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Phosphorus removal by various filter materials in subsurface flow constructed wetlands

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Author's contribution

Publication I: The author designed the experiment unit and is partly responsible for the fieldwork (about 50%), data collection (about 50%) and analyses (about 70%), and for writing the manuscript (about 90%).

Publication II: The author designed the experiment unit and is partly responsible for the fieldwork (about 50%), data collection (about 50%) and analyses (about 70%), and for writing the manuscript (about 90%).

Publication III: The experiments have partly been carried out based on the author's conceptual ideas. The author participated in experiment design, data collection and analysis.

ABSTRACT

In order to follow European Union (EU) 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. Constructed wetlands (CWs) are the most appropriate means of wastewater treatment when pollution loading is 50–500 PE, especially in rural areas, but systems for 2000–5000 PE are also practiced. Phosphorus removal is a critical issue in conventional treatment plants and also in constructed wetland treatment systems. The majority of Estonian 800 wastewater treatment plants are small biological treatment plants, which can only achieve from 20–30% phosphorus removal. These systems are not designed for intensive nutrient removal, and hence the acceptable degree of purification is difficult to achieve. Combined wastewater treatment plants with biological-chemical steps can mostly achieve the required purification efficiency of phosphorus, but the whole system with high installation and maintenance costs is not often available to small enterprises. Thus alternative means for phosphorus removal from wastewater have been studied. The separate unit containing filter media with high and stable phosphorus removal is the most appropriate way to prolong phosphorus removal in CWs but also for extrapolating outflow water at conventional treatment plants.

The long-term (8-year) study in the Kodijärve sand planted CW filter media demonstrated an increasing trend in outlet P concentrations and decreasing annual P removal rate, showing the saturation processes in filter media. Saturation of filter media occurred 5–7 years after the starting of the system, and hence it is extremely important to search for filter media with high and stable phosphorus removal efficiency.

To search for potential filter media with high phosphorus sorption capacity, the sorption characteristics and particle size distribution of several local sands, gravels, glauconite-sandstone, LWA and calcareous waste products from the oil-shale industry were investigated. The batch experiments showed a very high P sorption capacity for oil shale fly ash, crushed ash block and the sediment from the oil shale ash plateau (on average 98.9%, 96.5% and 98.4% respectively at initial concentrations from 5–1000 mg PO_4^{3-} L^{-1}). No significant correlation between average grain size and uniformity (sorting coefficient) was noted, whereas local filter media, classified as gravels, sorbed P better than local sands. The high content of Ca, Mg, Al and Fe supported better sorption for these gravels.

To test the best filter material according to batch tests, sediment of ash plateau, at complex wastewater conditions at field scale, an experimental ash unit was installed in the outlet from the Kodijärve HSSF CW. Regardless of very high P removal efficiency (>98%) of ash material derived from oil-shale combustion in laboratory batch experiments, the retention in the pilot-scale filter was lower than expected. The decrease in P removal after satisfactory retention during the first four months in the Kodijärve ash unit was probably caused by the undersized filter unit. The increased flow rates and hence too short retention time were not sufficient for efficient removal processes (P removal 10–20%).

Mineralogical and laboratory binding capacity kinetic studies with the sediment from the ash plateau performed by my co-authors also indicated the good P-binding capacity (up to 65 mg P g^{-}1) of the hydrated oil-shale ash sediment, with a removal effectiveness of 67–85%. The results of the study indicate that the high phosphorus sorption potential of hydrated oil-shale ash is considered to be due to the high content of reactive Ca-minerals, of which ettringite Ca6Al2(SO4)3(OH)12 26H2O and portlandite Ca(OH)2 are the most important. Dissolution of ettringite and portlandite, and precipitation of Ca-carbonate and Ca-phosphate phases, was confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM)-EDS studies.

Experiments with oil-shale ash sediment were continued in order to achieve optimal hydraulic conditions and thus sufficient purification efficiency of the material. The pilot study with sufficient residence time and effective design showed very high phosphorus removal. Average P accumulation in ash sediment filters was 40 mg P kg^{-1}.Total phosphorus removal capacity in the horizontal ash filter (hydraulic loading ~50 L m^{-3} d^{-1}) at long-term was greater than 85%, and in vertical flow filters (at loading ~80 L m^{-3} d^{-1}) greater than 50%. The results of the pilot study allow one to claim that in HF ash sediment filters at water loading less than 50 L m^{-3} and in average inflow concentrations less than 10 mg L^{-1}, purification efficiency higher than 70% is guaranteed during at least a one year period.

Variations in the chemical and mineralogical composition of ash sediment after the study period supported the findings for removal mechanism analysed in earlier laboratory experiments. The content of ettringite in materials decreased after the wastewater treatment experiment, and the amount of calcite increased during the same period. That process refers to the precipitation of calcium released from the ettringite dissolution, resulting in the formulation of sparingly soluble Ca-phosphate.

Regardless of the extraordinarily good P removal in pilot filters, a study of full-scale filter systems should be carried out before the recommendation that ash sediment be extensively used in separate filters to treat outflow P in constructed wetlands but also in conventional treatment plants.

1. INTRODUCTION

Phosphorous is an important nutrient that is critically needed for the normal functioning of ecosystems. Nevertheless, excess phosphorous and nitrogen, is the main cause of euthrophication. The main input of phosphorous into nature occurs through its use in agriculture and from domestic wastewater. Whereas phosphorous can be regulated by balanced fertilization in agricultural use, wastewater needs proper treatment for the removal of phosphorous to level(-s) acceptable for natural systems.

Phosphorus removal in conventional small-scale wastewater treatment systems is a critical issue that has not yet been sufficiently solved. Moreover, continuing eutrophication, especially in fresh-water ecosystems, have led to increasing governmental regulatory pressure for the lowering of phosphorus concentrations through more enhanced phosphorus removal from wastewater. In Europe, the supplementary treatment of wastewater from houses and small rural communities specifically designed for phosphorous removal is becoming important for the improvement of environmental quality in streams and lakes (*Brix et al., 2001*).

To follow European Union (EU) regulations, wastewater sewerage and wastewater treatment plants **should also include a nitrogen and phosphorus reduction step** in all large settlements (10,000 individuals) by the end of 2009 and in all settlements of 2000 – 10,000 individuals by the end of 2010. Appropriate wastewater treatment in small settlements and densely populated villages must also be provided by 2010. According to 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 also means that urban areas and densely populated villages should be involved. These measures originating from the EU requirements should bring Estonian water bodies up to a good ecological condition by the year 2015 *(Riigikontroll, 2007*).

Pollution from small settlements in rural areas (<10,000 PE), villages and dispersedly populated areas substantially influences the condition of local water bodies. Only 65% of Estonian water bodies have been evaluated as being in good condition, and the remaining 35% have been described as in satisfactory or poor condition. According to Council Directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment, all of Estonian territory is classified as a sensitive area for any water pollution, and hence considerably stricter requirement are enforced compared with less sensitive discharge areas (*Keskkonnaministeerium, 2006.*). In 2003 half of Estonia's 856 wastewater treatment plants were not operating as required. Moreover, as a result of amortized sewerage pipes, 20–30% (60% in North-East Estonia) of wastewater infiltrates into the soil and groundwater before reaching the treatment plant.

The high phosphorous level in rivers and lakes has been considered to be the main problem in Estonian water protection, which demonstrates insufficient phosphorus reduction from the wastewater of small settlements and industrial wastewater (*Iital et al, 2003*).

The phosphorus concentration in natural river water is generally less than 0.05 mg P L^{-1}, whereas the recommended level of 0.10 mg P L^{-1} is considered as a criterion of pollution, and a higher concentration induces eutrophication in rivers (*Roots and Talkop, 1996*). In Estonian lakes, phosphorus limits the growth of emergent plants and phytoplankton (*Keskkonnaministeeriumi Info- ja Tehnokeskus, 2000*). Even at very low concentrations (10 µg P L^{-1}), it can cause eutrophication processes that deteriorate ecological conditions in lakes, rivers with slow flow and water reservoirs and thus also diminish esthetic value (*Donnert et al., 2002*). In closed water bodies with stagnant water and relatively simple ecosystem structure, oxygen transfer is difficult and self-purification performance poor. Therefore nitrogen and phosphorus tend to accumulate, which results in the propagation of blue-green algae, poor transparency, and malodour of the water.

Constructed wetlands

Subsurface flow constructed wetlands function very effectively in the treatment of the wastewater of small settlements and rural areas. Subsurface flow constructed wetlands (SSF CW) are known to be efficient in the removal of both biological oxygen demand (BOD_5) and total suspended solids (TSS) from wastewater. However, nitrogen (N) and phosphorus (P) removal is known to be somewhat problematic (*Brix et al., 2001, Vymazal et al., 1998*).

Subsurface flow and other treatment wetlands have been used for the purification of industrial wastewater (food production, paper industry etc.), mine water, agricultural water and also landfill leachate purification, and most often for domestic and rainfall water. Because of their great volume and slow purification processes, wetland systems are tolerant to changing hydraulic and nutrient loadings. This makes them more suitable than conventional treatment plants for the treatment of wastewater from tourist resorts, individual households, industries and other objects with variable wastewater flow rates and pollution loads. They can be also suitable for the after treatment of outflow water from conventional plants. Wetland treatment requires a great area, and hence the use of constructed wetlands for wastewater treatment is more suitable in sparsely populated areas. Optimal loading rates for subsurface flow CWs are between 50 and 500 PE. The systems can, however, also be designed for loadings of 2000 PE.

In Estonia subsurface flow and treatment wetlands systems have mainly been used for the purification of domestic wastewater, but also as after treatment for conventional plants. About 30 subsurface flow and treatment wetlands have been installed in Estonia to date.

Phosphorus removal in subsurface flow CWs is closely connected (associated) with the physical–chemical and hydrological properties of the filter material, whereas P is mainly sorbed or precipitated in filter media (*Faulkner and Richardson, 1989; Kadlec and Knight, 1996; Vymazal et al., 2000*).

Thus the removal of P in constructed treatment wetlands is a complicated process and moreover, the life expectancy of sub-surface flow CWs, especially as concerns phosphorous removal, depends on the filter media that are used for the construction (*Grüneberg and Kern, 2000*). Medium with a high phosphorus binding capacity is an important component of treatment wetlands (*Arias et al., 2001*).

The search for efficient and long-lasting filter media has been a key issue for more than a decade. However, the longevity of the sorption capacity of phosphorous is still the main topic (*Johansson Westholm, 2006*). When one uses local natural filter materials, the risk of clogging exists, whereas natural substrates always consist of silt and clay. In addition to good hydraulic conductivity, the chemical composition of the material is also important. As the phosphorus is removed via the sorption and precipitation processes, Ca, Fe and Al content is extremely important to guarantee efficient P removal. Thus filter media should be selected very carefully. Even if a medium with high P binding capacity has been selected, it will be 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 that case appropriate pre-treatment will also allow for a longer lifetime of the filter media, by decreasing the risk of clogging and allowing one to use finer reactive filter media with higher sorption capacity (*Hedström, 2006*).

Indicator parameters for efficient P removal in wetland filter

The sorption and precipitation of phosphorous are controlled by the properties of the substrate (Fe-, Al-, Ca-minerals, porosity), the physicochemical environment (pH, Eh, dissolved ions) and hydraulic parameters (loading rate, retention time) (*Kadlec and Knight, 1996; Faulkner and Richardson, 1989; Vymazal et al., 2000*).

Chemical composition of filter media

In a sand or gravel substrate, phosphorus is bounded to the media mainly as a consequence of adsorption and precipitation reactions with calcium (Ca), aluminium (Al) and iron (Fe). At pH levels greater than 6, the reactions are a combination of physical adsorption to iron and aluminium oxides and precipitation as sparingly soluble calcium phosphates. At lower pH levels, precipitation as iron and aluminium phosphates (strengite, variscite) becomes increasingly important (*Gerritse, 1993*). The capacity of the filter media to remove P may therefore be dependent on the contents of these minerals in the substrate. This hypothesis is supported by the observation that P-removal has been found to be particularly efficient in constructed reed beds containing ferruginous sand (*Netter, 1992*). However, P-removal efficiency is often high initially and then decreases after some time as the P-sorption capacity of the sand is used up (*Ciupa, 1996*).

Arias et al. (2001) found that The P-removal capacity of some sands would be used up after only a few months in full-scale systems, whereas that of others would persist for a much longer time. The most important characteristic of the sands that determined their P-removal capacity was their Ca-content. A high Ca content favours precipitation with P as sparingly soluble calcium phosphates, particularly at the slightly alkaline conditions typical of domestic sewage.

In situations where the wastewater to be treated is more acid, the Fe and Al content may be more important, as the precipitation reactions with these ions are favoured at lower pH levels (*Stumm and Morgan, 1981*).

