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Active filtration of phosphorus in Ca-rich hydrated oil shale ash filters: effect of hydraulic retention time and pollutants loading rate

Master's Thesis

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Abstract

Elevated phosphorus concentration is the main cause of surface water pollution and related problems, e.g. eutrophication of water bodies. Phosphorus concentration of only 10 μg per litre is already considerably effecting the aquatic environment. To address this problem new water quality regulations are determined for all European Union countries (Council of the European Communities, 2000). According to the regulations all contaminated water has to be treated before releasing it into water bodies.

Phosphorus removal from wastewater at large population or industrial sites can be solved in large-scale wastewater treatment facilities that usually apply coagulation with Al^- and Fe^- salts. For technical and economic reasons, nevertheless, these systems are not applicable at a smaller scale as in single houses and small enterprises or settlements in rural areas. For small-scale wastewater treatment, the treatment wetlands (TWs) can be used (Kadlec and Wallace, 2009); however, their P removal capacity is usually problematic. P removal in TWs is associated with the physical–chemical and hydrological properties of the filter material (Kadlec and Wallace, 2009). Many different natural materials, industrial by-products and man-made filter materials have been studied (Vohla et al., 2011). Highest P removal efficiency has been shown trough Ca-phosphate precipitation (i.e. active filtration) in Ca-rich alkaline filter materials (Vohla et al., 2011). The main reactive filter material that has been studied in Estonia is industrial by-product of oil shale industry – hydrated ash.

Current thesis is demonstrating the results of most recent research that has been done with hydrated oil shale ash. This work is part of research project "Sustainable technologies for phosphorus reduction in constructed wetlands: removal processes and long-term performance of hydrated oil-shale ash filters".

The aim of this thesis is to study the phosphates removal efficiency from municipal wastewater with hydrated oil shale ash in full-scale horizontal subsurface flow filters during first six months of experimentation. The on-going experiment imitates the size and wastewater production of one family household.

Our main objectives are: a) to monitor the impact of high organic, nutrients and solids loading rate on the removal of phosphorus in hydrated ash; b) to evaluate the effect of stable and highly variable hydraulic loading regime on the efficiency of hydrated ash filters; c) and to observe the spread of pollution inside the hydrated ash filters.

1. Theoretical background

According to European Union (EU) Water Frame Directive all the EU members are bound to achieve „good status" for all water bodies by 2015. „Good status" means both „good ecological status" and „good chemical status" (Council of the European Communities, 2000). This means that all countries have to treat contaminated water before releasing it into receiving water bodies. The degree of treatment required in the systems is determined by regulations, which may contain standards for suspended solids (SS), biochemical oxygen demand (BOD), nitrification and total phosphorus (TP), among others. Most wastewater treatment systems are able to fulfil the requirements for SS and BOD removal, and nitrification can also frequently be obtained. However, it is problematic to remove phosphorus (P) in on-site systems (Brix et al., 2001). In conventional biological treatment plants phosphorus is mainly efficiently removed with the help of coagulants (mostly Al^- and Fe^- sulphates). However, this method is not visible for small-scale conventional treatment plants and treatment wetland systems because of the high cost, and need of constant manpower and maintenance.

Nitrogen and phosphorus are the main cause of ecological water pollution problems. For 40 years, elevated phosphorus and nitrogen have been recognized as the main nutrients responsible for eutrophication of surface water (e.g. lakes and rivers; Edmondson, 1970, Schindler, 1977; Sharpley, 1994). Therefore phosphorus has to be removed from the wastewater to maintain the ecological balance of natural systems.

According to the Estonian regulations, wastewater treatment has to reduce nitrogen and phosphorus in all settlements with over 300 human equivalents (PE). Therefore there is an urgent need to find efficient and at the same time economically reasonable solutions also for smaller settlements and wastewater producers.

In order to prevent the entrance of P into receiving water bodies, recent studies have focused on alternative P-removal technologies that are economically achievable (Brooks et al., 2000). As an ecological engineering alternative to conventional and chemical based wastewater treatment methods, the use of subsurface flow (SSF) treatment wetlands (TW-s) in the removal of P, has been reported in many studies over the last three decades (Mitsch and Jorgensen, 1989; Kadlec and Knight, 1996; Pant et al., 2001; Korkusuz et al., 2005).

