1} and in 2V 4.8 mg L^{-1}; Fig. 11). In aerobic conditions in VF filters, the nitrate-nitrogen concentration in the indoor experiment increased from 29 to 140 mg L^{-1} on average, confirming the good nitrification. In the outdoor experiment the nitrogen in leachate was mostly in

the form of organic nitrogen and nitrate-nitrogen (average inflow concentration of NO_3-N 50 mg L^{-1}). Because of the aerobic conditions in the VF filters (Kadlec & Knight, 1996), denitrification efficiency was low in all studies, resulting in overall poor TN removal (e.g. average removal in second study of only 13%).

The median concentrations of different forms of nitrogen of the inflows and outflows in the third study at both sites are shown in details in Publication III. The behaviour of the Väätsa and Tapa filters differs significantly in the area of nitrogen removal. The best results for nitrification were achieved in the VF peat filters (Fig. 10 and 11), where ammonia nitrogen was reduced by 56% on average in TV1 and 97.5% in VV1 (Publication III). In the VF filters at Väätsa landfill, where the TN loading is more that 10 times higher than in Tapa (TN 180 and 12 mg L^{-1}, respectively), the nitrogen removal is low (>10%). In the Väätsa experiment, this was probably caused by the high concentrations of other contaminants, e.g. the high COD value and the NO_2-N concentration that may inhibit microbiological processes.
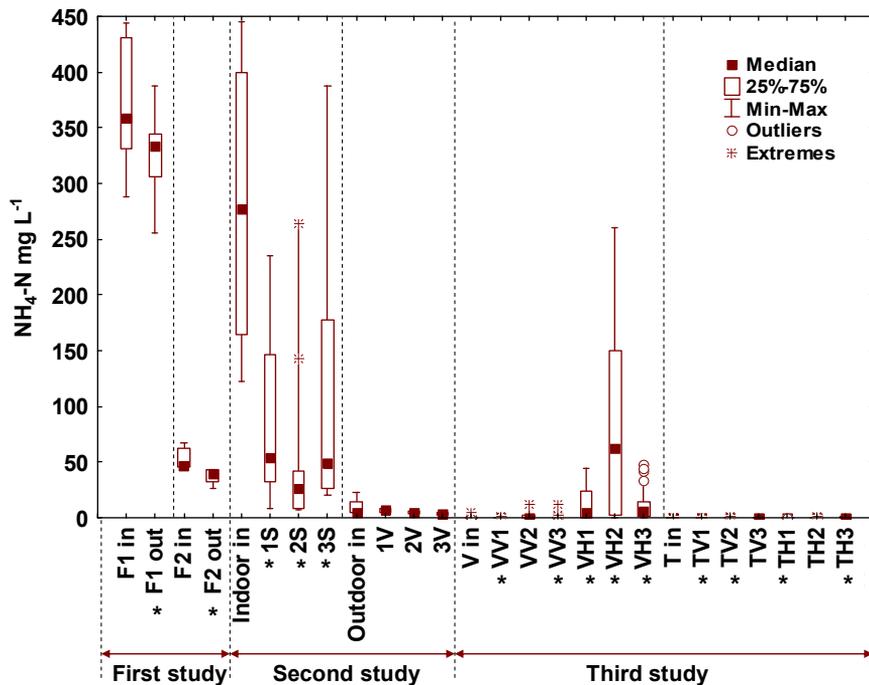
Figure 10. Changes in the ammonium-nitrogen (NH_4-N) concentration in the experimental filters; median inflow and outflow concentrations (mg L^{-1}). For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test).

In the Tapa experiment the TN removal in peat filter TV1 was 78% and in the combined peat/hydrated ash filter TV3 51%. The results show that mineralized peat can nitrify NH_4-N even at low inflow concentrations (0.44 and 0.023 mg L^{-1} at Väätsa and Tapa respectively; efficiency in VV1 97.5% and in TV1 55.6%). In the Tapa experiment the inflow NO_3-N concentration was only 9 mg L^{-1} (inflow TN concentration 12 mg L^{-1}), but all peat filters showed a remarkable performance in the reduction of NO_3-N, i.e. 72–92% (Table 2 and Fig. 6 in Publication III). Analogous results in nitrification were achieved in Canadian studies, where the hybrid peat filter showed an efficiency of 97% during two years of operation (Kinsley et al., 2004), and the pilot scale peat filter efficiency of 85.3% (Hu and Gagnon, 2006). Interestingly, the nitrogen forms and their removal efficiency in the peat filters in the third study (Publications III) show some seasonal dependency (Fig. 5 and 6 in Publication III).

Mæhlum (1998) indicated that nitrification may be limited due to lack of oxygen. The amount of oxygen in filter materials was not directly measured, but the intermittent loading of leachate during the experiment to VF filters was selected in order to increase the natural inflow of oxygen through the top and the bottom of the filter body. In all experiments the amount of oxygen was measured from the inflow and outflow of the filters. The results show that all VF filters increase the amount of oxygen in water (e.g. 95% on average in 1S).
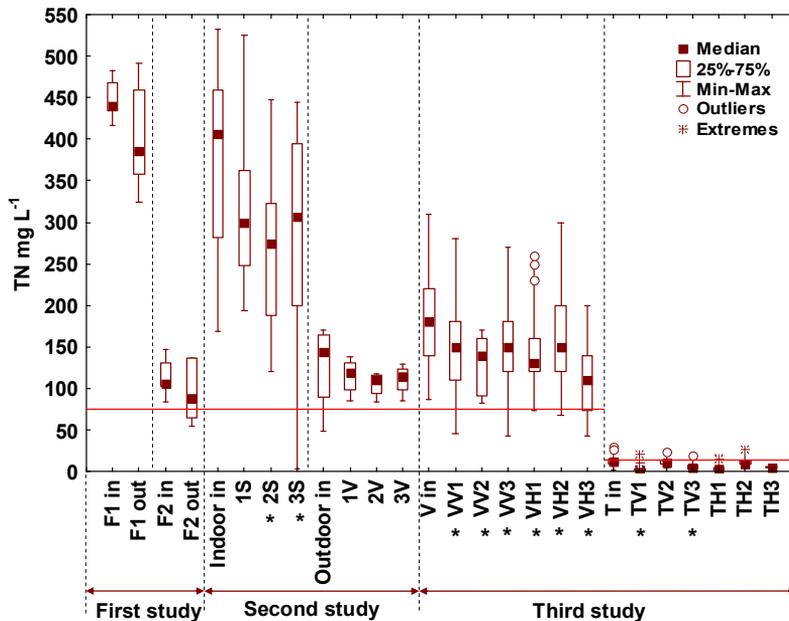
Figure 11. Removal of total nitrogen (TN) in the experimental filters; median inflow and outflow concentrations (mg L^{-1}). For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test). Target concentrations according to Estonian regulations (RT I 2001.69.424) are marked with the red lines.