Brix et al. (2001) suggests that in order to sustain effective long-term P-removal in subsurface flow constructed wetlands, it is necessary to promote precipitation reactions of insoluble P-salts, by eventually amending the media with a material containing a high P-binding capacity and/or a material that releases precipitation minerals.

The solubility diagram from *Snoeyink and Jenkins (1980)* shows that $Ca(OH)_2$ dissolves when the pH is less than 11.3, depending on the total Ca^{2+} concentration. *Adam et al. (2007)* () reported that in Filtralite P precipitation of $Ca(OH)_2$ requires a high total Ca^{2+} concentration and high pH. On the other hand, dissolution of $Mg(OH)_2$ requires pH values lower than 8.6. The combination of Mg^{2+} and Ca^{2+} in the solution may precipitate P over a wide pH interval.

Oxidation conditions

Oxidation conditions can influence P removal, while in anaerobic conditions the P that is bound with iron (Fe) compounds due to the reduction of Fe^{3+} to Fe^{2+} may be released as phosphates (PO_4^{2+}) and Fe^{2+} (*Faulkner and Richardson, 1989*). In addition, the reduction of Mn^{4+} can cause the release of P from phosphate minerals. Anaerobic conditions in sulphate-rich soils produce H_2S, and the formation of ferrum sulphate can release phosphorus bound in Fe (*Kadlec and Knight, 1996; Roden and Edmonds, 1997*). In an aerobic water environment, phosphorus can release at high temperatures, when bacterial activity is high and microanaerobic conditions take place in the upper layer of the soil material. The amount of P released in the described aerobic environment is, however, 10 times lower than in anaerobic conditions.

Porosity, grain size, and density

Soil porosity can be defined as the ratio of soil pores to total soil volume. Soil pores can be related or non-related, and aggregation between the pores influences water permeability. The water permeability decreases and residence time increases when the amount of small particles grows. The average porosity of clean sand and gravel materials ranges between 30 and 45%. Plants may also block part of the pore volume in treating wetlands, whereas organic and mineral matter accumulates during the purification process. The important physical properties of the filter media are porosity, grain size and density (*Roseth, 2001; Brix et al., 2000*). For example, according to the Danish EPA regulation, the effective grain size d_{10} = 0.0–2.0 mm and d_{60} = 0.5–8.0 mm. The uniformity coefficient d_{60}/d_{10} should be <4 to ensure satisfactory hydraulic conductivity and minimize the risk of clogging (*Brix et al., 2000*). For natural sands, the recommended effective grain size (d_{10}) should be 0.2–0.5 mm, and the uniformity coefficient (d_{60}/d_{10}) less than 5.0 (*Johansson, 1997*). Filter media should not consist of clay, and the content of particle sizes under 0.1 mm is not permitted to exceed 0.5%. By explanation, d_{10} is the grain size that makes up over 10% of the dry weight sample, and d_{60} is the grain size that makes up over 60% of the dry weight sample. Smaller grain size can demonstrate better phosphorus removal efficiency due to the greater surface area and contact/ residence time. Grain size is not always decisive in the phosphorus removal process (*Johansson, 1997*). When hydraulic conductivity is very low, problems with filter clogging can take place. For example, organic soil and clay minerals have a much greater ion exchange capacity than mineral materials such as gravel (*Kim and Geary, 2000*). Clays have large surface area, but clogging problems, and surface erosion often occurs when these materials are used as filter media to improve phosphorus removal (*Farahbakhshazad and Morrison, 2000*). As the surface of porous materials is homogenously coated with sorption sites, larger grain size can nevertheless demonstrate a good potential for P removal (*Anderson and Rosolen, 2000*).

Hydraulic conductivity and residence time

Hydraulic conductivity and porosity are also important properties of the filter media.

Hydraulic conductivity is the main determined property when water infiltrates through the soil. Soil structure and the number of pores influence hydraulic conductivity. Porosity also designates the size of the surface area in the soil and thus the necessary sorption sites for P removal (*Johansson, 1997*). For the efficient functioning of the sorption process, a sufficient contact time/residence time is also needed. In the case of high hydraulic conductivity, rapid water flow through the substrate offers limited opportunities for contact between water and substrate. Thereby it is necessary to keep hydraulic conductivity at a level that allows the sorption mechanism to function (*Faulkner* *and Richardson, 1989*). Residence time in the wetland can be defined as the ratio of water volume in a wetland to the volumetric amount of water that passes through the wetland. Essentially, the measurement of residence time means the measurement of water contact time in the system. It is believed that little/slight seasonal influence on the purification efficiency of the cold climate wetlands where the biological reduction processes of the waste components take place is caused by sufficiently long residence time. Hence in cold climate wetlands, the efficient residence time is 4 weeks (*Mander et al., 2001*).

Sorbents for phosphorus removal

A great variety of different types of materials For P retention in CWs are described. Traditionally, locally available sands and soils have been used as filter media in sub-surface 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)* also brought out the fact that regardless of the great amount of existing scientific data, the potential and efficiencies of different materials and studies cannot be compared and generalized. The most reliable data on the recommendation of efficient filter media is based on studies performed in full-scale systems.

Various tested filter materials cannot be compared due to their very different chemical and physical properties. Even the same type of material, for example slag or sand, differs in terms of origin and treatment method (*Arias et al., 2001*). Differences also occur when different methods and conditions of study are used (load, temperature, study period, methods of determination etc.). These are the main reasons why a great variety of reported results have been described even for the same type of material. Most of the studies that demonstrate the phosphorus retention capacity of various materials have been conducted in the laboratory. Only a few materials out of the extensive group that has been tested so far have also been studied in full-scale systems.

Natural substrates

A great number of **natural substrates** have been tested to retain P from wastewater in constructed wetland systems. Sands (*Arias et al., 2001; Del Bubba et al., 2003; Farahbakhshazad and Morrison, 2000; Rodgers et al., 2004; Vohla et al., 2005; Xu et al., 2006; Vohla et al., 2007*), gravels (*Tanner et al., 1999; Mann and Bavor, 1993; Mann, 1997; Korkusuz et al., 2005; Vohla et al., 2005; He et al., 2007; Hatt et al., 2007*), limestone (*Johansson, 1999a; Drizo et al., 1999; Hill et al., 2000; DeBusk et al., 2004; Strang and Wareham, 2006*), shell sand - natural carbonatic material mainly produced by shells, snails, and coral alga with a grain consistentcy similar to sand or gravel (*Roseth, 2001; Søvik and Kløve, 2005*; *Adam et al., 2006*), opoka - bedrock material from south-eastern

Poland rich in Ca, Si, Al and Fe (*Johansson, 1999a; Johansson and Hylander, 1998; Johansson and Gustafsson, 2000; Brogowski and Renman, 2004*), .wollastonite — a calcium metasilicate mineral (*Brooks et al. 2000; Hill et al., 2000; Hedström, 2006*), shale — an argillaceous rock, derived from the lower limestone group of the carboniferous system (*Drizo et al., 1997; Drizo et al., 1999; Pant et al., 2001*), bauxite, a naturally occurring mixture of minerals rich in hydrated aluminium oxides and ferric oxides and low in alkali metals, alkaline earths and silicate (*Drizo et al., 1999; Akhurst et al., 2006; Altundoğan and Tümen, 2003*), maerl, the dead deposits of calcareous red algae (Corallinaceae) found growing in shallow waters around the coast of north-west Europe and the western Mediterranean (*Gray et al., 2000*), dolomite (*Karaca et al., 2004; Pant et al., 2001*), marble (*Gervin and Brix, 2001*; *Brix et al., 2001*), different type of soils_*(Johansson, 1999a; Hill et al., 2000; Braskerud, 2002; Lin and Banin, 2005; Zhang et al., 2007*)**,** zeolite**,** a hydrated aluminium-silicate mineral with the aluminium and silicon polyhedra linked by the sharing of oxygen atoms *(Drizo et al., 1999*) and peat (*Talbot et al., 1996; Bulc et al. 1997; Kõiv et al., 2007; Kõiv et al., 2008*) are most often tested**.**

In recent years the need for reactive materials that can effectively retain P has encouraged scientists to also test commercially available **man-made products** such as Light Weight Aggregates (LWA; also called Leight Expanded Clay Aggregates or LECA). LWA is manufactured by running palletized clay aggregates through a rotary kiln at 1200°C, the chemical composition differs according to the parent material, whether clay or shale (*Mæhlum, 1995; Johansson, 1997; Drizo et al., 1999; Hill et al., 2000; Farahbakhshazad and Morrison, 2000, Forbes et al., 2004)*. In addition calcite**,** commercially available as white cat litter (*Arias et al., 2003*) and gas concrete (*Oguz et al, 2004*), have been tested. Special substrates for P removal have also been worked out. Filtralite P is the first and also the most widely used (*Zhu et al, 1997; Zhu et al., 2003; Heistad et al., 2004; Adam et al., 2007; Adam et al., 2006*). It is a special LWA made from natural mineral clay illite with natural additives, and is manufactured by running palletized clay aggregates through a rotary kiln at 1200°C. It has a high pH (10), and high Ca and Mg content. Filtra P (*Gustafsson et al., 2008*) is also a special product used to retain P, made by Maxit Group Finland Oy. Filtra P is produced after heating a mixture of limestone, gypsum and Fe oxides.

Very good results have also been described when testing different kinds of **by-products** that are produced in large amounts, mainly by industries. Coal fly ashes (*Donnert et al., 1999; Oguz, 2005; Agyeia et al., 2000; Agyeia et al., 2002; Khelifi et al., 2002; Ugurlu and Salman, 1998; Cheug and Venkitachalam, 2000; Drizo et al., 1999; He et al., 2007*) and blast furnace slag, which is a porous nonmetallic co-product produced in the iron and steel industry (*Mann and Bavor, 1993; Sakadevan and Bavor, 1998; Johansson 1999b; Johansson and Gustafsson, 2000; Grüneberg and Kern, 2001; Cameron et al., 2003;*

Shilton et al., 2006; Drizo et al., 2006; Korkusuz et al., 2007) but also burnt oil shale (*Drizo et al., 1999*), sediment of oil shale ash (*Vohla et al., 2005; Vohla et al., 2007; Kaasik et al., 2008*), iron-ore (*Grüneberg and Kern, 2001*), ochre (precipitated $Fe(OH)_3$ and FeO·OH) from mine water treatment plants (MWTPs) (*Heal et al. 2005*), red-mud, waste by-product during the alkaline leaching of bauxite (*Carucci et al., 2002; Liu et al., 2007; Roberge et al., 1999*) and sand (used for the precipitation of iron from drinking water), have most often been studied.

Some studies have been conducted by burning natural substrate before to enhance the P removal of material, for instance oyster shells. Oyster shells are generated as a by-product from the oyster culture (*Kwon et al., 2004; Seo et al., 2005*). Calcinated alunites have been also shown better P removal than natural ones (*Özacar, 2006*). Alunite, KAl3(SO4)2(OH)6, is a mineral that is not soluble in water in its original form. It is formed by the hydrothermal alteration of tuff. *Brogowski and Renman (2004)* have demonstrated that heating of opoka gradually activates its sorption capacity. A Swedish company uses the same technology to produce wastewater treatment product Polonite® from excavated raw opoka.

Reuse and plant availability

In addition to chemical composition, which determines the sorption capacity of the filter media, availability at the local base is also important. At this point, an important demand is that material should be free of heavy metals and toxic compounds. For example, slag originating from the steel industry can effectively sorb phosphorus, and in saturated slag the phosphorus is also available for plants. A problematic issue when using slag in wastewater treatment is the possible heavy metal content. In LECA material, phosphorus is bound mainly with Al- and Fe-compounds. Al-compounds and phosphorus formulate compounds are known to be difficult for plants to obtain (*Johansson, 1997; Krogstad et al., 2005, Kvarnstrom et al., 2004*). In addition, producing LECA is a process with a huge energy demand, which is why the benefit of using LECA as substrate is doubtful (*Drizo et al., 1999*). The material that is enriched with P can be used as a fertilizer, provided that P is available to the plants, and the contents of toxic compounds and pathogens do not restrict such use. Most of the materials are characterised by high pH values (9–12), which create an unfavourable environment for bacteria (*Renman et al., 2004*). Phosphorus-sorbing materials with additional beneficial characteristics may be used. For example, lime can be used to counteract acidification so as to improve soil structure (*Rex, 2000).*

The adsorption and precipitation of phosphorus in constructed wetlands are very complex phenomena and can occur simultaneously. The media can both adsorb the phosphate ion and/or promote its precipitation by supplying the solution with metals, which can react with phosphorus to produce sparingly soluble phosphates (*Del Bubba et al., 2003*). In addition, calcium present in the wastewater itself can promote phosphorus precipitation (*Maurer et al., 1999*). In such complex conditions the quantification and investigation of the phosphorus sorption process using a long-term base can provide useful data, while establishing an additional filter bed for P removal and evaluating potential filter media for phosphorus sorption in constructed wetlands.