1.1. Treatment wetlands and phosphorus removal

According to the newest wetland terminology by Fonder and Headley (2013) the treatment wetlands (TWs) are artificially created wetland systems designed to enhance and optimise certain physical and/or biogeochemical processes that occur in natural wetland ecosystems for the primary purpose of removing contaminants from polluted waters. In TWs special vegetation, substrates and microbial communities are used to gain the best performance. Treatment wetlands can be implemented as two different technological systems according to the water hydrology: the surface flow (SF) and subsurface-flow (SSF) treatment wetlands– in last ones the flow direction can be horizontal or vertical. In SSF system, the water is maintained below the surface of the wetland body, usually made up of gravel or some other substrate, and planted with the emergent macrophytes. For more complex and efficient treatment the different TW types are used as hybrid systems (i.e. different wetland types are combined and co-used; Vymazal et al., 2010).

TWs are becoming increasingly popular for wastewater treatment because of their lower cost, multi-functionality and low maintenance requirements combined with a good performance (Kadlec & Knight, 1996, Noorvee et al., 2007). Treatment wetlands operation and maintenance costs are much lower compared to conventional treatment systems (Vymazal et al., 2010). Subsurface flow treatment wetlands (SSF TWs) have been efficiently used for purification of municipal wastewater, industrial wastewater (paper industry, food production etc.), agricultural wastewater, mining water and storm-water and even for landfill leachate (Maehlum, 1995, Noorvee et al., 2007, Westholm, 2010).

In Estonia, subsurface flow treatment wetlands have mainly been used for the purification of domestic wastewater, but also for after-treatment of the effluents of conventional treatment plants. Until today about 32 TW systems have been installed in Estonia (however some of them are already out of usage).

TW systems are tolerant to changing hydraulic and nutrient loadings because of their great buffering volume and less sensitive purification processes. This makes them more suitable than conventional treatment plants in cases of variable wastewater flow rates and pollution loads, e.g. for the treatment of wastewater from tourist resorts, individual households, industries, and for treatment of storm-water. The only limiting factor is that TWs requires a greater area, and therefore are more suitable in sparsely populated areas, for small settlements and rural areas where the optimum loading rates are between 50 and 500 PE. They can be also suitable for the after-treatment of effluent of the conventional treatment plants.

SSF TWs are efficient in the removal of both organic matter and solids, however, nitrogen (N) and phosphorus (P) removal is known to be somewhat problematic (Brix et al., 2001, Vymazal et al., 1998). Though, good nitrogen removal is usually achieved with right usage of aerobic and an-aerobic treatment processes. Whereas P is mainly removed from water in filter media trough sorption and/or precipitation. Therefore, phosphorus removal in subsurface flow TWs is closely connected with the physical–chemical and hydrological properties of the filter material (Vymazal et al., 2000).

1.2. Phosphorus removal with reactive filter materials

Reactive filter materials for phosphorus (P) sorption have been greatly studied in past two decades. They are available for both phosphorus and ammonium sorption, even though phosphorus sorbents have attracted the most attention for their usage in smaller wastewater treatment systems (Brix et al., 2001).

The efficient P removal from wastewater is complicated process. Active filtration in Ca-rich materials relies on chemical reactions. The effectiveness of P removal depends on the activity of Ca ions, ionic strength of the solution and the forms and activity of the phosphates. Calcium phosphate precipitation is happening when pH is over 7 (Noorvee et al. 2007).

In sub-surface flow CWs, the major removal mechanisms of phosphates are adsorption and precipitation (Zhu et al, 1997; Vymazal, 2001). During adsorption the phosphates attach to charged surfaces of filter materials (namely on iron and aluminium oxides). Precipitation means that negatively charged ortho-phosphates are bonds with positively charged ions (namely calcium, iron, or aluminium) provided by the filter media, forming insoluble compounds (Noorvee et al., 2007). The sorption and precipitation of phosphorus are controlled by the properties of the filter material (e.g. content of Fe-, Al-, Ca-minerals, porosity), the hydraulic parameters (loading rate, porosity of and retention time in material) and the physicochemical environment (pH, electrical conductivity, content of dissolved ions; Faulkner and Richardson, 1989; Kadlec and Knight, 1996; Zhu et al, 1997; Vymazal et al., 2000). Good results in phosphates removal have been achieved with Ca-rich reactive filter materials, e.g. metallurgical slags and ashes (Shilton et al., 2005; Kaasik et al., 2008).