In the second study (Publication II), we found a significant negative correlation ($R^2 = 0.36$–0.77) between the temperature and O_2 content of the leachate (Fig.3a, b in Publication II). When the temperature decreased, the O_2 diffusion to the leachate in the vertical flow filters was considerably better. This also positively affected the removal efficiency of organic matter, and especially nitrification. According to Kadlec & Knight (1996), nitrification occurs at an optimum temperature of about 30ºC, and at 5ºC the nitrification rate is only 15% of the rate at 20ºC. In the first study the temperatures of raw and pre-treated leachate during the summer period in Väätsa were 14.8±0.3ºC and 18.0±1.6ºC respectively, and during the third study the average temperature of leachate was 12.2ºC and wastewater 9.1 ºC (higher in summer period, e.g. average 18.6ºC in leachate). Thus favourable conditions for the creation of nitrifying bacteria were ensured.

The drawback was evident in HF peat filters VH3 and TH3 (Publication III), where the NH_4-N concentration in outflow increased significantly (Fig. 5 and 6 in Publication III). Such behaviour suggests that the anaerobic conditions in saturated filters initiated the intensive decay of the organic matter in peat, which is also evident from increased BOD and COD values (Fig. 7 and 8) in the outflows from these filters, being supported by increased organic N values (Table 2 in Publication III).

As expected, low nitrification and overall nitrogen removal was detected in filters filled with alkaline hydrated ash (slightly better results in VF hydrated ash filters, e.g. median efficiency of 25% in 3V). The highly alkaline conditions (Fig. 6) in the horizontal flow hydrated ash filters probably inhibited the microbial processes, and as a result there were only slight changes in the TN concentrations in effluents (some hydrated ash filters even increased the ammonium-nitrogen concentration in water; Fig. 10).

3.1.5. Removal of phosphorus

Most of the inflow phosphorus in leachate (in all studies) and wastewater (in the third study) was in the form of PO_4-P. In the course of the first study (Fig. 12), the raw and pre-treated leachate had a much lower total phosphorus concentration than during the following experiments, a median of 1.4 and 1.2 mg P L^{-1} respectively, which is already sufficient to fulfil the Estonian discharge limit for landfill leachate (RT I 2001.69.424).

According to pairwise t-tests, the inflow and outflow values were significantly different ($p \leq 0.005$) in the first study (Fig. 2 in Publication I), with the TP falling by an average of 49% in F1 and F2. However, the experimental period in the first study was not long enough to estimate the overall capacity of peat filters for phosphorus removal.
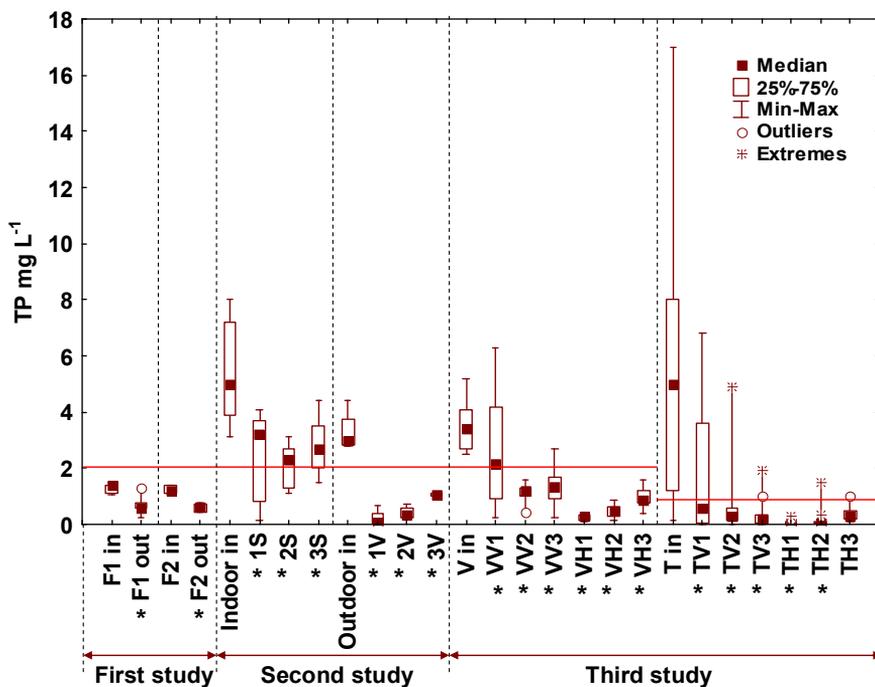
Figure 12. Removal of total phosphorus (TP) in the experimental filters; median inflow and outflow concentrations (mg L^{-1}). For abbreviations of filters, see Materials and Methods. *outflow value differs significantly from the inflow value (p<0.005, according to the Wilcoxon Matched Pairs test). Target concentrations according to Estonian regulations (RT I 2001.69.424) are marked with the red lines.

In the second study (Publication II) the average reduction of total P in peat filters 1S and 1V during the first 6 months was 77% and 93% for indoor and outdoor experiment respectively (Fig. 2 in Publication II). In peat/hydrated ash filters 2S and 2V the average reduction was 71% and 88%, and in ash sediment filters 3S and 3V 46% and 68% respectively. As demonstrated by an indoor experiment (Fig. 3 in Publication II), the P removal efficiency in peat filters decreased during the last 6 months in operation, whereas it remained stable in other filters that were partly or completely filled with hydrated oil shale ash.