Objectives

(1) To determine the physical and chemical resistance, possible limiting factors and P removal capacity of the best media, based on batch tests - sediment from the oil shale ash plateau for the first time in real wastewater treatment system as tertiary treatment for P removal in the Kodijärve horizontal subsurface flow (HSSF) CW (*Paper I, Vohla et al., 2005; Paper II, Vohla et al., 2007*).

(2) To analyse the sorption characteristics of locally available substrata (materials) that can be used as reactive filter media for sustainable phosphorus removal in constructed wetlands. Batch experiments and particle size distribution were among the first analyses to test the physical and chemical characteristics of various filter materials (*Paper I*).

(3) To analyse the long-term variations in P retention capacity, accumulation pattern and possible mechanisms responsible for long-term effective P retention in horizontal subsurface flow (HSSF) planted sand filter in the Kodijärve constructed wetland (CW) in Estonia (*Paper II*).

(4) The mineralogical study/experimental work was performed by my co-authors with the purpose of determining the mineralogical properties of the ash sediment and clarifying the phosphorus removal mechanism and binding capacity in the ash plateau sediment (*Paper III, Kaasik et al., 2008*).

(5) To determine the treatment capacity of hydrated oil-shale ash in pilot-scale vertical and horizontal flow filters designed to reduce phosphorus in municipal wastewater from the town of Tapa and landfill leachate in Väätsa, Estonia (project “Perspective use of waste products from the oil-shale industry for phosphorus removal from wastewater” during 2006–2007, supported by the EU through Enterprise Estonia (registration code EU23687).

2. MATERIALS AND METHODS

2.1. Phosphorus retention dynamics of Kodijärve HSSF CW

2.1.1. Site description

The Kodijärve HSSF CW (located in south Estonia, constructed in October 1996; *Mander et al., 2001*) purifies wastewater from a hospital for about 40 persons. The wastewater flows from the septic tank into two parallel vertical subsurface flow (VSSF) beds constructed in summer 2002. Outflow from the VSSF beds passes through the HSSF wetland (sand filter), and from the outlet the water flows into the experimental phosphorus retention filter. The HSSF wetland system consists of two beds (chambers) filled with Ca-, Mg- and Fe-rich sand. Before sieving, the uniformity coefficient (d_{60}/d_{10}) for the sand was 0.51. The average grain size before sieving was 0.07 mm (for detailed information see *Paper I*).

2.1.2. Water and soil analyses

Soil analysis of the Kodijärve treatment system
Every October from 1997–2004, 54 soil samples were taken at three depths: 0–10, 20–30 and 60–70 cm, at 18 sites (9 from either bed) located around the water sampling wells, for analyses P at the Laboratory of Plant Biochemistry of the Estonian Agricultural University. Data on accumulated P collected from sampling sites in the HSSF filter beds were analysed and the cumulative accumulation and annual accumulation (mg kg^{-1}) in the left and right beds were compared (C and N content in soil was also measured and analysed; for detailed information see Paper II). The horizontal heterogeneity of accumulated P was also studied by dividing both beds according to the direction of water flow. According to the non-normal distribution of most datasets, the median values and also the minimum and maximum values were calculated.

Water analysis of the Kodijärve treatment system
Once a month from 1997–2004, water samples were taken from eighteen 50-mm polyethylene sampling wells (9 in the left and 9 in the right bed), from the inlet and outlet of the HSSF filter beds and from the P retention filter. Samples were analysed for SS, BOD_7, NH_4–N, NO_3–N, NO_2–N, total N, SO_4–S, PO_4–P, total P and total Fe according to *APHA (1989)* in the lab of Tartu Environmental Research Ltd. Since 2000, during each sampling session the redox potential and pH were also measured from the sampling wells using

Mettler–Toledo portable equipment. Based on the sampling data, retention rates for P (g m^{-2} yr^{-1}) in the left and right beds were calculated and compared. The variations between the two beds were verified using the Wilcoxon Matched Pairs Test, and the t-test was used for independent samples. According to the non-normal distribution of most datasets, Spearman Rank Order Correlation was used to characterize the relationship between water quality parameters.

2.1.3. Retention and removal calculations for the HSSF filter

Phosphorus input and output values for the Kodijärve HSSF CW were calculated by multiplying the P concentration and water discharge, which was averaged over the period between the sampling events, and divided by the area. The input of P into the system is defined as a P load (g m–2 d–1). The mass removal rate in g P m–2 d–1 (*Kadlec and Knight, 1996*) was calculated, with the aim of minimizing the effects of input concentration and hydraulic loading.

2.2. Laboratory experiments of phosphorus sorption in filter media

The phosphorus ad sorption characteristics of different potential filter materials were investigated similar to *Zhu et al (1997)* and *Roseth (2001)* in batch experiment, established by shaking 3 g of material with a 75 ml solution containing 0, 5, 10, 100, 300, 700 and 1000 mg L–1 PO43-P, supplied as KH2PO4 on a horizontal shaking machine for 48 hours. Before the analyses, the samples were set to rest for 30 minutes and then filtrated through a 0.45 μm filter. Terminal phosphate concentration was determined colorimetrically for the PO43-P using the molybdate method described by *Murphy and Riley (1962)* (in accordance with *APHA, 1989*). The amount of sorbed P was calculated as the difference between the initial and the final concentrations.

2.2.1. Materials

For phopsphorus sorption tests 14 local materials rich in Ca-, Mg-, Fe and Al-compounds was gathered, including sands, gravels, glauconite-sandstone, LWA, crushed ash block, oil shale fly ash and the sediment from the oil shale ash plateau.

Natural sands and gravels were collected from various quarries in southern Estonia. Natural sands and gravels from the Rootsi, Kodijärve, Palupera, Aru-küla and Kopa quarries were used. Crushed Palupera gravel was pretreated (crushed, sieved and washed) in the quarry.

At Sub-Ordovician age (~ 480 million years), **glauconite sandstone** is fine-grained well-sorted sandstone that consists of green color Fe-rich stable claymineral–glauconite- round granules with size of 0.1–1.5 mm. The glauconite content can amount to 50–70% (*Raukas and Teedumäe, 1997*). Glauconite is a widespread mineral (deposits are found in the USA, Russia, Germany, Belgium, etc.) containing iron and aluminium silicates as major components (*McRae, 1972*). That is why glauconite is considered to be a potential industrial raw material for mixed coagulant production. In Estonia glauconite is found in the form of round pellets blended with sandstone. The reserves of glauconitic sandstone in the main phosphorite deposits in Estonia amount to over 4 billion tons (*Viiding, 1984*). Glauconite sandstone consist of SiO_2 up to 57%, Quartz sand 19%, Al_2O_3 9%, Fe_2O_3 18%, CaO 3%, MgO 4% and K_2O 7% (*Pozin, 1970; Anso, 1947; Vilbok, 1949*). *Kuusik and Viisimaa (1999)* have tested glauconite as a coagulant by performing sulphuric acid treatment. Thus aluminium and iron sulphates are the main active elements in tested dual glauconite coagulant.

Estonian LWA (the local product name is Fibo) is a porous material made from local clay, and is expanded at high temperatures in a rotary furnace at 1150°C *(http://ee.maxit-cms.com, 07.04.08)*. It is a commercially available building and filling material that is used also for insulation and drainage. Lightweight aggregates (LWA) or light–expanded clay aggregates (LECA) have shown both good water permeability and phosphorus sorption capability (*Johansson, 1997; Zhu et al., 1997; Harris and Maehlum, 2003; Jenssen and Krogstad, 2003*). LWA is also available in large quantities at low cost.

Ash block is a by-product, used for construction, and is made from local raw materials (oil-shale fly ash, natural sand and water). To achieve a porous structure, Al-powder is added during the production process *(www.silbet.ee, 07.04.08)*.

Oil shale fly ash and sediment of oil-shale ash

Kerogenous oil-shale used at the 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 40–60% of the mineral matter), and the ash remaining after combustion is due to the thermal decomposition in fireboxes (peak temperatures 1500 1C) of carbonate minerals and subsequent reactions with flue gases rich in free lime (CaO) and anhydrite ($CaSO_4$). Coarser ash is removed from the bottom side of the fireboxes using water and the slurry is transported through the pipe systems to the waste heaps (plateaus). The fly ash is caught in the dust chambers (cyclones) and is transported also hydraulically through the pipe systems to the plateaus (*Puura, 1989*).

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 most important products in the tested material are: ettringite [Ca_6 A_{l2} $(SO_4)_3$ $(OH)_{12}\cdot 26H_2O$] (15.2%); hydrocalumite [$Ca_2Al(OH)_7\cdot 3H_2O$] (4.1%); portlandite [$Ca(OH)_2$] (6.8%), and Ca-carbonates [$CaCO_3$] (28.0%) (Tabel 1; *Paper III*).

Hydrated sediment from the oil-shale ash plateau consists of hydrous fly- and firebox ash compartments (Figure 1). The mineral part of the used oil-shale ash consists mainly of CaO (29.22%) and SiO2 (25.96%), but Al2O3 (6.25%), Fe2O3,(3.56%) K2O (2.97%) and MgO (3.42%) are also represented (*Paper III*).

Table 1. Average mineral composition (wt%) of oil-shale ash and hydrated plateau sediment (data for fresh ash after *Kuusik et al., 2005*) (*Paper III*).

Mineral	Fresh ash, wt%	Ash-plateau sediment, wt%
Quartz	6.4	9.6
Orthoclase	6.3	6.9
Clay minerals	3.4	3.1
Ca/Mg-silicates	24.1	16.6
Periclase	3.0	2.1
Melilite	10.3	5.3
Anhydrite	11.0	
Lime	28.0	
Calcite/vaterite	4.5	28
Portlandite	2.1	6.8
Ettringite		15.2
Hydrocalumite		4.1
Gypsum		2.3

Figure 1. Hydrated oil shale ash sediment in ash plateau.

The trace element (including heavy metal) content in oil-shale ash is typically higher than in raw oil-shale (e.g. *Pets and Haldna, 1995; Saether et al., 2004)*, but heavy metal concentrations are below the critical limits, and unhydrated fly-ash has been used for the liming of acidic soils in Estonia and northwestern Russia (*Pets et al., 1985*) (Table 2).

The chemical composition of oil shale raw ash and the sediment of oil shale ash are given in Table 1 and Table 2.

Table 2. Average chemical composition of major oxides (wt%) and selected trace element (ppm) content in hydrated plateau sediments.

	Ash-plateau sediment		**Ash-plateau sediment**
In wt%		In ppm	
SiO_2	25.96	Ni	27.0
Al_2O_3	6.25	Sc	6.0
Fe_2O_3	3.56	Mo	3.7
MgO	3.42	Cu	8.6
CaO	29.22	Pb	42. 1
Na_2O	0.11	Zn	50.3
K_2O	2.97	Ni	25.4
TiO_2	0.36	As	15.1
P_2O_5	0.13	Cd	<0.1
MnO	0.04		
Cr_2O_3	<0.01		
LOI	27.98		
TOT/C	2.22		
TOT/S	1.63		

LOI — loss of ignition, TOT/C — total C, TOT/S — total S.

Estimated amount of ash, that is disposed to plateaus by thermal power plants in northeast Estonia, is around 280 Mt (Otsa, 2006).

2.3. Particle size distribution of various substrates for P removal

Particle size distribution was determined using dry- and wet-sieving techniques and pipette analyses to calculate the uniformity coefficient (σ) and determine the possible correlation between the phosphorus removal and the particle size (M) of the local potential filter materials. The particle size for the oil-shale fly ash could not be determined due to its chemical composition. Oil-shale fly-ash consists of an average of 42% CaO, which reacts easily in contact with water and forms $Ca(OH)_2$ and forms cement minerals (portlandite, etringite etc.). Thus we were unable to perform wet sieving. According to *Kikas (1988)*, the main particle sizes for oil-shale fly ash are 0.002–0.063 mm and 0.063–0.125 mm.

2.4. Chemical composition of tested substrates

The Fe, Al, Ca and Mg content (g kg^{-1}) for local sands and gravels (except for glauconite sandstone) were determined earlier in the laboratory of Tartu Environmental Research Ltd.

The chemical composition of the oil-shale ash sediment was determined using standard ICP-ES and ICP-MS techniques at ACME Analytical Laboratories Ltd., Vancouver, Canada (*Paper III)*.

2.5. Experimental filter unit in Kodijärve

The sediment from oil-shale ash plateaus (waste heaps), which was determined to be the most effective filter material on the basis of the batch experiments (*Paper I*), was used for further analysis in an experimental unit installed in the outflow ditch of the Kodijärve HSSF CW in summer 2002.

The outlet from the wetland is also the inlet to the ash unit (more detailed description in *Paper I and II*). During the first two months, samples were taken once a week, then once after two weeks and after that once a month. Terminal phosphate concentration was determined according to *APHA (1989)* in the laboratory of Tartu Environmental Research Ltd.