Various tested filter materials are not comparable with each other 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).

Another problem is that filter media might become saturated after few years. An obvious and sustainable solution would also be a separate filter unit containing replaceable material with a high P binding capacity (Brix et al., 2001). In such systems, appropriate pre-treatment will also allow for a longer lifetime of the filter media, by decreasing the risk of clogging (Platzer & Mauch, 1997) and permitting the use of finer reactive filter media with higher sorption capacity (Hedström, 2006). Phosphorus sorption sites may be also blocked by organic matter or the sorption may be reduced by competitive sorption of organic anions or metal complexation (Nilsson, 1990; Bird and Drizo, 2010; Nilsson et al., 2013).

Earlier studies (e.g. Chen et al. 2002, Adam et al. 2007) have shown that P removal is inhibited in the presence of competitive anions such as Cl^-, SO_4^{2-}, CO_3^{2-} and also organic compounds whereas wide super-saturation of pore-water with respect to Ca and phosphate is required for the precipitation of stable Ca-phosphate phases (Arias et al., 2003; House, 1999; Liira et al., 2009).

There is a large amount of literature showing high efficiency of phosphorus removal with different materials. Those studies are mostly made in laboratory with synthetically made solutions not containing any organic matters. Limited studies with real wastewater effluents show that the organic matter and solids concentrations in wastewater can dramatically shorten the lifetime of filters. For example, Bird and Drizo (2010) have reported that P removal efficiency and filter life were significantly higher in steel slag filters fed with agricultural effluent with lower organic matter content than domestic sewage. Nilsson et al. (2013) has made a dynamic column experiment using on-site wastewater under real-life treatment conditions and the results showed that the Polonite material P removal increased with lower BOD concentration. It is important to further examine the impact of organic matter and other pollutants on the phosphorus removal efficiency of such materials with the aim of optimising the use of reactive filter materials in wastewater treatment.

1.3. Investigated reactive filter materials

In last decades different filter materials for P removal in TWs have been investigated. Most of research has been made in laboratory but in recent years also full-scale studies have been conducted with real wastewater. The investigated filter materials can be divided into three groups, natural substrates, industrial by-products and industrially produced (i.e. man-made) products.

Most popular naturally-occurring filter materials for P removal are:

- Limestone (Baker et al. 1998; Hill et al. 2000; Comeau et al. 2001; Hylander et al. 2006; Chazarenc et al. 2010).
- Shell and shell sands: natural CO_3-rich material mainly consisting of shells, snails, and coral (Roseth, 2000; Arias and Brix, 2005; Adam et al., 2007).
- Wollastonite: a calcium meta-silicate mineral (Brooks et al., 2000; Hill et al. 2000; Hedström, 2006).
- Opoka: bedrock material from south-eastern Poland rich in Ca, Si, Al and Fe (Johansson and Gustafsson, 2000; Hylander et al., 2006).
- Marble: non-foliated metamorphic rock composed of recrystallized carbonate minerals, most commonly calcite or dolomite (Brix et al., 2001; Gervin & Brix, 2001).
- Zeolite: a hydrated aluminium-silicate mineral with the aluminium and silicon polyhedral linked by the sharing of oxygen atoms (Sakadevan and Bavor 1998; Drizo et al., 1999; Gikas & Tsihrintzis, 2012).
- Peat: organic material, formed in wetlands. (Talbot et al., 1996; Bulc et al. 1997; Kõiv et al., 2009).

By-products of industrial processes have also been investigated for re-use as reactive filters:

- Metallurgical slags: commonly porous by-products of iron and steel production; many types are available. Melter slag: is a co-product of the steel making process that converts iron sand to iron by adding coal and limestone to the iron sand. (Drizo et al., 2006; Shilton et al., 2006; Lee et al., 2010). Electric arc furnace steel slag: is a by-product of the manufacturing of steel by the electric arc furnace process (Drizo et al. 2002; Bird and Drizo 2010; Claveau-Mallet et al., 2013). The slag is formed through the addition of lime, which is designed to remove impurities from within the steel. Blast Furnace Slag: is produced in steel plants derived from slag forming minerals, consists limestone (Sakadevan & Bavor, 1998; Johansson & Gustafsson, 2000; Cameron et al. 2003; Hylander et al., 2006; Korksuz et al. 2005; Korkusuz et al., 2007; He et al. 2007; Lee et al. 2010; Westholm, 2010; Nilsson et al. 2013).