The dynamics of TP removal in the third study suggest the same as the results of the second study, that at both experimental conditions the TP removal capacity of peat in VF filters gradually decreases over the first 6–7 months of operation (however, during that first period of time the efficiency was quite good, 67% in VV1 and 58% in TV1; Fig 12). This effect was well demonstrated in the Väätsa experiment, where the decrease in efficiency shows a trend close to power law (Fig. 2 in Publication III). The same is evident in the Tapa experiment (Fig. 2 in Publication III), where the higher contamination rate and

varying loading caused an even faster decrease in removal capacity, and the filter lost its P-binding capacity after 5 months in operation. Moreover, the data from the longer experiment (in Väätsa landfill) show some phosphorus mobilization after saturation was achieved (Fig. 12).

Whereas the peat filters exponentially exhaust their binding capacity after the initial phase, the combined peat/hydrated ash filters in the third study show a rather gradual (linear) change. In both sites the peat/ash filters VV3 and TV3 show similar efficiency at the beginning of the experiment, namely 67% and 94% for the Väätsa and Tapa experiments respectively (Fig. 2 in Publication III). The longer effective performance of combined peat/ash filters is directly related to the additional (or supporting) P-binding effect of hydrated ash (Publication III). However, the hydrated ash filter is very sensitive regarding retention time, and its efficiency in VF regime with short contact time seems to be quite low compared to the peat material, which controlled the phosphorus removal in VF filters during the first few months of the experiment. Nevertheless, when the peat filter becomes saturated, the phosphorus precipitation in the ash material begins to dominate at lower efficiency, but for at least twice as long a period as the peat filter (Publication III).

Phosphorus removal in HF peat filters VH3 and TH3, which were installed after the combined VF peat/ash filters VV3 and TV3, was more complex (Fig. 2 in Publication III), and the outflow TP concentration shows quite a great variation, and therefore the removal efficiency was very unstable. In both cases the P was not removed during the initial stages of operation at low TP concentrations in the inflow from VF filters VV3 and TV3, and at least at the Tapa site, mobilization of P was observed (Fig. 12). However, the filters did show good binding capacity (up to 90%) after 5–6 months of operation, when the concentration of TP in inflow increased due to the failure of VF peat/ hydrated ash filters VV3 and TV3. In the Väätsa experiment the removal efficiency of TP also increased during the 7–12 month period of operation, when the efficiency was 32%, compared to the earlier period, when the efficiency was only 11%. Interestingly, our results suggest that in saturated HF peat filters (Publication III), phosphorus removal was initiated only if the TP in the inflow was above 1.5 mg L^{-1}. The nature of this phenomenon is not clear, although this may suggest that the phosphate molecules need to be bound to complexes (the formation of larger molecular aggregates) to be adsorbed to peat particles.

Earlier studies (Mann, 1990; Kadlec and Knight, 1996; Richardson et al., 1996) suggest that the reduction of P in mineralized peat may occur through the sorption, sedimentation and combination of complex compounds. Alternatively, some P may be bound to the biofilm (Mann, 1990; Richardson et al., 1996), and the phosphorus can easily be transformed from organic to inorganic forms. Importantly, the phosphorus forms chemical complexes with organic and in-organic ligands, which can be adsorbed into the soil or be removed by preci-pitation (Mæhlum, 1998). In aerobic and alkaline wetland conditions P appears in dissolved complexes together with Ca and Mg ions, and with Fe or Al ions in

aerobic soil with acidic to neutral pH Nieminen and Jarva, 1996; Mæhlum, 1999). The content of the Mg and Ca in peat from the experiments of the first study increased significantly, whereas the pH of the peat was neutral.

Talbot et al. (1996) showed in a lab-scale experiment that the efficiency of peat in P removal from an initial 14 mg P L^{-1} was a median 44%. Average effluent parameters over a 2-year study for the septic tank and peat filter system demonstrated no removal of PO_4-P and 12% for TP. Bulč et al. (1997) demonstrated that phosphorus removal efficiency from leachate over a 5-year study was on average 63%. Rizzuti et al. (2002) found that peats with higher N and P retention capacities also have humic acid contents between 5 and 7% (unfortunately the content of humic acid in our peat was not analyzed).

Our results from the third study (Publication IV) show that because it is a highly alkaline and reactive filter material, hydrated oil shale ash is unsuitable for the removal of organic matter and nitrogen (the best median removal efficiencies for BOD_7 and TN were only 50% in VH2 and 13% in VH1 respectively; Fig. 7 and 11); nevertheless, the P-removal in both experiments, despite the significantly different wastewater compositions and P loading dynamics, is remarkably good (Fig. 1 in Publication IV). The median removal efficiency of TP in the VF hydrated ash filters of the Väätsa and Tapa experiments was 58% and 89% respectively.

During the operation of the VF hydrated ash filters (VV2 and TV2), the subsequent HF filters VH2 and TH2 removed 68.9% and 82.4% of remaining TP from the outflows of the VF filters. After the VF filters were switched off, the median removal efficiency of TP in HF filters even increased to 85.4% and 99.2% in the Väätsa and Tapa experiment respectively. In the HF hydrated ash filters VH1 and TH1 (subsequent to VF mineralized peat filters VV1 and TV1), the median removal efficiency was 88.6% in Väätsa and 86.1% at the Tapa site.

Interestingly, the removal efficiency of phosphorus in the hydrated ash filter was not (significantly) affected by wastewater or leachate composition (Fig. 2 in Publication IV), although the concentrations of several known inhibitors such as magnesium, sulphate and chloride (Salimi et al., 1985; Chen et al., 2002; Shilton et al., 2005) were considerably higher in landfill leachate at Väätsa than in municipal wastewater at the Tapa site. The somewhat higher removal rate in the Tapa filter systems (Fig. 1 in Publication IV) was because of lower content of non-phosphate P (polyphosphates, organic phosphorus etc.) than in Väätsa, whereas the PO_4-P removal rate in both systems was statistically the same (Fig. 2 in Publication IV).

Phosphorus removal is strongly affected by ionic and organic inhibitors in the case of the adsorption mechanism, when the competing ions or organic carbon compounds block the adsorption sites on suitable crystal surfaces such as calcite (e.g. Vdović and Kralj, 2000; Berg et al., 2005a). Homogenous precipitation of Ca-phosphate, however, is not as strongly influenced, and whereas magnesium is known to inhibit the growth of the most stable Ca-phosphate crystalline form hydroxyl-apatite (HAP), other phases such as octa-calcium phosphate (OCP) and di-calcium phosphate di-hydrate (DCPD) are less affected

(House, 1999). Typically poorly-crystallized or amorphous DCPD, OCP and tri-calcium phosphate (TCP) form as precursor phases in solutions containing Ca and P, and are only then re-crystallized into thermo-dynamically stable HAP over time (Valsami-Jones, 2001). Consequently, we suggest that the P removal in hydrated ash occurs through precipitation discrete amorphous Ca-phosphate phases by either homogenous precipitation or heterogeneous nucleation on suitable crystal surfaces. The P-removal efficiency of the ash then depends on the availability of dissolved Ca.