2.6. Mineralogical analyses

The phosphorus-binding capacities of the ash sediment were studied in open containers using various amounts of hydrated oil-shale ash sediment of different particle sizes and contact surfaces. Together with the phosphorus content in the solution treated with ash sediment, mineralogical and scanning electron microscope (SEM) analyses of the material were also performed. The mineralogical composition of the samples was studied using powder X-ray diffraction (XRD) in unoriented preparations (more detailed data in *Paper III*). The quantitative mineral composition was determined through full-profile Rietveld analysis using Siroquant^{TM} code (*Taylor, 1991*).

Scanning electron microscopy and microanalyses (SEM and SEM-EDS) of ash-sediments were carried out on Zeiss DSM940 and JEOL 845 SEM instruments. The samples were coated with gold (SEM) or chromium (SEM-EDS) prior to the analyses.

Phosphorus-binding capacity measurements from the 0.01 M NaCl solution containing PO4 $^{3-}$ had concentrations ranging from 5 to 300 mg L^{-1} (1.6–98 mg P L^{-1}). The samples were agitated in an orbital shaker for 48 h. All of the abovementioned analyses were performed by my co-authors (*Paper III*).

2.7. Water and soil analyses from Tapa and Väätsa pilot systems

The data about the pilot filter systems in Tapa and Väätsa are gathered from the EU/Enterprise Estonia project No EU23687 on "Perspective use of waste products from the oil-shale industry for phosphorus removal from wastewater" (2006–2008) (*Kirsimäe et al. 2008*). A publication based on these results is under preparation and therefore, the manuscript is not included in current PhD thesis. However these data provide with important information about experiments in the pilot scale filters with hydrated oil-shale ash and confirm the main postulates from previous experiments.

2.7.1. Site description

The composition of inflow water at both sites is shown in Table 3. It is evident that the composition of inflowing water at both sites, the landfill leachate and municipal wastewater, both treated in conventional systems, had significantly different compositions. The wastewater treatment system of Tapa town generally has a good purification efficiency, and problems only occur in the removal of TP, which has a considerably higher variability. The inflow quality in Väätsa landfill is quite stable, but the treatment plant is unable to reduce the water quality to limit values (Table 3). The main problems in leachate at Väätsa are related to very high COD values and nutrient concentrations.

Table 3. Median inflow values of the variables (mg L^{-1}) in the Väätsa and Tapa treatment systems and limit values from the Estonian regulations (RT I 2003.83.565).

		BOD_7	**COD**	**TP**	**TN**	**TSS**	**pH**
Estonian regulations	landfill leachate	25	125	2.0	75	25	6–9
Väätsa leachate	1–6 months	12.3	526	2.9	142.7	54	8.8
	7–12 months	25.4	1050	4.1	214.8	75	8.7
Estonian regulations	wastewater	15	125	1.0	15	15	6–9
Tapa wastewater	1–6 months	1.9	<50	4.7	12.7	7.0	7.8

Whereas at Väätsa landfill the leachate had a relatively stable total phosphorus (TP) concentration varying between 2.5 and 5.2 mg L^{-1}, at the Tapa treatment plant the TP content in the inflow varied between 0.14 and 13.0 mg L^{-1} and had higher TP loading in filters. Most of the inflow P in both sites was in the form of PO_4-P.

To determine the treatment capacity of hydrated oil-shale ash in vertical and horizontal flow filters designed to reduce phosphorus in municipal wastewater from the town of Tapa and landfill leachate in Väätsa, Estonia. Two identically designed pilot experiments were conducted using the following filter systems: (a) a vertical flow (VF) ash filter, followed by a horizontal flow (HF) ash filter and horizontal ash filter receiving water from the peat filter (peat filter data are not included in this thesis). In our experiments, one treated municipal wastewater over 6 months and another treated landfill leachate over 12 months. In both cases, effluent from a conventional treatment (aerated activated sludge treatment) plant was used. The median inflow value of total phosphorus (TP) concentration was 3.4 mg P L^{-1} in Väätsa landfill leachate and 4.9 mg P L^{-1} in municipal wastewater from Tapa.

Identical pilot-scale experiments 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. Small, insulated houses were built for both experiments, in order to avoid the freezing of filters during the winter period. The VF filters had a volume of 0.86 m^3, and HF filters 1.24 m^3. Filters were filled with a 1.1 m thick layer of material.

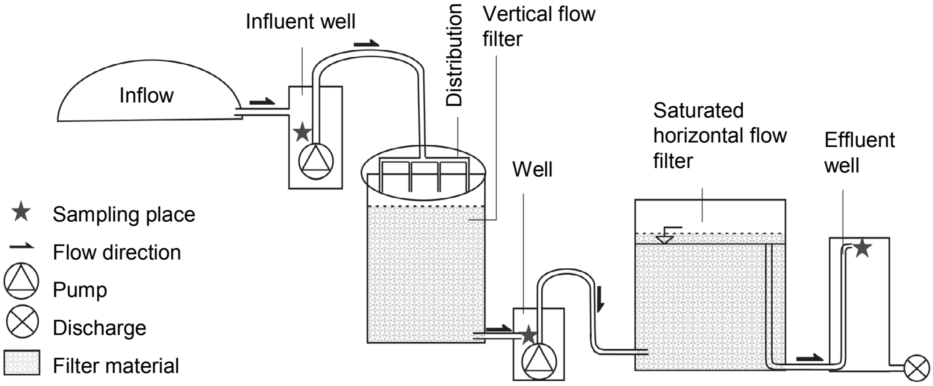

Figure 2. Experimental design of pilot systems in Tapa and Väätsa. Adapted from Kõiv et al, 2008).

The loading rate was 76 mm d^{-1} for VF filters, and 53 mm d^{-1} for HF filters. The average flow rate for all filters was 60 L d^{-1}. To provide maximal saturation and good contact between filter media and wastewater, the inflow water was pumped from the collecting well to the horizontal filter at the bottom, and an outflow pipe collected the water in the upper part of the filter (Figure 2).

The water samples from the inflow and outflow of the pilot systems (onsite systems) were taken once a week during the whole period of operation, according to standard procedures (ISO 5667–10:1992). In both experiments total phosphorus (TP) and $PO_4^{3-}$and pH were determined in a certified Tartu Environmental Research Ltd. laboratory using standard methods (*APHA, 1989*).

3. RESULTS AND DISCUSSION

3.1. Phosphorus retention dynamics of Kodijärve HSSF CW

Average P inlet and outlet concentrations in the Kodijärve CW system were 14.6± 5 mg P L^{-1} and 3.2 ± 1.8 mg P L^{-1}. The average calculated purification efficiency for the whole system was 78.4%, and the mass removal rate for the same period was 0.14 g m^{-2} yr^{-1}. There are some differences in the purification efficiencies between the filter beds. During the investigation period, the average P removal efficiency in the right bed was slightly higher (81%) than in the left bed (70%). This could be the result of the anaerobic conditions in the left bed. During the period 2000–2002, redox potentials (Eh) in the right and left bed were 34 ± 27 and – 39 ± 9, respectively. Anaerobic conditions prevail in soil when Eh is below –100 mV (*Kadlec and Knight, 1996*), but Fe that is bound with P can be released as the result of reduction even if Eh is below 250 mV (*Faulkner and Richardson, 1989*). The calculated average mass removal rate between the beds did not vary significantly (0.13 g m^{-2} d^{-1} for the left bed and 0.14 g m^{-2} d^{-1}. for the right one). In 1997–2002 the horizontal flow sand-plant filter had an average loading of 55.7 g m^{-2} yr^{-1}.

The average inlet concentrations of P did not vary significantly, but the fluctuating flow rates and thus the loading of P in the last year may be the reason why purification efficiency in the filter bed has been changeable. Likewise, *Mander and Mauring (1997)* have found a positive correlation between nutrient loading and purification efficiency. Although the outlet concentrations in the Kodijärve sand planted filter system showed a slowly increasing trend from 1997–2002 (Figure 3), the purification efficiency of phosphorus has been quite good (63–95% respectively). For instance, recent studies (*Harrison et al., 2000*) and reviews (*Van Buuren et al., 1999*) on the performance of sand filters have reported removal efficiency of only 40% total phosphorus (TP) at loading rates of 10 g BOD_5 m^2 d^{-1} in the filter.

In the same time, the average annual calculated phosphorus retention fell from 74.5 to 24.7 g m^{-2} yr^{-1}. This was followed by constantly high Fe outwash due to anaerobic conditions from the filter media (negative retention from 2 to 3.7 g m^{-2} yr^{-1}; Figure 3). *Tanner et al. (1999)* showed a substratum TP accumulation rate of 22.8–25.2 g $m^{-2}yr^{-1}$ in a gravel (SiO_2 75%, Al_2O_3 12.7%, Fe_2O_3 1.6, CaO 1.5%, MgO 0.3%) filled wetland system that purified dairy farm wastewater during a 5-year-peiod. Our system achieved the same value after 5 years of operation. Substantial quantities of accumulated TP representing the TP found in surface sludge (in the absence of sorbing gravel surface) suggest that much of the accumulated TP was likely to be in organic forms or associated with organic matter.

In the sand or gravel substrate, phosphorus is bounded to the media mainly as a consequence of adsorption and precipitation reactions with calcium (Ca), aluminium (Al) and iron (Fe). *Arias et al. (2001)* found that The P-removal capacity of some sands would be used up after only a few months in full-scale systems, whereas that of others would persist for a much longer time. The most important characteristic of the sands determining their P-removal capacity was their Ca-content.

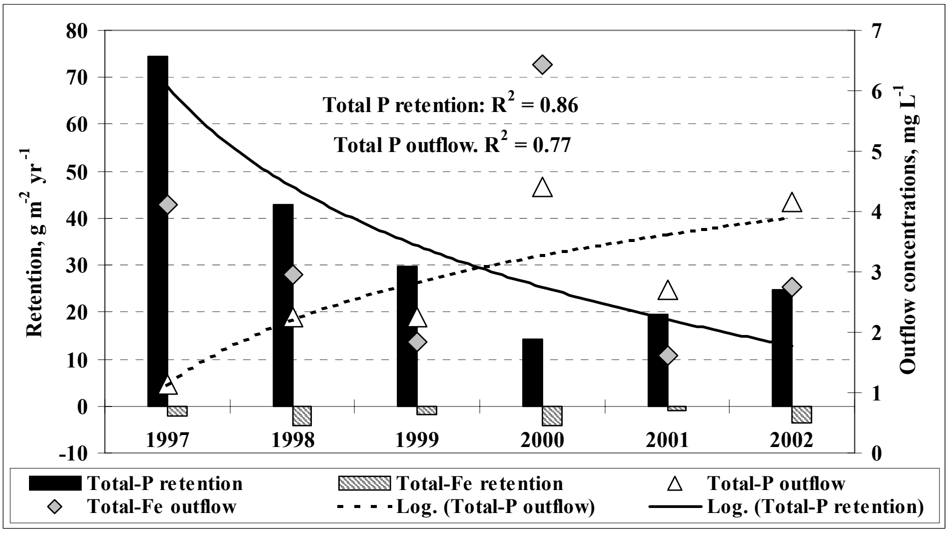

Figure 3. Retention (g m^{-2} yr^{-1}) and outflow concentrations (mg L^{-1}) of total P and total Fe in the Kodijärve HSSF CW during the period 1997–2002.

The good phosphorus removal capacity in Kodijärve is probably supported by the Ca-, Mg- and Fe-rich sand. Analyses showed that the Ca, Mg and Fe contents were 41.5, 8 and 2.4 g kg^{-1} respectively.

After five years of operation, the cumulative phosphorus retention in the Kodijärve HSSF CW was 52.8 kg (based on water inflow and outflow data), of which the majority (88.1%) was adsorbed in soil. However, like the total P retention of the system, annual P accumulation in the soil also decreased. Assimilation by plants (6.1%) and microbial immobilization (4.4%) supported the removal process *(Mander et al., 2003)*. Gaseous phosphorus fluxes are believed to play some role in phosphorus retention in anaerobic environments (*Gassmann and Glindemann, 1993)*. According to *Devai et al. (1988)* and *Gassmann and Glindemann (1993)*, gaseous P losses in the form of phosphine and phosphane (PH_3) in Kodijärve might be no more than 10 g P from 1997–2001, which is <0.02% of P retained in the system (*Mander et al., 2003)*.

Kadlec and Knight (1996) showed that initial P removal rates from wetland systems in the U.S.A. are often in excess of 90% but decline sharply after only 4–5 yr of cumulative P addition. In the gravel system, the main P removal mechanisms were supposed to be filtration, biological assimilation and plant uptake *(Korkuzus et al., 2005)*.