- Fly ash: a by-product of coal or oil shale combustion. Coal fly ash: is produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas (Drizo et al., 1999; Agyeia et al., 2000; Cheug and Venkitachalam, 2000; Agyeia et al., 2002). Hydrated oil shale ash: Kerogenous oil shale used in Estonian thermal power plants leaves large amounts of ash after combustion. The ash remaining after combustion is due to the thermal decomposition (peak temperatures 1500 ◦C) of carbonate minerals and subsequent reactions with flue gases rich in free lime (CaO) and anhydrite (CaSO4). The ash is transported to waste heaps (plateaus) through a pipe system in water slurry at an ash–water ratio of 1:20. (Vohla et al., 2005; Kaasik et al., 2008; Liira et al., 2009; Karabelnik et al., 2012).
- Red mud: iron and aluminium based by-product of alumina production from bauxite (Liu et al., 2011).

There are also some man-made filter materials that have been made with purpose of P removal in TW systems, for example:

- Lightweight clay aggregates (LWA; also called Light Expanded Clay Aggregates or LECA): produced by modifying natural clays to improve phosphate removal capacity through heating clay aggregates through a rotary kiln at 1200°C (Mæhlum, 1995; Johansson, 1997; Brix et al., 2001; Jenssen et al., 2005; Öövel et al., 2007; Jenssen et al., 2010).
- Pollytag: is sintered pulverized fly ash treated with limestone and diatomite (Tsalakanidou, 2006)
- Filtralite P: is expanded clay product especially produced and investigated for P sorption in wastewater treatment and has a high Ca and Mg content (Heistad et al. 2006; Adam et al. 2007).
- Nordkalk Filtra P: expanded granules consisting of lime, iron and gypsum (Renman, 2008; Vilpas et al., 2005 cit. Hedström 2006).
- Polonite: a product manufactured from the cretaceous rock opoka and is intended for use in wastewater treatment. Polonite is manufactured by heating opoka to 900 °C,

causing calcium carbonates to transform into calcium oxides, which are more reactive. (Brogowski & Renman, 2004; Hylander et al. 2006; Renman and Renman, 2010).

1.4. Calcium-rich active filter materials for P sorption

Good removal of P by filtration through reactive media has been demonstrated in recent years especially with calcium-rich “active” filter materials. Several batch- and column-studies have been made, but not as many full-scale studies with real wastewater. Potential materials for the active filtration of P that have been also studied in full-scale with real wastewater are: natural wollastonite, limestone; industrial by-products, such as metallurgical slags (e.g. steel slag and blast furnace slag) and ash, e.g. hydrated oil shale ash; and also man-made products, such as Filtralite®-P.

The natural materials have had different efficiency when used for treatment of real wastewater. For example, P removal with natural limestone has been studied by Hill et al. (2000) and Comeau et al. (2001). Hill et al. (2000) performed a full-scale experiment using wastewater from dairy farm. The experiment lasted 1.5 years and during that time the P retention was on average only 4.3%. Comeau et al. (2001) designed three stage P-retaining TW systems for trout farm using limestone in horizontal flow bed which TP removal efficiency was 78%. Brooks et al. (2000) studied the capacity of wollastonite in vertical up flow columns for treatment of secondary wastewater. With hydraulic residence times varying from 0.6 to 7.5 d in this experiment the removal rate higher than 80% (up to 96%) was achieved when the residence time was >40 h. Hill et al. (2000) tested wollastonite tailings (a by-product of mining activities that produced wollastonite and garnet) that showed mean reduction in P concentrations of only 28%.

Recently, most studied and tested filter materials in full-scale are industrial by-products and specially slags. However, different studies show also very variable efficiency of this material. For example, Cameron et al. (2003) demonstrated that the experimental slag filters reduced TP up to 99% and they reported that the pH value of the effluent rose up to 11.0. Korkusuz et al. (2005) studied the P-removal efficiency of slag from iron and steel company from Turkey during 11 months lasting experiment with vertical subsurface flow reed beds and the average removal of TP was only 45%. On contrary, Lee et al. (2010) achieved almost 100% efficiency with steel slag that was used in experiment with three hybrid and three integrated saturated flow pilot-scale filters. TWs Research group in Sweden (Westholm, 2010) has testes blast furnace slag (BFS) for P removal already for the last decade. However, their field trials with real wastewater have shown only 40-53% P sorption capacity.