Kaasik et al. (2008) have shown that hydrated oil shale ash is composed of several Ca-phases, including calcite and vaterite as Ca-carbonate phases – $CaCO_3$ and γ-$CaCO_3$, respectively; ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$, hydrocalumite $Ca_2Al(OH)_7*6H_2O$, portlandite $Ca(OH)_2$, C_2S belite β-Ca_2SiO_4, merwinite $Ca_3Mg(SiO_4)_2$, melilite $(Ca,Na)_2(Al,Mg,Fe)(Si,Al)_2O_7$, pseudo-wollastonite $CaO*SiO_2$. About 20-30% of the ash consists of amorphous glass-like aggregates of (alumino-) silicate composition. These phases are dissolved at different rates, (a) providing Ca-favouring phosphate precipitation and (b) increasing the pH to alkaline (>9.0, Fig. 1 in Publication IV), which promotes P speciation towards PO_4^{3-} (Berg et al., 2005b).

Likewise, our results show that the removal rate of phosphorus in hydrated ash filters depends significantly on the concentration of P in solution (Fig. 3 in Publication IV). The removal efficiency is low (<50%) at low P concentrations (<0.2 mg L^{-1}), and efficiency increases abruptly when the phosphorus concentration is higher than 0.5 mg L^{-1}. This suggests different removal mechanisms upon P loading.

3.2. Changes in the composition of filter materials during the experiments

The removal of contaminants from leachate and wastewater is linked to chemical changes in the filter material. The results are mainly affected by interactions between the type of the filter material, water quality, hydraulic loading rates, and duration of treatment.

In the third study, the content of heavy metals (e.g. Zn, Pb, Cu, Cd, Hg, As, Ni, Cr) in the initial filter materials and in the mineralized peat and hydrated ash after the experiments was also determined, and no concentrations exceeding the limits were detected.

3.2.1. Changes in the composition of the mineralized peat

In Table 4 the chemical composition of the well-mineralized peat before and after the experimental studies is presented and the results show that the landfill leachate and municipal wastewater mostly had a significant influence of the chemical composition of the peat.

Surprisingly, before the first study, the content of organic matter in peat was almost twice as low (only 37%) as the average in other experimental studies (Table 4), which could be due to the small stones/mineral particles that were found in the peat, and this affected the lab analysis. The content of organic matter in the peat decreased, which was probably caused by the slight mineralization of the peat material.

In the first study the initial content of Ca, Mg and K in the well-mineralised peat was relatively high in comparison to other studies (Table 4). After the experiments of all studies, the concentration of Ca, Mg, N and especially K in peat increased significantly (e.g. median 96% in first study). The main reason for this could be the adsorption of these elements from the leachate and wastewater to the peat. The additional content of Ca and Mg also supported P removal from leachate. The pH of the peat slightly increased during the majority of experiments, and only in Tapa experiment did we see some decrease in pH value.

The relatively good results in phosphorus removal (analysis from the influents and effluents of the filters) are also confirmed by the chemical analysis from the filter materials. Before the experiments, the content of phosphorus in mineralized peat was about 0.03% (Table 4). In indoor experiment (filters 1S and 2S) the concentration increased on average threefold (to 0.08–0.09%) and was twice as high as the original values in the outdoor experiment (about 0.05%). As expected, in third study the VF filters had higher P concentration in the top layer of the peat, on average 0.05–0.07%, and in the bottom layer the content of P was much lower, on average 0.03–0.05%, and as expected the HF peat filters had insignificant changes in the content of P.

As mentioned above, probably the main removal mechanism for phosphorus in peat is most likely adsorption on the surface of the material and this is evidently limited by suitable sorption sites on peat fibres, and removal efficiency falls while the sorption sites become saturated. Likewise, the reduction of P in mineralized peat may also occur through the sedimentation and combination of complex compounds (Mann, 1990; Kadlec and Knight, 1996; Richardson et al., 1996). For the pilot-scale VF peat filter at Väätsa landfill, we estimate the maximum P binding capacity at given experimental conditions to be in the order of 81 mg kg^{-1} of P for dry peat or ~20 g m^{-3} of phosphorus, assuming the dry density of peat to be 246 kg m^{-3}.

Table 4. The chemical composition (wt %) of well-mineralized peat before (initial values) and after the experimental studies.

		pH	P	Ca	K	Mg	N	Organic matter
First study	**Initial value**	6.70	0.002[a]	8.294	0.093	1.416	0.500	37.20[b]
	F1 and F2	7.10	0.004[a]	9.178	2.177	2.149	0.600	36.90[b]
Second study	**Initial value**	6.93	0.031	3.070	0.050	1.150	0.670	63.46
	1S	7.33	0.082	4.290	0.560	1.610	1.050	54.49
	2S	7.36	0.096	6.230	0.510	1.410	0.980	47.21
	1V	7.71	0.055	4.080	0.540	1.580	0.790	56.59
	2V	7.98	0.051	5.070	0.540	1.830	0.750	52.93
Third study	**Initial value**	7.23	0.033	5.095	0.080	1.200	0.680	57.28
	VV1-1	7.48	0.072	4.693	0.834	1.749	1.095	51.47
	VV1-2	7.36	0.044	5.536	0.841	2.556	0.907	54.81
	VV1-3	7.48	0.035	5.381	0.811	2.300	0.706	53.60
	VV3-1	7.35	0.051	5.845	0.914	2.516	0.980	53.97
	VV3-2	7.38	0.042	4.827	0.895	2.238	0.852	57.42
	VH3	7.68	0.029	6.411	1.011	2.126	0.662	56.00
	TV1-1	6.90	0.066	5.719	0.105	1.458	0.842	52.72
	TV1-2	6.97	0.042	6.573	0.124	1.691	0.651	50.06
	TV1-3	7.05	0.037	6.667	0.126	1.986	0.536	45.79
	TV3-1	6.97	0.073	4.679	0.125	1.381	0.853	52.52
	TV3-2	6.95	0.053	4.074	0.123	0.748	0.765	56.19
	TH3	7.35	0.030	5.40	0.50	0.80	0.67	55.73

[a] In the first study, only the content of plant-available phosphorus (the AL method) in peat was analysed
[b] It is likely that some stones/mineral particles affected the analysis and the measured values are doubtful

Peat is a porous, complex material containing lignin and cellulose as major constituents. These constituents contain polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers that can be involved in chemical bonding (Viraraghaven, 1993). This polar nature gives peat a high specific adsorption capacity for suspended and dissolved solids, such as transition metals and polar organic molecules. As demonstrated also by our results, the particulate and highly porous nature of peat makes it an effective physical filter (Pérez et al. 2005).