3.1.1. Soil P accumulation in HSSF filter from 1997–2004

During the wetland performance of 8 years, the concentration (based on soil P data) of P in the filter sand increased significantly, from 14 to 117 mg P kg^{-1} respectively. On the other hand, the annual accumulation of soil P decreased from 14.1 mg kg^{-1} in 1997 to 4.4 in 2000, and a negative annual accumulation (−6.5 mg kg^{-1}) was observed in 2004. No significant differences in P accumulation between the right and left bed were observed. Average annual soil P accumulation in the sand filter fluctuated. Since a significant part of soil P is accumulated as lactate soluble P via the sorption process, fluctuations in accumulated P rates are probably influenced by some release of P caused by the anaerobic conditions in the filter bed. The fluctuating phosphorus concentration in soil is probably caused by the iron release from filter beds. The amount of released iron from the filter from 1997–2003/2004 is approximately 13 kg. Comparing the phosphorus and iron outflow concentrations between the beds, the concentrations of total P, PO_4–P and total Fe in the outflows from the right and left beds differed significantly ($p<0.05$). Average outflow concentrations for total P and total Fe were lower in the right bed (4.4 mg P L^{-1} and 1.6 mg Fe L^{-1}) than in the left bed (5.1 mg P L^{-1} and 3.2 mg Fe L^{-1}). The low average redox potential (−22±11 mV) in the left bed during the period 1997–2004 (in right bed 40±24 mV) also shows that the high Fe and P concentration in the outflow were most likely induced by the anaerobic conditions in the sand filter. *Rustige et al. (2003)* found that in typical subsurface flow sand based wetlands constructed in the 1980s, the Eh in HSSF wetlands was normally 600–700 mV. Minimal Eh (200 mV) was observed in spring. A relative minimum of P removal was also reached at that time.

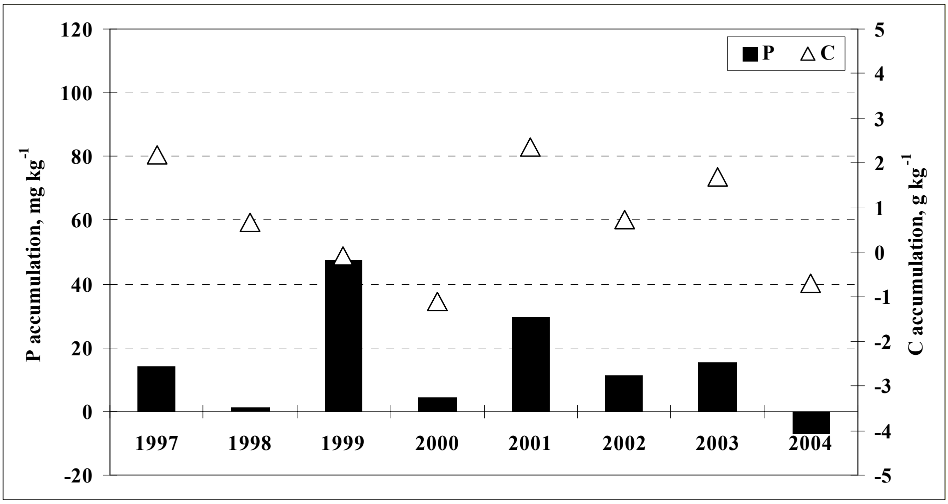

Figure 4. Annual carbon accumulation (g kg^{-1}) and P retention g m^{-2} yr^{-1} in Kodijärve HSSF sand filter from 1997–2004.

As can be seen in Figure 3, the C and P annual accumulation values are also quite similar. Organic amendments are a source of water-soluble C that can directly affect P solubility through three mechanisms. Organic molecules may: (1) specifically sorb to soil minerals, competing with P for sorption sites; (2) combine with surface-bound aluminum or iron to form soluble organic-metal compounds substituting for, and releasing, previously sorbed P; or (3) sorb to soil particles at nonspecific sorption sites, increasing the surface negative charge of the particle and resulting in reduced electrostatic attraction of P to the soil surface (*Traina et al. 1986*). The above-mentioned mechanisms may also play an important role in P removal processes at the Kodijärve sand filter (Figure 4).

The distribution of wastewater in sand filter beds may be another reason for the formation of anaerobic zones. The Kodijärve sand consists of 20.5% of fine silt (particles with grain size <0.006 mm), which certainly increases the surface area and creates sorption sites for P, but may form impermeable zones and cause clogging in the filter bed (*Anderson and Rosolen, 2000; Farahbakhshazad and Morrison, 2000*). On the other hand, a significantly higher cumulative concentration of P in the upper layer of the filter material in the outflow zone of the right bed supports the existence of anaerobic microsites in deeper layers. In the left bed the differences were not as great, although an “island” was found in the middle of this bed where the concentrations were remarkably lower than in the other closer areas of the bed.

Anaerobic conditions in Kodijärve filter sand additionally lead to sulphate reduction. Iron oxyhydroxides were converted to iron sulphides (Fe_2S) and phosphate released into the water column (*Kadlec and Knight, 1996; Roden and Edmonds, 1997*). Sulphates were positively correlated with Eh (R=0.69) and negatively with phosphates (R=−0.59) and total phosphorus (R= −0.62) (Paper II).

In its original state, Kodijärve sand consist largely of Ca (41.5 g kg^{-1}), but also Mg (8 g kg^{-1}), Fe (2.4 g kg^{-1}) and Al (1.5 g kg^{-1}). *Del Bubba et al. (2003*) showed that Danish sands (tested for phosphorus removal), contained much less Ca (0.2–69.9 µg g^{-1}), Mg (0.08–2.23 µg g^{-1}), Al (0.32–4.18 µg g^{-1}) and Fe (1.21–8.47 µg g^{-1}). The study found that sands with high Ca content were most suitable to be used in HSSF constructed reed beds.

As expected, relationships between water quality characteristics in Kodijärve demonstrated significant correlation values between various wastewater parameters in the water sampling wells of the filter beds (*Paper II*). For instance, the BOD_7 value showed a positive correlation with the NH_4–N, Total N, PO_4–P and Total P concentrations, and a negative correlation with redox potential, NO_2–N, NO_3–N, SO_4, and dissolved O_2 concentrations.

Total N and Total P concentrations were strongly correlated. Dissolved O_2 enhances higher NO_2–N, NO_3–N and SO_4 concentrations, whereas lack of oxygen causes significantly higher NH_4–N, Total N and Total P concentrations. It was somewhat of a surprise to us that the water table showed a significant correlation only with dissolved O_2 concentration (R^2=−0.56). Likewise, water temperature showed a significant positive correlation with NH_4–N, Total N, PO_4–P, and Total P concentrations. This is probably due to better oxygen solubility in cooler water, which enhances nitrification and phosphorus removal processes. Similar results are shown in *Rustige et al. (2003)*. PO4 and total P concentrations in water were negatively correlated with Eh and SO4 concentration. This presumably refers to enhanced biological phosphorus removal, where phosphates are immobilized and stored as polyphosphates in the aerobic stage and released after decomposition in the anaerobic or anoxic stage (*Bitton, 1994; Kunst and Mudrack, 1988; Alas et al., 2003*). *Rustige et al. (2003)* described reversible P accumulation in a vertical flow CW. In that case the equilibrium concentrations of the aqueous phase rises continuously with the amount of total accumulated P. The removal only takes place with an increase in input concentrations. The regeneration of adsorbing capacity in vertical flow filters can be achieved by changing the regimes to achieve fluxes in redox situation. New amorphous structures of Fe probably enhance P removal *(Lantzke et al., 1999).*

3.1.2. Horizontal distribution of P in soil

Soil data were also studied by dividing both beds into three zones according to flow direction, as follows: the inlet zone, the central zone and the outlet zone. Comparing the long-term horizontal heterogeneity in accumulation of P from 1997 to 2004, the average cumulative accumulation (the average amount of P in mg per kg in the sampling zone that has been retained in filter media) demonstrated a significant decrease towards the outlet zone in all cases. *Rustige et al. (2003)* also found a similar filtration effect in HSSF wetland media. Accumulation between the right and left beds in Kodijärve did not differ significantly.

3.2. Batch experiments and particle size distribution

3.2.1. Batch experiments

P retention efficiency for ash materials was near 100%, even at very high concentrations of P (700–1000 mg PO_4^{3-} L^{-1}). No sign of saturation was noted during the tests. Efficiency for crushed ash block 98.9%, for oil shale fly ash 96.5% and for sediment of oil shale ash 98.4% was observed. Maximal sorption (at a concentration of 1000 mg PO_4^{3-} L^{-1} or 326.1 mg P L^{-1}) of P, calculated as decreased amount of P in mg per 1 g material, for the ash materials was 293.5 mg P g^{-1} for ash block, 325.3 mg P g^{-1} for oil shale ash sediment and 326.0 mg P g^{-1} for oil shale fly ash (Figure 5). For the gravels, maximum sorption was 97.8 and 143.5 mg P g^{-1}. Both LWA materials and Rootsi sand had the lowest sorption values in all tested concentrations (0–16.3 mg P l^{-1}) (Figure 5). Observed maximum sorption for Kodijärve was 65.2 mg P g^{-1}. The same value was measured for Palupera sand. Based on maximum sorption value, however, the Kopa coarse and red sand showed an even higher value than the Kodijärve sand (*Paper I*). Both Kopa sands indicated very low sorption values at initial P concentrations between 5–300 mg P L^{-1} (sorption 0.26–3.26 mg P L^{-1}). This might refer to precipitation, while supersaturation and crystal growth at high phosphate concentrations take place (700 and 1000 mg PO_4^{3-} L^{-1}). At higher initial concentrations the sorption value increased over 70 mg P L^{-1} (Figure 5).

3.2.2. Grain size distribution

Natural materials were classified according to *Jaanisoo et al.* (1998) as sand and gravels. The average grain size for Estonian sands was found to be 0.07–1.01 mm and 0.92–1.84 mm for gravels (Palupera crushed gravel and Aruküla gravel. We did not find any significant correlation between average grain size and uniformity (sorting coefficient) and the P removal efficiency of the tested filter media. According to the results of grain size distribution, we classified natural materials as sands and gravels.

Only Palupera sand and Kopa coarse sand contained particles with fractions over 0.5 mm (63% and 44%). Kodijärve sand (the fraction >0.5 mm was missing) and glauconite-sandstone (0.8% of particles over 0.5 mm) had the finest texture. All other sands had more than 10% of particles >0.5 mm. The 0.06–2 mm fraction, classified as the sand fraction, was probably the most important factor for P removal in tested filter media (a correlation of R2=0.86 was found) (*Paper I*).

Average P removal efficiency among different South-Estonian sands was between 8.6–27.2%. In Norway the grain size limit for filter media in CWs suggest less than 0.5% of particles under 0.1 mm. The content of fine silt (<0.006 mm) in natural materials used in our work varied from 2.9–36.4%. All sands and gravels with a grain size <0.006 mm made up more than 0.5% of the total. Hence the risk of clogging and poor hydraulic conductivity is most likely to appear when, for instance, one chooses Kopa (26.4%) or Kodijärve sand (20.5%), which contained fine silt much more than other materials. To enhance hydraulic conductivity and minimize the risk of clogging, the sieving and washing of natural materials is needed before use in CWs.

The grain size of LWA, crushed ash block and crushed sediment of oil shale ash fell in a range between the gravel and sand fractions (2–60 mm and 0.006 –2 mm).

Chemical composition

The average P sorption capacity was higher for gravels (Palupera crushed gravel (50.3 %) and Aruküla gravel (32.6%)). Analyses showed that Aruküla and Palupera gravels were rich in Ca, Mg, Fe and Al compounds (140, 41, 7.8, 3.5 and 20, 12, 9.6, 5 g kg^{-1} respectively).

This was clearly the reason for their better sorption efficiency. The determination coefficient (R_2) between sorption efficiency and summarized Ca, Mg, Fe and Al content was 0.56. The importance of Ca, Mg, Fe and Al content in filter media (R^2= 0.93) has also been observed by *Zhu et al. (1997).*

The determined Ca content in substrates varied between 1–140 g kg^{-1} for dry weight. The greatest amounts of Ca were observed in Palupera gravel and the smallest in Estonian LWA. Mg, Fe and Al contents in tested materials were much lower than Ca. The moderate efficiency of Estonian LWA in the batch test is probably explained by the lower Ca content than Norwegian LWA. Both Estonian LWA and Swedish LWA exhibited poorer P removal efficiency than Norwegian LWA, probably due to their different chemical composition (*Johansson, 1997*). To enhance the P removal capacity of LWA, which has a sufficient hydraulic conductivity for CWs, *Johansson (1997)* suggests mixing with Ca-rich materials or Norwegian LWA.