Nilsson et al. (2013) compared two materials (BFS and Polonite) and also investigated the effect of organic load on P removal under real-life treatment conditions. At the high BOD concentration (median 120 mg/L), the mean monthly P removal ranged between 47 and 97% in Polonite and-8 and 71% in BFS, with a mean total reduction of 76% in Polonite and only 22% in BFS.

Electric arc furnace (EAF) steel slag is another industrial by-product that has been efficiently used as filter material for P removal in TW-s. Shilton et al. (2006) presents a decade of experience for P removal by active slag filters at a full-scale treatment plant. The average total phosphorus (TP) removal efficiency of their slag was 77% during the 5-year period. Bird and Drizo (2010) have investigated the effects of total suspended solids daily mass loading rates and of alternating feeding and resting periods on EAF steel slag filters in dairy farm in Vermont. This experiment showed average TP removal efficiency of 74%.

Some man-made products have shown also promising results in P removal. For instance, Filtralite P^{TM} that was studied by Heistad et al. (2006) in wastewater treatment system (consisting of aerobic bio-filter and an up-flow saturated filter) for use in single houses for 3 years. The tested system demonstrated excellent total phosphorus removal throughout the experiment (average 99.4% removal).

1.5. Hydrated Oil Shale Ash

In Estonia, hydrated oil-shale ash has been used for P removal in TW-s. Hydrated oil shale ash is a Ca-rich industrial by-product that results from the burning of Kerogenous oil shale used in Estonian thermal power plants.

Hydrated oil shale ash has been studied as a potential filter material for TW-s in Estonia for almost ten years. Current thesis is showing the results of most recent research with hydrated oil shale ash.

1.5.1. Formation 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 (temperatures from 1300 to 1500 °C) of carbonate minerals and subsequent reactions with flue gases rich in free lime (CaO) and anhydrite ($CaSO_4$). The fly and bottom ash is transported to waste heaps through a pipe system in water slurry at an ash–water ratio of 1:20. The lime and anhydrite already begin to react with water in the ash removal system and the hydration processes continue in open plateaus (waste heaps), resulting in different secondary Ca-minerals (hydrated oil shale ash): ettringite [Ca_6 A_{12} $(SO_4)_3$ $(OH)_{12}\cdot 26H_2O$], hydrocalumite [$Ca_2Al(OH)_7\cdot 3H_2O$], portlandite [$Ca(OH)_2$], and Ca-carbonates [$CaCO_3$] (Kaasik et al. 2008).

1.5.2. Composition of oil-shale ash and ash sediment

The mineral composition of fresh ash from power plants is dominated by free lime (CaO), anhydrite ($CaSO_2$), quartz (SiO_2), C_2S belite (β-Ca_2SiO_4), merwinite ($Ca_3Mg(SiO_4)_2$), orthoclase ($KAlSiO_8$), melilite ($(Ca,Na)_2(Al,Mg,Fe)(Si,Al)_2O_7$) and periclase (MgO). The ash also contains minor amounts of calcite ($CaCO_3$) and tricalcium-silicate C_3S, tricalcium-aluminate C_3A and pseudo-wollastonite (CaO-SiO_2). About 20–30% of the ash consists of amorphous glass-like materials of (alumo-) silicate composition (Kuusik et al., 2005), which form after the partial melting and thermal decomposition of silicate minerals (K-feldspar, clay minerals; Table 1).

The chemical composition of the hydrated oil shale ash corresponds to its mineral composition– the major oxides are CaO (on average 29.2%), SiO_2 (on average 25.9%) and Al_2O_3 (on average 6.3%; see Table 1; Kaasik et al., 2008). The trace element (including heavy metal) content in oil-shale ash is typically enriched compared with raw oil shale (e.g. Pets & Haldna, 1995; Saether et al., 2004), yet the heavy metal concentrations (Kaasik et al., 2008) are below the critical limits, and the un-hydrated fly ash has been used for the liming of acidic soils in Estonia and north-western Russia (Pets et al., 1985).

The composition of the ash-plateau sediments can be considerably variable depending on the advancement of digenetic processes, specifically the carbonization of the surface layers of the plateau sediments (Kuusik et al., 2005).

Table 1. Mineral and chemical composition (wt %) of the hydrated oil shale ash (Kaasik et al., 2008; Liira et al., 2009).