3.2.1. Changes in the composition of the hydrated oil shale ash

In Table 5 the chemical composition of the hydrated oil shale ash before and after the experimental studies and the average chemical composition of the hydrated ash according to Kaasik et al. (2008) are presented.

Compared with the average hydrated oil shale ash (Table 5; Kaasik et al., 2008), the hydrated ash used in the second study had a higher content of SiO_2 and Al_2O_3 (Table 5). The average content of Si is 12.1%, and in hydrated ash in the second study 17.8%, and in the third study 12.5%. The content of aluminium in average hydrated ash is 1.65%, and in our material 2.46% and 1.71% in the second and third studies respectively (Table 5). The content of Ca in initial material is higher in the third study (22.17%), but the initial hydrated ashes mostly have similar chemical compositions. The chemical composition of the hydrated ash depends on the combustion and deposition technology, and at higher temperatures increases the content of Si-rich minerals. Composition can also vary considerably depending on the progress of diagenetic processes, specifically the carbonization of the surface layers of the plateau sediments (Kuusik et al., 2004).

Changes in the composition of the hydrated oil shale ash are best visible from the results of the third study (Publication IV). The mineralogical and chemical analyses of initial hydrated ash and used material (Table 5) indicate significant mass-transfer through the filters, of which the most important is the dissolution of ettringite and the precipitation of additional $CaCO_3$, which has evidently also used up additional Ca from the wastewater and leachate (e.g. 90% of Ca and 99% of Mg was removed from leachate and wastewater in ash filters). The ettringite content in all filters decreased drastically, from a median of 20% to 7.5% in VF and to 2.0% in the HF filters. At the same time, the content of $CaCO_3$ (calcite) increased from about 23% in initial ash to up to 26% in the HF filter. These results are also confirmed by the chemical analyses from the hydrated ash (Publication IV).

Table 5. The chemical composition (wt %) of hydrated oil shale ash before (initial values) and after experiments and average chemical composition according to Kaasik et al. (2008).

Average composition		pH	P	Si	Ca	Al	Fe	K	Mg	S	C
	Initial value	12.3	0.05	12.1	20.9	1.65	1.25	1.23	2.05	1.63	2.22
Second study	Initial value	N/A	0.061	17.83	15.50	2.46	1.61	1.70	2.90	1.27	1.96
	2S	N/A	0.078	16.57	15.36	2.26	1.49	1.58	2.70	0.21	4.06
	3S	N/A	0.078	15.68	16.86	2.11	1.56	1.33	3.12	0.53	3.84
	2V	N/A	0.061	17.22	16.29	2.32	1.56	1.29	3.00	1.19	2.35
	3V	N/A	0.065	15.68	18.00	2.12	1.60	1.16	3.30	1.30	2.65
Third study	**Initial value**	12.32	0.052	12.51	22.17	1.71	1.27	1.29	2.28	1.63	2.35
	VH1	10.44	0.066	11.45	21.86	1.55	1.24	0.83	2.72	0.83	4.30
	VV2-1	11.88	0.071	12.36	21.92	1.67	1.30	0.93	2.27	1.29	3.34
	VV2-2	12.07	0.062	11.98	22.33	1.64	1.28	0.76	2.35	1.00	3.13
	VV2-3	11.86	0.071	11.41	22.49	1.55	1.25	0.77	2.71	1.08	3.87
	VH2	11.42	0.066	11.80	22.41	1.60	1.33	0.78	2.38	0.92	3.71
	VV3-3	9.71	0.068	11.78	21.67	1.61	1.23	0.92	2.44	0.57	4.52
	VV3-4	10.52	0.065	11.38	22.00	1.58	1.25	0.85	2.71	0.6	4.46
	TH1	12.54	0.063	12.46	24.30	1.71	1.37	0.77	2.22	1.50	2.18
	TV2-1	12.47	0.070	12.11	23.69	1.68	1.30	0.78	2.48	1.49	2.68
	TV2-2	12.31	0.067	12.92	23.46	1.80	1.36	0.96	2.39	1.65	2.08
	TV2-3	12.39	0.063	11.72	23.44	1.62	1.29	0.79	3.23	1.40	3.23
	TH2	12.59	0.064	12.38	24.54	1.71	1.39	0.80	2.55	1.56	2.31
	TV3-3	12.23	0.066	12.07	23.26	1.66	1.28	0.68	2.84	1.42	2.93
	TV3-4	12.51	0.068	12.45	24.13	1.70	1.42	0.72	2.24	1.59	2.06

The results suggest a statistically significant increase in phosphorus in all filter systems (Fig. 5 in Publication IV), whereas almost all TP was removed from the inflow leachate, (R^2=0.99) and the efficiency was high throughout the test period. The chemical composition of the filter materials after the experiment period of the third study (Table 5) show that P content in the hydrated ash increased during the experiments, e.g. from 490 mg kg^{-1} in the initial ash to 706 mg kg^{-1} in VV2 and to 665 mg kg^{-1} in VH2 and 693 mg kg^{-1} in TV2 to 612 mg kg^{-1} in TH2, and to 657 mg kg^{-1} in VH1 and 612 mg kg^{-1} in TH1 at the end of the experiments (Fig. 5a in Publication IV). The data shows that the VF ash filters VV2 and TV2 removed most of the P from the influent during the 5 months they were in operation. More importantly, the P accumulation in all of the HF filters does not show any signs of saturation (Fig. 5b in Publication IV).