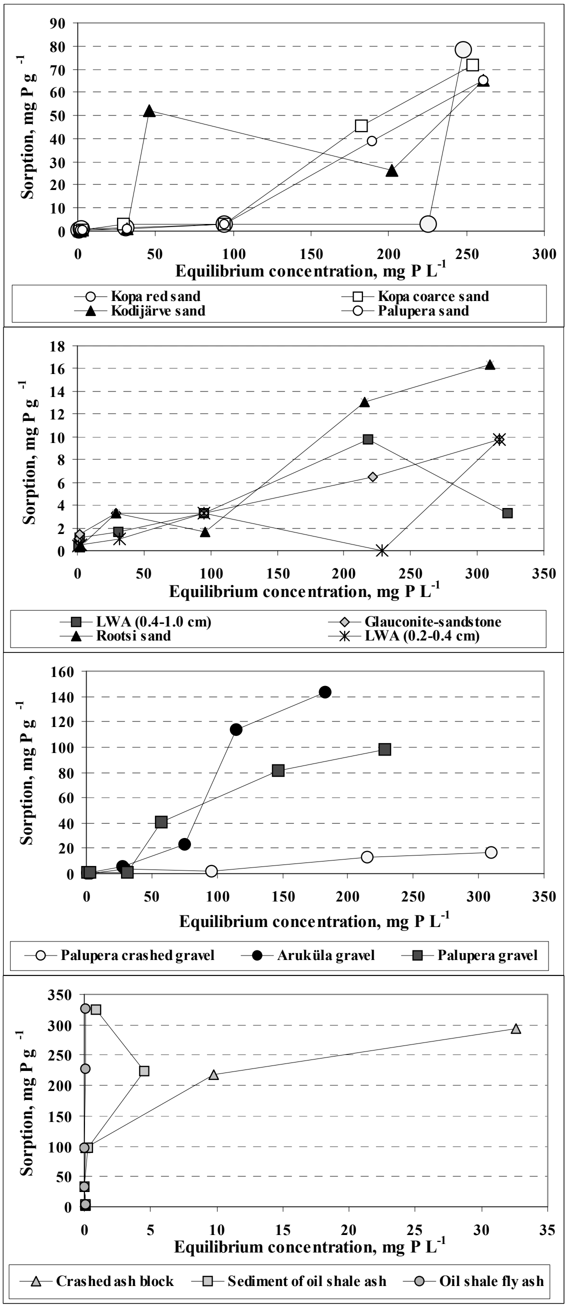

Figure 5. Phosphorus sorption capacity of potential filter media in batch experiments (using phosphate solution 5–1000 mg L^{-1}). Equilibrium concentration is the final P content in the solution.

Uniformity

Uniformity coefficient (d_{60}/d_{10}) of South-Estonian natural sands was found to be between the values of 1.5–8.0. Based on the recommended value (<4) according to *Brix et al. (2000)*, the most appropriate sands for constructed wetlands were Kopa coarse sand, Rootsi sand, glauconite-sandstone and Kodjärve sand (d_{60}/d_{10}=2.6; 2.6; 2.1 and 1.5). The fact that their uniformity value is under 4 provides sufficient residence time in filter soil and also minimises the risk of clogging. Roseth (2001) reported the uniformity for different sands from coastal areas (shellsands) as being between 2.7–5.6, and for natural sands 2.0–2.9. For tested LWA the uniformity number was 3.9 (*Roseth, 2001*).

3.3. Experimental phosphorus retention unit in Kodijärve

During the first 4 months of the ash filter experiment, the efficiency of P removal was about 71%, resulting in an average concentration of 1.9 mg P L^{-1} in the outlet. However, increasing average annual water discharge (2.2–3.8 L min^{-1}) led to a short hydraulic retention time (1.5–2 days) and water overflow in the filter. The high water table in the ash unit could not be dropped down because of technical problems in design. Hence the upper water layer was not in direct contact with the material at the bottom. Increased flow rates and hence too short retention time was not sufficient for efficient removal processes (P removal 10–20%). Longer contact time and effective distribution between the ash and water, promotes the dissolution of Ca^{2+} and high pH, and thus precipitation processes with phosphates (also in *Paper III*, *Kaasik et al., 2008*). P removal efficiency decreased, resulting in an increase in outlet concentrations from 3.5 to 6 mg P L^{-1} (R_2=0.57). Biofilm development on filter particles could also influence retention by clogging the active surface and pores.

During the study period the visual structure of oil shale ash from the plateau remained stable, no degradation processes were observed, in contrast to the ash block (that was also considered to be a potential filter media). During the filtration of wastewater through the ash blocks, the material hydrolyzed (Noorvee, personal communication). The cold season and freezing temperatures could, however, influence the microstructure of the material, whilst removal efficiency slowed down after the filter successively froze and melted. Thus the physical stability is appropriate for the use of ash sediment in filter systems, but the maintenance of removal efficiency can be guaranteed by isolating the filter at cold temperatures.

In addition to P removal, other wastewater components were also determined and analysed. For the period September 2002–December 2004, average Fe removal in the ash filter was found to be 52%. A slight increase in SO_4 in the outflow compared to the inflow data was found (from 33.2 mg L^{-1} to 34.2 mg L^{-1}).

Sulphates are probably a product of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 24H_2O$) degradation (*Myneni et al., 1998*). SO_4 outflow concentrations were lower than the permitted value established by the Estonian effluent quality requirements for wastewater systems for <2000 population equivalents (PE).

3.4. Mineralogical analyses

The basic results of the mineralogical/kinetic study demonstrated phosphorus retention predominantly via precipitation processes with Ca-phases. The content of the most reactive Ca-phases (ettringite and portlandite) decreased drastically, and after prolonged treatment with P solution, these minerals disappear from the sediment. The increased content of calcium carbonates at the same time suggests both carbonization of the portlandite and precipitation using the Ca released from the dissolution of ettringite.

The observed changes suggest that the unstable calcium-rich minerals such as ettringite and portlandite (probably also hydrocalumite) in the hydrated ash sediment control the removal of phosphorus, providing Ca2+ and the source of stable nuclei in which the crystals of phosphate can form. Mineralogical analyses show that the phosphorus is bound in the oil-shale ash sediment as a hydrated calcium phosphate Ca3(PO4)2 nH2O or as a β-form of calcium phosphate Ca3(PO4)2,

$$2PO_3^{-4} + 3Ca^{2+} + nH_2O = Ca3(PO4)2 \cdot nH2O, \qquad (1)$$

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:

$$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O = 6Ca^{2+} + 2Al(OH)_3 + 3SO_4^{-2} + 29H_2O;\ pH\sim10:7, \qquad (2)$$

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

$$CaCO_3 = Ca^{2+} + CO_3^{2-}, \qquad (4)$$

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 Ca2+ released from the ettringite.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

The precipitation of Ca-phosphates is confirmed by the SEM-EDS spectra of these precipitates (Figure 6). The highest removal capacity of 65 mg P g–1 and effectiveness of 67–85% in all experiments was measured.

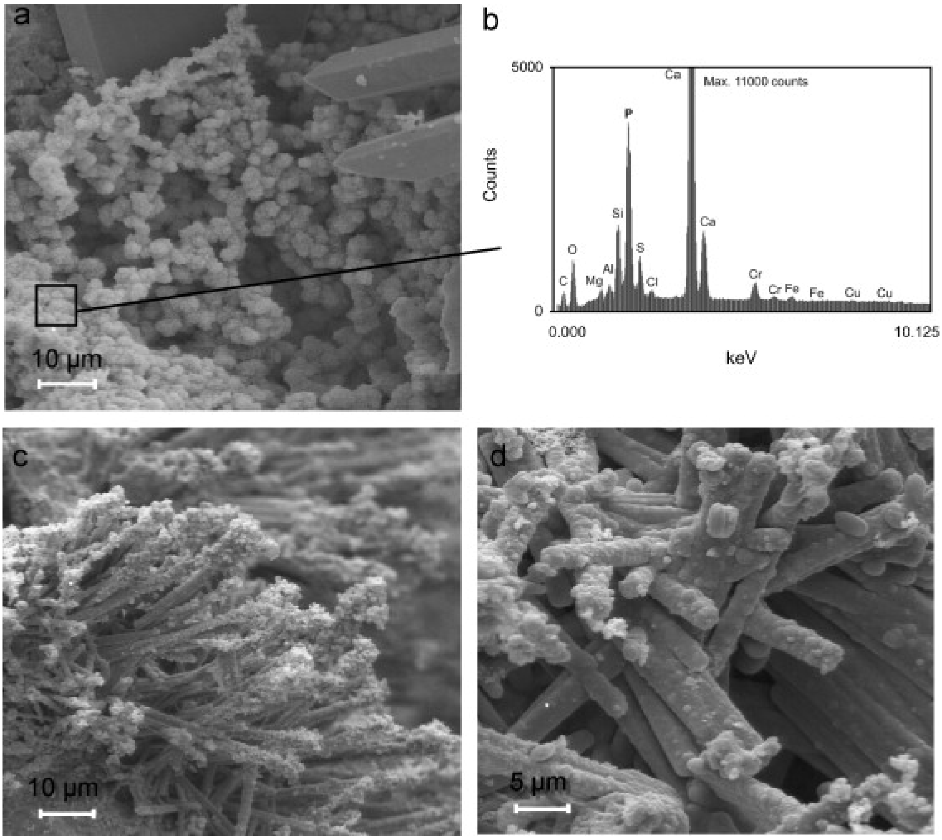

Figure 6. SEM images and EDS analyses of the treated ash. (a) Calcium phosphate aggregates on the hydrated ash sediment after treatment with the phosphorus-containing solution. Note the authigenic gypsum crystallites in the upper right corner of the image; (b) SEM-EDS analysis spectrum of the hydrated ash sediment surface after treatment with the phosphorus-containing solution. The sample was Cr-coated prior to analysis. (c) Calcium-phosphate aggregates on the ettringite needles after treatment with 100 mg L^{-1} phosphorus-containing solution; (d) calcium-phosphate overgrowths on ettringite after treatment with a 1000 mg L^{-1} phosphorus solution. Note the shape of the overgrown/replaced ettringite crystallites (*Paper III*).

Ettringite can constitute up to 25% of the hydrated ash sediment, and it is clearly the most reactive mineral in the hydrated ash sediment. The equilibrium dissolution of ettringite provides free calcium ions that act as stable nuclei for phosphate precipitation. Other potential substrates for P adsorption are surfaces of devitrified alumosilicate glass phases, whose importance will increase over time.

3.5. Phosphorus removal in pilot systems at Tapa and Väätsa treatment plants

Continious study with hydrated oil-shale ash was carried through in pilot systems at Tapa and Väätsa treatment plants, to find out the limits for phosphorus loadings and filter design.

Whereas at Väätsa landfill the leachate had a relatively stable total phosphorus (TP) concentration varying between 2.5 and 5.2 mg L^{-1}, at Tapa treatment plant the TP content in the inflow varied between 0.14 and 13.0 mg L^{-1} and had higher TP loading on filters (Figure 7). Most of the inflow P in both sites was in the form of PO_4-P.

Despite the significantly different phosphorus loadings, dynamics and short retention time, we found that the reduction of TP in the VF ash filters (VV2 and TV2) during the first 6 months was quite good. Vertical flow ash filters combined with sequential horizontal ash filters were studied for 4 months. In order to test the higher inflow P load in horizontal ash filters (VH2 and TH2), the vertical filters were later switched out from the system.

The Väätsa VF filter (VV2), which had lower and more stable inflow concentrations, did not show a higher reduction (median value 58%). The VF ash filter at the Tapa site (TV2), which operated under variable phosphorus concentrations, resulted in 89% removal.

However, the horizontal ash sediment filters VH1 and TH1 (receiving the inflow from vertical peat filters) at both sites did show efficient TP removal, namely 86% and 89% for the Väätsa and Tapa experiments, even at very low median P loads (0.6 and 0.27 mg P L^{-1}) (Figure 7, 8). Low inflow concentrations at horizontal ash filters were achieved by pretreatment with vertical peat filters. Higher inflow concentrations for the ash filters (VH1 and TH1) was presented after the saturation of pretreating peat filters for 4–5 months (Figure 7 and 8).