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

1.5.3. P-retention mechanism in hydrated ash

The previous mineralogical researches with hydrated oil shale ash have indicated that the high P-binding potential is due to the high ratio of reactive calcium minerals. For example, Kaasik et al. (2008) and Liira et al. (2009) have shown that hydrated oil shale ash contains several potential Ca sources with different solubility. The most efficient Ca release into solution and highest phosphorus removal rate was suggested to occur due to reactions between reactive Ca-(sulphoaluminate)-sulphate-hydroxide phases (ettringite, Ca-aluminate and portlandite), whereas in later stages of the reaction, the existing and/or authigenic calcite and/or vaterite (γ-$CaCO_3$) precipitates controlled P-binding processes.

Molle et al. (2005) have reported that geochemical behaviour of ettringite can be compared to natural Ca-phosphate – apatite. Therefore similarly to apatite ettringite creates suitably high and stable pH of the solution and good kinetics for secondary Ca-phosphate crystallization, by providing a high number of nucleation sites on its needle like crystallites (Kaasik et al., 2008; Liira et al., 2009). Poorly-crystallized or amorphous octa-calcium phosphate (OCP), dicalcium phosphate di-hydrate (DCPD) and tri-calcium phosphate (TCP) form as precursor phases in solutions containing Ca and P, and are only then recrystallized into thermo-dynamically stable hydroxyl-apatite (HAP) over time (Valsami-Jones, 2001). This shows that the P removal in hydrated ash occurs through precipitation of the discrete amorphous Ca-phosphate phases by either homogenous precipitation or heterogeneous nucleation on the suitable crystal surfaces. The P removal efficiency of the ash depends on the availability of the dissolved Ca, whereas the removal efficiency does not depend on the Ca concentration in inflow wastewater and the Ca is significantly removed from effluent during filtration (Kõiv et al., 2010).

1.5.4. The effectiveness of hydrated oil shale ash based on a research so far

In Estonia oil shale fly ash and the sediment from oil shale ash plateau were first studied in the batch experiments (Vohla et al., 2005; Kaasik et al., 2008). These experiments showed the average P removal effectiveness 96.5% (Vohla et al. 2005) and 67–85% (Kaasik et al., 2008) in different experiment. Because of these promising results a further research has been conducted.

Laboratory experiments with hydrated oil shale ash confirmed a good removal efficiency (up to 91% at loading 1.66 $gP \cdot m^{-2} \cdot d^{-1}$) of hydrated ash in the experiment that tested the effect of different hydraulic retention time on treatment efficiency (Liira et al., 2009).

During last decade several on-site medium- and large-scale experiments have been performed to further test the capacity of hydrated ash in treatment of different types of real wastewaters: e.g. municipal wastewater, landfill leachate, grey water. On- site pilot-scale experiment for treatment of grey water was established in 2009 in order to study the treatment capacity of hydrated oil shale ash. In this experiment a median reduction of TP in the hydrated ash filter was 89% and median effluent concentration of 0.55 mg P/L was achieved (Karabelnik et al., 2012). Medium-scale on-site experiment with pre-treated landfill leachate showed 68% removal of P with hydrated ash filters and 88% removal with filters that had mineralized peat and hydrated ash in same filter (Kõiv et al., 2009). Large-scale on-site experiments for after-treatment of landfill leachate (experiment lasted one year) and municipal wastewater (experiment lasted half a year) was conducted with aim to further studied the phosphorus binding capacity of and mechanisms in hydrated oil shale ash (Kõiv et al., 2010). The results of this study showed that for hydrated ash the hydraulically saturated horizontal sub-surface flow design is the best option that ensures a sufficient retention and reaction time inside this filter material. The horizontal flow (HF) filters of both experiments demonstrated efficient P removal (median removal of phosphates 99%) regardless of variable pollutants concentrations and several inhibitors.

1.6. Objectives of the thesis

The aim of this experiment is to study the full capacity and lifetime of hydrated oil shale ash in phosphorus removal from real high-strength wastewater.

The main objective of this dissertation is to:

- study the efficiency of hydrated oil shale ash in pilot-scale horizontal subsurface flow filters designed to reduce phosphorus in municipal wastewater;
- determine the pre-treatment efficiency of septic tank and vertical down-flow filters in organic matter and nitrogen removal;
- evaluate the effect of different hydraulic loading regimes on phosphorus removal capacity of hydrated ash;
- investigate the impact of high organic, nutrient and solid loading rate on the removal of phosphorus in hydrated ash.