Table 5 shows that the leachate and wastewater had a significant influence on the chemical composition of hydrated ash. The changes in chemical composition are also reflected in the mineralogical analyses. The increase in calcium carbonates (calcite, vaterite) is explained by the single reaction between portlandite $Ca(OH)_2$ and dissolved CO_2 in the solution, or by the precipitation of the Ca^{2+} released from the ettringite. The hydrated ash showed a significant increase in phosphorus concentration (on average 20%, Table 5). Mineralogical analyses show that the P is bound in the oil shale ash as a hydrated calcium phosphate $Ca_3(PO_4)_2 \times nH_2O$ or as a β-form of calcium phosphate $Ca_3(PO_4)_2$ (Kaasik et al., 2008).

$$2PO_4^{3-} + 3Ca^{2+} + nH_2O = Ca_3(PO_4)_2 \times nH_2O, \qquad (1)$$

where the activity of Ca^+ and pH is controlled by the solubility/dissociation of reactive Ca-phases – most importantly ettringite or portlandite, and to a lesser extent calcite:

$$Ca_6Al_2(SO_4)_3(OH)_{12} \times 26H_2O = 6Ca^{2+} + 2Al(OH)_3 +$$
$$+ 3SO_4^{2-} + 29H_2O, \qquad pH \sim 10.7 \qquad (2)$$

$$Ca(OH)_2 = Ca^{2+} + 2OH^-, \qquad pH\ 12–13 \qquad (3)$$

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad (4)$$
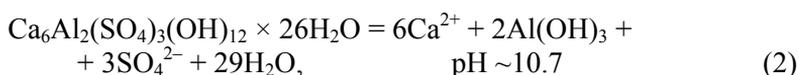
In summary, we suggest that the Ca-rich alkaline filter materials such as hydrated oil shale ash, C-type coal ash (Kirk et al. 2003), crushed gas-concrete (e.g. Berg et al., 2007) and Filtralite®-P type lightweight aggregates (e.g. Adam et al., 2007) are effective and cheap filter materials for P-removal in different wastewater compositions, due to the direct immobilization (active filtration) of P into a stable mineral phase.

3.3. Main results of the literature review of the filter materials for phosphorus removal from wastewater in treatment wetlands

A great variety (more than 30 main categories and over 80 subtypes) of both natural and man-made materials plus industrial by-products have been applied as filter media for phosphorus retention in constructed wetlands (Publication V).

The majority of these materials have a pH value >7.0 and high Ca and/or CaO content. The highest P-removal capacities were reported for various industrial byproducts (up to 420 g P kg^{-1} for some furnace slags; Mann and Bavor, 1993), followed by natural materials (maximum 119.6 g PO_4-P kg^{-1} for heated Opoka; Brogowski and Renman, 2004) and man-made filter media (maximum 12 g P kg^{-1} for Filtralite; Jenssen and Krogstad, 2003). We found a significant positive Spearman Rank Order Correlation between the P retention and CaO and Ca content of filter materials (R_2 = 0.51 and 0.43, respectively), whereas the relation of P retention to pH level was weak (R_2 = 0.22) but significant. Thus the main process of P retention used in constructed wetlands is precipitation. Although very few investigations have been performed in the long-term saturation time of materials, most of the calculations based on the batch experiments suggest, and some data from full size systems confirm, that the P retention capacity of most filter materials significantly decreases after a 5-year period of application.

Interestingly, in the type of constructed wetland systems where all contaminants (TSS, BOD, TN, TP etc.) are removed in one filter bed, the clogging of substrate active particle surfaces and pore spaces with organic matter (litter, biofilm etc.) can lead to decreasing P removal. Also, clogging decreases the hydraulic retention time in the filter. An obvious and sustainable solution would be a separate filter unit containing replaceable material with a high P binding capacity (Brix et al., 2001). In that case, appropriate pre-treatment would allow for a longer lifetime of the filter media, by decreasing the risk of clogging or even decreasing the pH and allowing one to use finer reactive filter media with higher sorption capacity (Hedström, 2006).

Some new and possibly promising materials such as Opoka, Filtralite, and hydrated oil shale ash with extremely high P sorption rates should be evaluated for efficiency of P removal over longer periods. Also, well-monitored long-term experiments in full size systems are needed. The recyclability of saturated materials used as fertilizer plays an important role in the further application of the technology of treatment wetlands. Therefore adequate experimental studies are needed to ensure the applicability of recycled filter media. The successful use of filter media also depends on their availability at the local level and the possibility of harmful side-effects such as contamination of the environment due to the high concentration of heavy metals.

The follow-up research on filter materials for phosphorus retention should be focused on their hydraulic parameters combined with the analysis of how to avoid possible clogging. Likewise, more attention should be devoted to investigating obvious constraints such as poor hydraulic conductivity, low surface area or high content of undesirable contaminants such as heavy metals.

4. CONCLUSIONS

The quality of the treatment of different types of wastewater in subsurface flow constructed wetlands depends largely on the selection and suitable combination of filter materials for efficient removal of different pollutants, such as nitrogen (N) and phosphorus (P). Several laboratory and field experiments have demonstrated that peat in subsurface flow filters can effectively remove nutrients, mineralize organic material, and retain pathogenic bacteria and heavy metals. Various ashes have been effectively used for the removal of different contaminants from wastewater, but the suitability of well mineralized peat and hydrated oil shale ash has not been particularly thoroughly studied.

Mineralized peat showed the best results in vertical flow (VF) filters, due to the suitable aerobic conditions for nitrification and the removal of organic pollution. The remarkable efficiency of well mineralised peat in the reduction of BOD values (up to 95%) and NH_4-N concentrations (up to 93%) from landfill leachate and municipal wastewater encourages us to use peat filters in combination with conventional treatment methods (Publications I–IV). In contrast, the removal efficiency of organic matter and nitrogen in hydrated oil shale ash filters was very low, which is probably due to the high alkalinity. High pH inhibits the biological treatment processes in this material.

Phosphorus reduction in mineralized peat filters (70–99% during 6 months in operation; Publication III) suggests that the main process that controls its removal from wastewater and leachate is related to sorption phenomena, which is evidently limited by suitable sorption sites on peat fibres, and removal efficiency falls while the sorption sites become saturated. For the pilot-scale VF peat filter at Väätsa landfill, we estimate the maximum P binding capacity at given experimental conditions to be in the order of 81 mg kg^{-1} of P for dry peat or ~20 g m^{-3} of phosphorus, assuming the dry density of peat to be 246 kg m^{-3}.