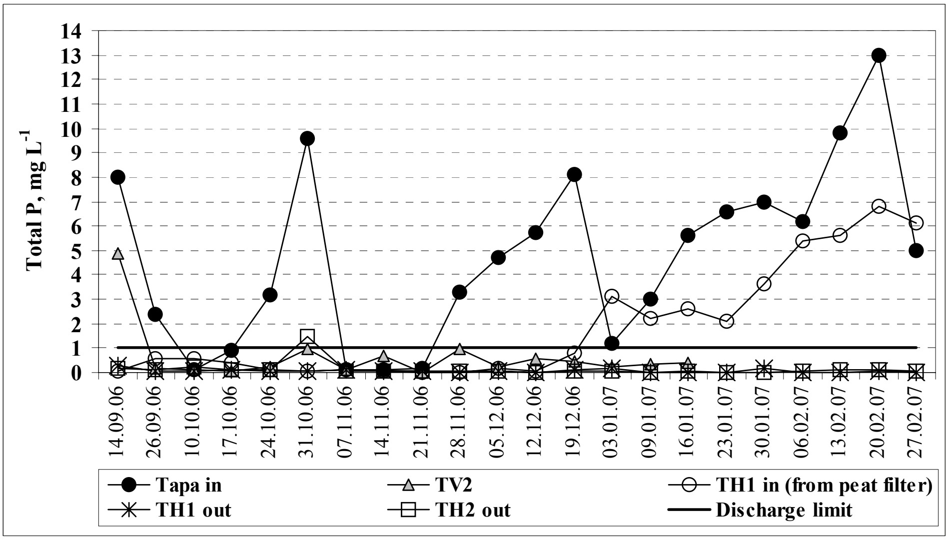

Figure 7. Inflow and outflow concentrations of total phosphorus (TP) in the Tapa experiments. The explanation of filters (TV2, TV1, TH1 and TH2) is described in Materials and Methods.

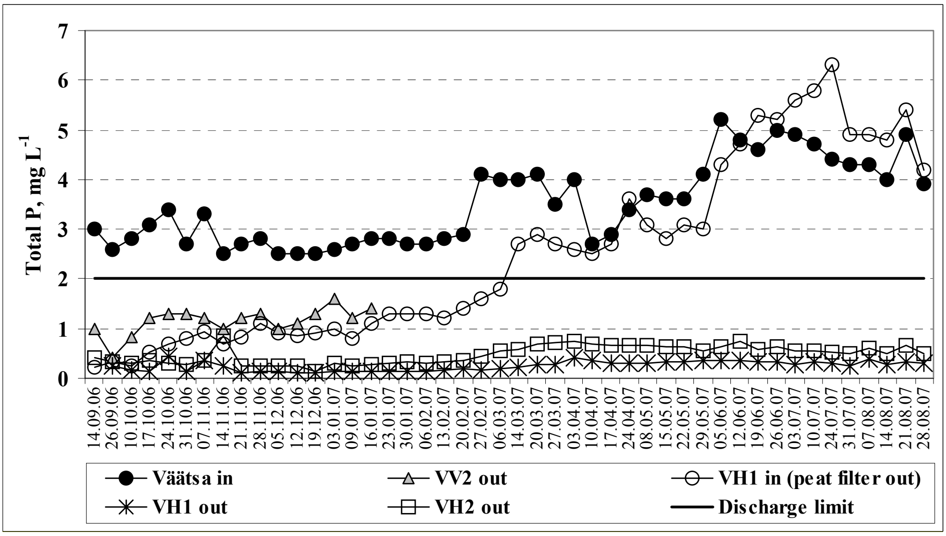

Figure 8. Inflow and outflow concentrations of total phosphorus (TP) in the Väätsa experiments. The explanation of filters (VV2, VV1, VH1 and VH2) is described in Materials and Methods.

In HF ash filters (treating outflows from vertical ash filter for 1–4 months and after that the water from the Väätsa treatment plant), showed even better P retention at both study sites - 93% for TH2 and 83% for VH2 (Figure 8).

The dynamics of TP removal suggest that at given experimental conditions the TP removal capacity of HF ash filters (TH1, VH1) slightly increases due to the increasing inflow values (from saturating peat filters) after the first 4–7 months of operation. Despite the increasing concentration, the outflow values remain very stable. A slight increase in outflow values after 6 months of operation was observed, and since then the concentrations in both horizontal filters remained at the same level.

The pH variation at the outflow of each filter shows a clear dependence on filter material properties. If the pH of the inflow was quite constant at both sites, i.e. 8.7 and 7.7 for Väätsa landfill leachate and Tapa wastewater respectively, then in the VF ash filters the pH increased to 11.4 in TV2 and 10 in VV2. The pH of water from horizontal ash filters (receiving inflow from VF peat filters) increased to 11.5 in TH1 and VH1. From horizontal filters receiving water directly from treatment plants, the pH increased to 12 in TH2 and 11.7 in VH2. High pH values in outflow were due to the dissolution of Ca-phases (portlandite and ettringite) present in the ash material. The pH value from combined VF filters (50% peat and 50% ash sediment) was significantly decreased, to a tolerable pH 7–9, by subsequent HF peat filters (*see at Kõiv et al., 2008*). Hence the effective design, peat filters after the ash sediment filters, is recommended to reduce the high pH to meet the permitted discharge values (pH 9.0) and even afford an additional P removal effect (*Kõiv et al., 2008*). In Filtralite P systems the initial pH was also 12.7, which decreased to 11 after several months of operation. Other filter materials (slags; *Drizo et al., 2002*) with alkaline components would also cause a high effluent pH. Possible solutions in addition to the polishing filter are aeration and dilution (*Saltnes and Føllesdal, 2005*).

The effective performance of ash filters is directly related to the main removal process through the precipitation of stable Ca-phosphate phases as a hydrated calcium phosphate $Ca_3(PO_4)_2 \times nH_2O$ or as a β-form of calcium phosphate $Ca_3(PO_4)_2$ (Figure 8; *Paper III*).

Variations in chemical and mineralogical composition after the pilot study supported the findings for removal mechanism analysed in earlier laboratory experiments. Ettringite content in materials after the wastewater treatment experiment decreased, and the amount of calcite simultaneously increased. That process refers to the precipitation of calcium released from the ettringite dissolution, and accompanied by the formulation of sparingly soluble Ca-phosphate and phosphorus removal from wastewater. Average P accumulation in pilot ash sediment filters (on the assumption that ash density is 900 kg m^{-3}) was 40 mg P kg^{-1}. Total phosphorus removal efficiency in the horizontal ash filter at long-term using hydraulic loading ~50 L m^{-3} d^{-1} more than 85% was achieved, and in vertical flow filters at loading ~80 L m^{-3} d^{-1} removal efficiency higher than 50% was determined.

Removal efficiency in VF ash filters was somewhat lower (on average 60%). The reason for that phenomenon is the rapid water infiltration through the porous soil (1 m thick layer, porosity ~60%), whereby sedimentation processes are unable to proceed with sufficient efficiency. The results of the pilot study allow one to claim that in the HF ash sediment filters at water loading less than 50 L m^{-3} and at average inflow concentrations lower than 10 mg L^{-1}, purification efficiency above 70% is guaranteed during a one-year period. That limit is based on a leachate filters treatment study in which higher contamination rate and complex composition in receiving water were determined. Hence the purification quality of P can even be improved by the efficient pre-treatment of water. In the Tapa experiment, where the inflow water was well purified and only high P concentrations were presented, purification exceeded 80% in horizontal ash filters, in the event the inflow concentration exceeded 0.2 mg P L^{-1}.

Below 0.05 mg L^{-1}, the horizontal ash filters could not achieve remarkable purification. In Väätsa the same type of filter system (vertical peat + horizontal ash) did not show low enough concentrations to affect purification. The lowest inflow concentration (from peat filter) for the horizontal ash filter was 0.22 mg L^{-1}.

Data from Tapa and Väätsa pilot systems verify earlier hypothesis (*Paper I; Paper II*) that sufficient residence time guarantees the effective phosphorus removal in reactive hydrated oil-shale ash filters. The hydraulic loading tests, carried recently through in laboratory, also demonstrated that phosphorus removal in ash filters is linearly dependent on residence time (*Kirsimäe et al., 2008*).

4. CONCLUSIONS

Subsurface flow and other treatment wetlands have been successfully used for the purification of industrial wastewater (food production, paper industry etc.), mine water, agricultural water, landfill leachate, but also for domestic and rainfall water purification. Because of their great volume and slow purification processes, wetland systems are tolerant to changing hydraulic and nutrient loadings. This makes them more suitable than conventional treatment plants for the treatment of wastewater from tourist resorts, individual households, industries and other objects with variable wastewater flow rates and pollution loads. Wetland treatment demands a great area, and hence the use of constructed wetlands for wastewater treatment is more suitable in sparsely-populated areas. Optimal loading rates for subsurface flow CW are between 50–500 PE. The systems can, however, also be designed for loadings 2000 ie.

Phosphorus removal in subsurface flow CW is strictly connected with the physical–chemical properties of the filter material, whereas P is mainly sorbed or precipitated in filter media (*Faulkner and Richardson, 1989; Kadlec and Knight, 1996; Vymazal et al., 2000*).

Thus removal of P in constructed treatment wetlands is a complicated process and moreover, the life expectancy of sub-surface flow CWs, especially considering phosphorous removal, depends on the filter media that are used for its construction (*Grüneberg and Kern, 2000*). The medium with a high phosphorus binding capacity is an important part of the treatment wetland system (*Arias et al., 2001*). Using natural substrata like sand or gravel, the phosphorus removal efficiency will decrease after some years of operation, and thus it is important to find local filter media with high and stable phosphorus removal.

The purification efficiency of phosphorus in the horizontal subsurface flow (HSSF) sand filter in Kodijärve after 5 years of operation varied from 63–95%. However, the slowly increasing trend in outlet P concentrations (R^2=0.77) and decreasing annual P removal rate (from 74.5 to 24.7 g m^{-2} yr^{-1}) offers clear evidence of possible saturation processes in the filter media.

The dynamics of soil phosphorus (P) accumulation in the sand filter of a horizontal subsurface constructed wetland (HSSF CW) was studied intensively in the period 1997–2004. Concentrations of soil P in the filter media (coarse sand) in the HSSF beds after 8 years of operation showed an increasing trend (R^2= 0.99). In the cumulative accumulation pattern of P, a decreasing filtration trend towards the outlet zone was observed. The variations in annually accumulated soil P are probably influenced by anaerobic conditions and P release. Average redox conditions for the filter beds were −22±11 mV in the left bed and 40±24 mV in right bed.

Better aeration conditions in the sand filter may enhance the efficiency of P removal and accumulation by preventing the reduction of Fe and the release of

PO_4-P. A separate reactive filter for phosphorus after treatment with filter media, which guarantees high and stable phosphorus removal capacity and is not rich in Fe, is a possible solution to prolong the lifetime of constructed wetlands. Sufficient and effective hydraulic conductivity and water distribution in the filter supports maximal retention. Hence grain size distribution is also an important characteristic for filter media.

Several "islands" of accumulated P in sand refer to the water channel established in the filter, which are also signs of decreasing hydraulic conductivity and water distribution. Previous observation is also supported by the large silt fraction (grain size <0.006 mm) in sand (20.5%), which can cause clogging conditions.

The batch experiments showed a very high P sorption capacity for oil shale fly ash, crushed ash block and oil shale ash plateau sediment (on average 98.9%, 96.5% and 98.4% respectively at initial concentrations from 5–1000 mg PO_4^{3-} L^{-1}). No saturation trend was noticed. No significant correlation between average grain size and uniformity (sorting coefficient), whereas local filter media classified as gravels sorbed P better than local sands. The high Ca, Mg, Al and Fe content clearly guarantee better sorption in the case of these gravels. The high content of Ca, Mg, Al and Fe clearly supported better sorption for these gravels.

The decrease in P removal after the satisfactory retention during the first four months in the Kodijärve ash unit was probably caused by the undersized filter unit. The high water table in the ash unit could not be dropped down because of technical problems in design. Hence the upper water layer did not have direct contact with the material at the bottom. Increased flow rates and hence too short retention time was not sufficient for efficient removal processes (P removal 10–20%). Longer contact time and effective distribution between the ash and water promotes the dissolution of Ca^{2+} and high pH, and thus precipitation processes with phosphates (also in Paper III, *Kaasik et al., 2008*). Decreased P retention after the freezing of ash material is a sign that in future the ash filters should be kept isolated in the cold season. The possible influence of biofilm development on filter particles during the warm season could also lead to earlier saturation, by clogging the active surface and pores. It has been proven that high pH also inhibits bacterial activity. Hence optimal retention time, which will enhance pH, is one of the design criteria for an oil shale ash filter.

The results of the complex mineralogical and laboratory sorption kinetic research indicate that the capability of hydrated oil-shale ash sediment to remove phosphorus is relatively good, up to 65 mg P g–1, and effectiveness at different loadings is in the range of 67–85%. The high phosphorus-binding potential of hydrated oil shale ash is considered to be due to the high ratio of reactive calcium minerals, of which portlandite Ca(OH)2 and ettringite Ca6Al2(SO4)3(OH)12 26H2O are the most important. Dissolution of ettringite and portlandite, and precipitation of Ca-carbonates and Ca-phosphate phases was confirmed by XRD and SEM (SEM-EDS) studies.

Experiments with oil-shale ash sediment were continued in order to achieve optimal hydraulic conditions and thus sufficient purification efficiency of material. The pilot study (supported by Enterprise Estonia) with sufficient residence time and effective design showed very high phosphorus removal >85% during the 1-year study.