2. Materials and Methods

2.1. Site description

We have onsite full-scale experiment with two parallel working sub-surface flow filter systems for treatment of municipal wastewater of Nõo settlement which is located in South-Estonia and the population of Nõo rural municipality is 3972 (Statistics Estonia database). The volume rate of wastewater in Nõo Wastewater Treatment Plant is approximately 500 m^3/d – 300 m^3/d on workdays and 200 m^3/d on weekends. Wastewater comes to the conventional biological activated sludge treatment plant from households in the settlement, school Nõo Gymnasium, butchery "AS Nõo Lihatööstus" and carpet cleaning company "AS Berendsen". Nõo high-strength wastewater is compared with typical municipal wastewater concentrations in Table 2. Also the composition of raw wastewater that is used in our experimental system is shown on the Table 2.

Table 2. Median pollutants content (mg/L) of influent to the experimental system, typical municipal wastewater (Henze et al., 2008) and effluent of Nõo conventional treatment plant, and limit values from Estonian regulations (RT I, 04.12.2012).

Parameters:	**COD**	**BOD_7**	**TSS**	**TN**	**TP**
Unit:	mg/L				
Estonian regulations (<300 PE)	150	40	35	- (60)*	- (2)*
Nõo wastewater (influent of the experiment)	1026	555	260	115	29
Typical municipal wastewater	750	350**	400	60	15
Outflow of Nõo biological treatment plant	150	40	120	12	4

* For treatment plants of 300-1999 PE

** 5 days biochemical oxygen demand (BOD_5)

The experimental system was established in September 2013 and will be working until August of 2015. The study is carried out using mechanically treated (with grid) wastewater from Nõo Wastewater Treatment Plant. We are using in our experimental system about 0.5

m^3/d of wastewater per parallel imitating wastewater production of one family household- approximately 5 human equivalents (PE).

2.2. Experimental design

For having highest efficiency in ortho-phosphates (o-PO_4) precipitation the removal of organic matter, nitrogen and solids has to be always addressed first. Therefore, pre-treatment and primary treatment of wastewater is essential. The purpose of current experiment is to see the full potential of hydrated ash in case of high organic, solids and nutrients loading rate. The roll of pre-treatment and primary treatment in this experiment is to lower the loading rates but not to eliminate them.