The results of our research show that active filtration using hydrated oil shale ash or other Ca-rich alkaline materials such as C-type coal ash, crushed gas-concrete and Filtralite®-P type lightweight aggregates is an effective and cheap method for P-removal at different and largely variable wastewater compositions. Nevertheless, we show that the effectiveness of the active filtration depends on the inflow P-concentrations and the method is not suitable for the removal of trace amounts of phosphorus at low inflow concentrations (<0.5 mg L^{-1}; Publication IV).

The results of our studies suggest the excellent P-removal efficiency of the alkaline hydrated oil shale ash filters using different real wastewater compositions and P loadings. The hydrated ash showed the best results (median efficiency >90%) in P removal in horizontal flow filters (HRT 5–7 days, accumulation of P 100–180 mg P kg^{-1}), whereas saturation was still not achieved (Publication IV). In the vertical flow ash filters the retention time was much shorter, and the average efficiency was generally 60%–90%. The results of the complex mineralogical research indicated that the high P-binding potential of hydrated oil shale ash is considered to be due to the high ratio of reactive

calcium minerals, of which portlandite and ettringite are the most important. Ca-rich alkaline filter materials applying active filtration for P-retention have proven their effectiveness for use in small-scale CWs and SSF filters. The active filtration technique uses the direct immobilization of phosphates into low soluble forms by the dissolution of Ca-phases into pore water and the precipitation of Ca-phosphates. Potential materials for the active filtration of P include metallurgical slag and high Ca content industrial products, in which Ca occurs in CaO form (lime) and/or Ca-silicates.

The hydrated ash filter does not ensure complete (*sensu stricto*) removal of P, but is sufficiently effective for PO_4-P-removal in the presence of different (mostly inorganic) inhibitors at variable P concentrations exceeding 0.5 mg L^{-1}. The precipitation mechanism is only effective at P-concentrations exceeding 0.5 mg L^{-1} and at lower concentrations P-removal is probably governed only by adsorption.

Further research is needed to identify the P-removal capacity of the hydrated ash filters in the presence of high organic concentrations and different forms of phosphorus. The remarkable efficiency of the combination of hydrated ash and mineralized peat in the reduction of P encourages us to use these materials for the after-treatment of leachate and wastewater in full-scale treatment systems. The most efficient setup for phosphorus removal would be a combination of saturated/horizontal flow hydrated ash filter and vertical flow peat filter, which ensures efficient P-removal and sufficient water quality. Importantly, the peat filter would decrease the pH of the effluent from the highly alkaline hydrated ash filter system.

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SUMMARY IN ESTONIAN

PRÜGILA NÕRGVEE JA OLMEREOVEE PUHASTAMINE PINNASFILTRITES MINERALISEERUNUD TURBA JA HÜDRATISEERUNUD PÕLEVKIVITUHA ABIL

Käesoleva doktoritöö eesmärgiks on kindlaks teha hästi mineraliseerunud turba ja kaltsiumirikka hüdratiseerunud põlevkivituha efektiivsus prügila nõrgveest ja olmereoveest erinevate saasteainete, eelkõige fosfori (P) ja lämmastiku (N) eemaldamises ning orgaanilise aine lagundamises, kasutades neid materjale vertikaal- ja horisontaalvoolulistes pinnasfiltrites. Samuti on antud doktoritöö üheks osaks kirjanduse ülevaade erinevate filtermaterjalide kohta, mida on maailmas uuritud ja kasutatud fosfori ärastamiseks reoveest.

Parima veekvaliteedi saavutamine pinnasfiltersüsteemides erinevat päritolu reoveest N ja P ning orgaaniliste ühendite ärastamisel, sõltub kõige enam filtermaterjalide valikust ja nende sobivaimast kombineerimisest. Mitmed labori- ja välikatsed on näidanud, et pinnasfiltrites substraadina kasutatud turvas (enamasti vähelagunenud turvas) annab väga häid tulemusi toitainete ärastuses, orgaanika lagundamises ja ka patogeenide ning raskmetallide eemaldamises reoveest. Samuti on eelnevalt uuritud erinevat tüüpi tuha (nt. kivisöe tuha, puutuha) efektiivsust reoainete eemaldamises, samas kui hüdratiseerunud põlevkivituha ja hästi mineraliseerunud turba sobivus on põhjalikult uurimata.

Käesoleva doktoritöö raames viidi läbi kolm uurimust erinevate välikatsetega. Aastal 2003 rajati Väätsa prügilasse esimesed pilootkatsed (Publikatsioon I) prügila nõrgvee puhastamiseks. Uurimuse eesmärgiks oli kindlaks määrata hästi mineraliseerunud turba (edaspidi turba; pH 6,7–7,2) efektiivsus vertikaalvoolulistes pinnasfiltrites (filtri maht 1,0 m^3, hüdrauliline koormus 290 mm d^{-1}) reoainete eemaldamises toornõrgveest ja kohalikus puhastussüsteemis juba eelnevalt puhastatud nõrgveest (suublasse juhitav nõrgvesi).

Aastatel 2005–2006 toimus Väätsa prügilas teine uurimus (Publikatsioonid I ja II), mille raames rajati kaks paralleelset pilootkatset vertikaalvooluliste filtritega (mõlemas katses kolm filtrit mahuga 0,11 m^3, hüdrauliline koormus 41–82 mm d^{-1}), mis täideti turba ja hüdratiseerunud põlevkivituhaga (edaspidi tuhaga; pH 12,3) ning üks filter mõlemas katses mõlema materjaliga (ülemine 0,5 m turbaga ja alumine 0,5 m tuhaga). Uurimuse eesmärgiks oli välja selgitada ja võrrelda mineraliseerunud turba ja hüdratiseerunud tuha efektiivsus aktiivmudapuhasti väljavoolu ja puhastist loodusesse juhitava nõrgvee järelpuhastamises.