Average P accumulation in ash sediment filters (on the assumption that ash density is 900 kg m^{-3}), was 40 mg P kg^{-1}, and total phosphorus removal capacity in the horizontal ash filters (hydraulic loading 50 L m^{-3} d^{-1}) at long-term was higher than 85% and in vertical flow filters (at loading 80 L m^{-3} d^{-1}) higher than 50%.

Variations in chemical and mineralogical composition after the study period supported the findings for removal mechanism analysed in earlier laboratory experiments. After the wastewater treatment experiment, ettringite content in materials decreased, and at the same time the amount of calcite increased. The said process refers to the precipitation of calcium released from the ettringite dissolution, resulting in the formulation of sparingly soluble Ca-phosphate and phosphorus removal from wastewater.

The results of the pilot study permit one to claim that in HF ash sediment filters at water loading <50 L m^{-3} and in average inflow concentrations <10 mg L^{-1}, purification efficiency >70% during at least a one year period is guaranteed. That statue/limit is basing on leachate filters treatment study with more contaminated and complex composition in inflow water. Hence obtained outflow values can be improved by efficient pre-treatment of water. The effective design, peat filters after the ash sediment filters (*Kõiv et al., 2008*), is recommended to decrease the high pH (10–12) to correspond the permitted discharge values (pH 9.0).

Regardless to the extraordinary good P removal in pilot filters, a study in full-scale filter system should be carried through, before the ash sediment recommendation for the extensive use in reactive filters extrapolating outflow P in constructed wetlands or conventional wastewater treatment plants.

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SUMMARY IN ESTONIAN

Fosfori sidumine pinnasfiltersüsteemides erinevate filtermaterjalide abil

Pinnasfilter- ja tehismärgalasüsteeme on rakendatud väga erinevate reovete (tööstus-, kaevandus-, olme- ja põllumajanduse reovete, prügila nõrgvee ning sadevee) puhastamiseks. Pinnasfilter- ja tehismärgalasüsteemid taluvad võrreldes enamike teiste reoveepuhastussüsteemidega paremini hüdrauliliste ja ka reostuskoormuste kõikumisi. Nad on lihtsad ning kergesti hooldatavad. Selliste süsteemide kasutamine on eriti sobilik objektide juures (turismi- ja suvituspiirkonnad, individuaalmajapidamised, tööstus), kus reovee vooluhulga kõikumised on suured. Samuti sobivad pinnasfiltersüsteemid konventsionaalsetest süsteemidest väljuva reovee järelpuhastuseks. Pinnaspuhastite optimaalne reostuskoormus jääb vahemikku 50–500 ie, kuid filtersüsteeme võib rajada ka koormustele 2000 ie.

Fosfori eemaldamine pinnasfiltrites on rangelt seotud kasutatava filterpinnase keemiliste ja füüsikaliste omadustega, kuna fosfor materjalis peamiselt sorbeeritakse või sadestatakse (*Faulkner and Richardson, 1989; Kadlec and Knight, 1996; Vymazal et al., 2000*).

Seetõttu on fosfori eemaldamine keeruline protsess ning selle efektiivsus ja kestvus määravad filtri tööea pikkuse (*Grüneberg and Kern, 2000*). Sorptsioon ja sadestamine materjalis on lõplik protsess ning ajapikku materjal küllastub fosforiga. Seetõttu soovitatakse rajada eraldi asetsev fosforifilter, mille materjali saaks küllastumise korral välja vahetada. Kasutades kohalikke looduslikke materjale nagu liiv ja kruus võib fosfori sidumine langeda ja filter küllastuda juba peale paariaastast töötamist, mistõttu kõrge ning stabiilse fosfori sidumisvõimega materjali valik on oluline.

Antud töö keskendub pikaajalise fosfori sidumise dünaamika uurimisele Kodijärve taimestik-liivafiltris ning potentsiaalsete kohalikult kättesaadavate filtermaterjalide väljaselgitamisele.

Aasta keskmine fosfori sidumise efektiivsus Kodijärve horisontaalses heitveepuhastus-liivafiltris ulatus ajavahemikul 1997–2002 63–95%-ni. Suurenevad fosforikontsentratsioonid filtri väljavoolus (R^2=0.77) ning vähenev aastane fosfori sidumismäär (74.5 kuni 24.7 g m^{-2} a^{-1}) peegeldavad tõenäolisi küllastumisprotsesse süsteemis.

Fosfori (P) mullaandmetele põhinevat akumuleerumise dünaamikat Kodijärve horisontaalvoolulises heitveepuhastus-tehismärgalas analüüsiti põhjalikult kogu tööperioodi jooksul (1997–2004). Kumuleeruv fosforisisaldus filterpinnases (jäme liiv) 8 aasta pikkuse perioodi jooksul suurenes (R^2=0.9). Enamus seotud fosforist oli akumuleerunud filtri sissevoolu tsooni. Väljavoolu suunas fosfori akumulatsioon kahanes. Fosfori aastase akumuleerumise varieeruv bilanss on tõenäoliselt oluliselt mõjutatud fosfori desorptsioonist anaeroobsetel tingimustel. Keskmine redokspotentsiaal Kodijärve vasakus filterpeenras ulatus −22±11 mV-ni ning paremas 40±24 mV-ni.

Paremad õhustamistingimused liivafiltris suurendavad tõenäoliselt fosfori ärastamisvõimet ning akumuleerimist ning takistavad raua redutseerumist ja sellega kaasnevat fosfori desorptsiooni. Samuti on filtri tööea pikendamise üheks võimaluseks eraldiasetsev filter efektiivse materjaliga, mis garanteerib kõrge ja stabiilse fosfori ärastamisvõime ning ei ole rauarikas. Maksimaalse sidumisefektiivsuse tagab pinnasfiltris ühtlane veejaotus, mis omakorda on mõjutatud kasutatud filtermaterjali lõimisest. Mitmed kõrgema fosfori kontsentratsiooniga alad ehk nn „saared" liivas viitavad filtris tekkinud veekanalitele ja seega ebaühtlasele veejaotusele. Kodijärve filtris kasutatud liivamaterjali suur peenosise (terasuurus <0.006 mm) sisaldus (20.5%), tõenäoliselt põhjustas nii ebaühtlast veejaotust pinnases kui ka osalist filtri ummistumist.

Erinevate materjalidega läbi viidud fosfori sidumiskatsetel osutusid kõige efektiivsemateks põlevkivi lendtuhk, purustatud tuhaplokk ja hüdratiseerunud tuhasete, sidudes keskmiselt vastavalt 98.9%, 96.5% ja 98.4% vees sisalduvast fosforist (algne kontsentratsioon ulatus näiduni 5–1000 mg PO_4^{3-} L^{-1}). Küllastumistrendi ei näidanud materjalid ka väga kõrgete kontsentratsioonidega sooritatud sidumiskatsetel (700 ja 1000 mg PO_4^{3-} L^{-1}).

Lõimiseanalüüsi tulemuste põhjal leitud keskmise terasuuruse, ühetaolisuse (ühetaolisus koefitsient; d_{60}/d_{10}) ja fosfori ärastusvõime vahelist korreleeruvat seost analüüsi käigus ei tuvastatud. Küll aga demonstreerisid kõrgemat sidumisvõimet looduslikud pinnasmaterjalid, mis klassifitseerusid kruusadeks. Kruusade kõrgem ärastusvõime oli tõenäoliselt seotud ka nende kõrgema Ca, Mg, Al ja Fe sisaldusega. Kõige sobivamaks materjaliks pinnasfiltrites kasutamiseks osutusid ühetaolisuse koefitsiendi alusel Kopa jäme liiv, Rootsi liiv, glaukoniit-liivakivi ja Kodjärve liiv (d_{60}/d_{10}=2,6; 2,6; 2,1 and 1,5).

Eesmärgiga uurida materjali vastupidavust ning sidumispotentsiaali reaalses reoveesüsteemis, rajati Kodijärve pinnasfiltri väljavoolule katseline filterkeha, mis sisaldas laborikatsete põhjal ühte efektiivseimat materjali, hüdratiseerunud põlevkivituhka. Esimestel kuudel demonstreeris katseline tuhafilter rahuldavat sidumisvõimet, mis aga edaspidi üsna kiiresti langes. Selle peamine põhjus oli ilmselt ala-dimensioneeritud filter, kuna tehnilistel põhjustel ei olnud võimalik veetaset küllaldasele tasemele reguleerida. Pealmine veekiht voolas materjalist üle, ning selle kihi kontaktaeg jäi ärastusprotsesside toimimiseks liiga lühikeseks. Keskmine ärastuseffektiivsus filtris peale esimest nelja kuud ulatus vaid 10–20%-ni. Pikem viibeaeg ja efektiivne veejaotus tuhafiltris, tagab Ca^{2+} lahustumise materjalist, ning fosfaatide sadenemisprotsessi (lähemalt vt Kaasik et al., 2008). Ärastusvõime langus peale filtri suureosalist külmumist osutab filtri isoleerimise vajalikkusele külmal perioodil. Filtri töövõime langusele võis kaasa aidata ka biokile moodustumine materjali osakestele soojal perioodil, takistades sellega lahustumis- ja sadenemisprotsesse tuhamaterjali aktiivsetes poorides ning pinnal. Kõrgel pH väärtusel on bioloogiline aktiivsus pärsitud ning fosfori sidumisprotsess ei ole häiritud. Seega tõstab optimaalne viibeaeg filtris pH-d ja soodustab ärastusprotsesse tuhamaterjalis, olles üheks kriteeriumiks filtri projekteerimisel.

Laboratoorsed komplekskatsed hüdratiseerunud põlevkivituha mineraloogiliste omaduste ning sorptsiooni kineetika välja selgitamiseks kinnitasid eelnevaid tuhasette sidumisefektiivsusega seotud laboritulemusi (ärastus erinevatel P koormustel 67–85% ja sidumisvõime kuni 65 mg P g–1). Hüdratiseerunud põlevkivituhasette fosfori sidumispotentsiaal on kõrge arvatavasti tänu reaktiivsetele kaltsiumi mineraalidele, millest tähtsaimad on portlandiit Ca(OH)2 ja ettringiit Ca6Al2(SO4)3(OH)12 26H2O. Portlandiidi ja ettringiidi lahustumist ja Ca-karbonaatide ning Ca-fosfaatide sadenemist kinnitati ka röntgen-difraktomeetriliste (XRD) ja elektronmikroskoobi (SEM) uuringutega.

Optimaalsete hüdrauliliste tingimuste ning küllaldase ärastusvõime saavutamiseks hüdratiseerunud tuhasettefiltris jätkati katseid kohapealsetes spetsiaalselt disainitud filtrites Tapa olmereoveepuhasti ja Väätsa prügila nõrgveepuhasti väljavoolu veega. Katse tulemused demostreerisid üle 85%-list fosforis sidumist aastase perioodi jooksul. Keskmine P akumuleerumine tuha filtris ulatus 40 mg P kg^{-1}. Üldfosfori ärastusefektiivsus ulatus horisontaalvoolulises tuhasette filtris (hüdraulilisel koormusel 50 L m^{-3} d^{-1}) pikaajaliselt üle 85% ning vertikaalvoolulises filtris (koormusel 80 L m^{-3} d^{-1}) üle 50%.

Tuhasette keemilise ja minaraloogilise koostise muutused viisid filterkatsete lõppedes ettringiidi, mis on peamine Ca-ioonide allikas, lahustumiseni. Kohapealsete filterkatsete põhjal võib kinnitada, et hüdratiseerunud põlevkivituhasete seob üle 70% vees sisalduvast fosforist hüdraulilisel koormusel <50 L m^{-3} ja sissevoolu kontsentratsioonil < 10 mg PO_4^{3-} L^{-1} vähemalt aastase perioodi jooksul. Tuhafiltrite tegelik sidumisefektiivsus võib olla isegi kõrgem, kuna eespool toodud tulemused baseeruvad fosfori ärastuskatsetele nõrgveest, mis oli võrreldes tavalise olmereoveepuhastist väljuva veega saastunum ning keerukama koostisega. Sarnaselt teiste Ca-rikaste filtermaterjalidega tõstavad ka tuhafiltrid väljavoolu pH väärtust. Ühe võimalusena tagada kõrge pH väärtuse (10–12) alandamine lubatud väärtuseni (pH 9,0) tuhasette filtrite väljavoolus on järjestikune tuha ja turbafiltrite kasutamine (*Kõiv et al., 2008*).

Tulemuste põhjal võib hüdratiseerunud tuhasetet pidada efektiivseks materjaliks fosfori sekundaarseks ärastamiseks nii heitveepuhastus-tehismärgalasüsteemides kui ka konventsionaalsete puhastites. Vaatamata erakordselt heale fosfori ärastamisele tuhasette filtrite pilootseadmetes, tuleks katseid jätkata kindlasti ka täismahulises filtersüsteemis.

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III

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