Mõlema uurimuse (Publikatsioonid I ja II) tulemused näitasid, et vertikaalvoolulistes turbafiltrites toimib efektiivselt nitrifikatsioon (ammonium-lämmastiku sisaldus vähenes kuni 93%). Häid tulemusi saadi ka üldfosfori (TP) sidumises erineva puhastusastmega nõrgveest ja toornõrgveest (efektiivsus kuni 99%), samuti soodustasid aeroobsed tingimused vertikaalvoolulistes filtrites orgaanika lagundamist (biokeemilise hapnikutarbe (BHT_7) vähendamine kuni 95%). Kombineeritud turba/tuha filtrid näitasid samuti päris häid tulemusi

orgaanilise aine eemaldamises (efektiivsus 64–78%) ning ka tuhafiltrites (teises uurimuses) oli efektiivsus keskmiselt 50%.

Kolmas uurimus hüdratiseerunud tuhaga ja turbaga toimus aastatel 2006–2007 (Publikatsioonid III ja IV), kui neid filtermaterjale katsetati kahes paralleelses katses vertikaal- (maht 0,86 m^3) ja horisontaalvoolulistes (maht 1,24 m^3) filtersüsteemides eesmärgiga teha kindlaks hüdratiseerunud põlevkivituha P ärastusvõime eelpuhastatud prügila nõrgveest (nn. Väätsa katse, kestvus üks aasta) ja konventsionaalse puhasti läbinud olmereoveest (nn. Tapa katse, kestvus 6 kuud). Kuna eelnevad katsed hüdratiseerunud tuhaga näitasid head P-ärastuspotentsiaali, aga orgaanika ja lämmastiku eemaldamises oli efektiivsus limiteeritud, siis kombineeriti filtersüsteemides tuhka mineraliseerunud turbaga.

Hüdratiseerunud tuha P sidumise efektiivsus oli suurepärane mõlemas katses, horisontaalvoolulistes filtrites üle 90% (viibeaeg 5–7 päeva, koormus 53 mm d^{-1}; PO_4-P-st eemaldati keskmiselt 98–99%) ja vertikaalvoolulistes filtrites rohkem kui 50% (madalam efektiivsus arvatavasti põhjustatud lühikesest viibeajast). Stabiilset ja kõrget efektiivsust ei mõjutanud ka erinev reovee koostis ja reostusaste. Veeanalüüside tulemusi kinnitavad ka muudatused materjalide keemilises koostises: keskmine tuha P akumulatsiooni võime oli 100–180 mg P kg^{-1} ning arvutuslik kumulatiivne P-sidumisvõime ei näidanud märkigi vähenemisest kogu aasta väldanud katse jooksul (R^2=0,99).

Mineraloogiliste uurimuste tulemused näitavad, et selline kõrge P sidumisvõime on seotud reaktiivsete Ca-mineraalide (tähtsaimad ettringiit ja portlandiit) kõrge sisaldusega hüdratiseerunud tuhas, millest tulenevalt on põhiliseks protsessiks fosfori eemaldamisel reoveest P aktiivne filtratsioon ehk keemiline sadestamine Ca-fosfaadina. Aktiivse filtratsiooni käigus toimub materjalist kaltsiumi väljalahustumine ning moodustub raskestilahustuv Ca-fosfaat. Käesolevate uurimuste tulemuste põhjal on võimalik järeldada, et fosfori keemiline sadestamine hüdratiseerunud põlevkivituha (samuti teiste sarnaste omadustega Ca-rikaste materjalide nagu metallurgilised räbudega, kivisöetuha, purustatud gaas-betooni ja Filtralite®-P tüüpi kergkruusadega, kus kaltsium esineb materjalis CaO vormina (lubjana) ja/või Ca-silikaatidena) on efektiivne ja odav meetod erinevat tüüpi ja erineva reostusastmega reovee puhastamiseks (Publikatsioon V). Samas näitasid katsete tulemused, et aktiivse filtratsiooni efektiivsus sõltub reovee P-sisaldusest ning väiksema kui 0,5 mg L^{-1} fosfori kontsentratsiooni korral ei ole see meetod sobilik. Arvatavasti on väga madalate kontsentratsioonide korral põhiprotsessiks adsorptsioon.

Kõigi uurimuste tulemuste põhjal võib järeldada, et mineraliseerunud turvas on potentsiaalne filtermaterjal nõrgvee ja olmereovee järelpuhastuseks just perioodiliselt koormatavates vertikaalvoolulistes pinnasfiltrites. Samuti nagu tuhas, suurenes fosfori sisaldus märgatavalt ka mineraliseerunud turbas (maksimaalselt 81 mg P kg^{-1} turba kuivaine kohta), kuid kui tuhk ei näidanud horisontaalvoolulistes filtrites mitte mingeid märke küllastumisest, siis turba sidumisvõime ammendus juba 6 kuu jooksul. Arvatavasti toimub fosfori ärastus turbas adsorptsiooni teel ning see protsess on limiteeritud turbamaterjalis olevate vabade sorptsioonikohtade olemasolu poolt, seega kui sorptsioonikohad

küllastuvad, siis langeb ka materjali sidumisefektiivsus. Kolmandas uurimuses näitasid orgaanika lagundamises ja lämmastiku ärastuses parimaid tulemusi samuti vertikaalvoolulised turbafiltrid, kusjuures horisontaalvoolulistes turbafiltrites (arvatavasti anaeroobsete tingimuste domineerimise tõttu) ning tuhafiltrites (liiga kõrge aluselisus inhibeeris bioloogilisi protsesse) ei toimunud märgatavat orgaanika sisalduse vähenemist ja N eemaldamist.

Käesolevas doktoritöös käsitletud uurimustes mineraliseerunud turbaga ja hüdratiseerunud tuhaga saavutatud väga head tulemused näitavad, et kindlasti on vajalikud ka täiendavad täismõõtmelised katsed erineva reostuskoormuse ja fosforisisaldusega reovee puhastamiseks, selgitamaks nende materjalide efektiivsus reaalsetes pinnasfiltersüsteemides.

Fosforiärastuseks ja parima veekvaliteedi saavutamiseks on soovituslikuks ülesehituseks puhastussüsteem, kus veega küllastunud horisontaalvoolulisele hüdratiseerunud põlevkivituha filtrile järgneb perioodiliselt koormatav mineraliseerunud turbaga täidetud vertikaalvooluline pinnasfilter, mis vähendaks ka tuhafiltrist tulenevat kõrget pH väärtust.

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PUBLICATIONS

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