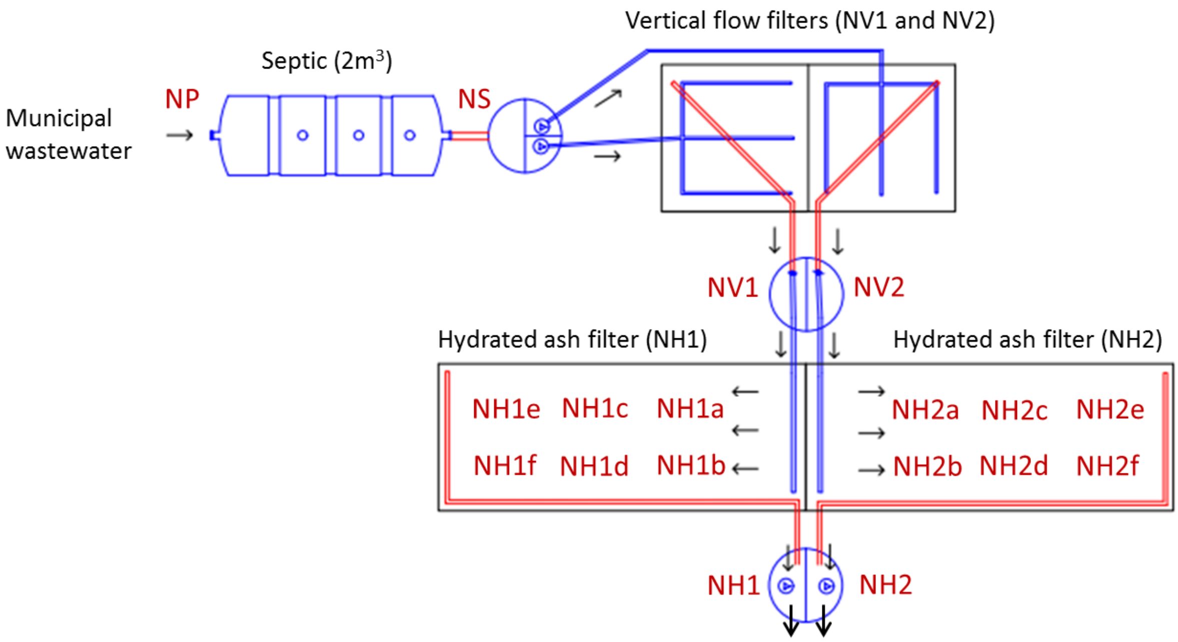

Figure 1. Experimental design of two parallel working systems: NP – wastewater inflow; NS – outflow of septic tank; NV1 and NV2 – outflow of vertical flow filters; NH1 and NH2 – outflow of hydrated ash filters; Letters "a" to "f" indicate sampling points (piezometers) inside ash filters.

As a pre-treatment step septic tank (NS; 2 m^3) is used in our experimental setup. Septic outflow is pumped to two parallel working filter systems (Fig. 1). Both systems consist of vertical subsurface flow filters (NV1 and NV2; volume 3 m^3 each) as primary treatment stage and subsequent horizontal sub-surface flow filters (NH1 and NH2; effective volume 8 m^3 each, Fig. 1) as secondary treatment stage.

2.3. Filter materials

Filter materials used in the system were chosen according the purpose of the filter. Vertical down-flow filters are filled with light-weight expanded clay aggregates (LECA). LECA is porous and has large specific surface area for adsorption of different pollutants and for growth of bio-film. VFs are expected to have good hydraulic conductivity and aerobic conditions. For achieving that the VFs are filled as follows: top 20 cm with 2-4 mm aggregates, middle 20 cm with 4-10 mm aggregates and bottom 25 cm with 10-20 mm to ensure good drainage. For better distribution the 10-20 mm LECA is used underneath the ¾ inch distribution pipes (that are covered with half-pipe with 110 mm diameter).

The filter material for the HF filters was mainly chosen on the basis of having good phosphates precipitation capacity. Therefore, crushed and sieved Ca-rich hydrated oil shale ash (fraction 4-16 mm, main properties described in Paragraph 1.5) is used in both HF filters.

2.4. Loading rates of the experiment

The parallel filter systems (NV1+NH1 and NV2+NH2) have the same organic and hydraulic loading rate of 3.83 m^3 of wastewater per week (Table 3). However, the NV1+NH1 system has stable hydraulic loading regime (periodical pumping of 0.55 m^3/d in every 40 minute) and therefore stable hydraulic retention time in the filter system. NV2+NH2 has variable loading regime (unstable hydraulic retention time) that imitates the wastewater production of average household - 5 days a week 0.4 m^3/d and 2 days 0.9 m^3/d. With applied mode the imitated loading rate to this system is more intense during the mornings and nights and also weekends, when family is usually at home. To mimic the situation and to see the effect of vacation period (i.e. no wastewater production for longer time) we gave the second system NV2+NH2 a one month resting period from 19th of December until 20th of January. To test the high hydraulic loading situation and to see the effect of extremely short retention time on our hydrated ash filters we have plan to apply higher hydraulic loading on the second system (NV2+NH2) during summer 2014.

Table 3. Design parameters of experimental system: NV1 and NV2 –vertical flow filters; NH1 and NH2 – hydrated ash filters.

Filter	Period	Hydraulic loadings				Filter surface area	Filter volume	Void volume	Retention time
		m^3/week	m^3/d	m^3/m^2/d	mm/d	m^2	m^3	m^3	days
NV1	Mon-Sun	3.83	0.55	0.14	137.5	4.0	2.8	-	-
NV2	Mon-Fri		0.40	0.10	100.0	4.0	2.8	-	-
	Sat-Sun		0.90	0.23	225.0	4.0	2.8	-	-
NH1	Mon-Sun		0.55	0.06	55.0	10.0	8.0	3.8	6.0
NH2	Mon-Fri		0.40	0.04	40.0	10.0	8.0	3.8	8.1
	Sat-Sun		0.90	0.09	90.0	10.0	8.0	3.8	3.6

2.5. Sampling

Water samples are taken as grab samples once every month's from the municipal wastewater (NP), septic tank effluent (NS), the outlet of the vertical flow filters (NV1; NV2) and outlet water from horizontal flow hydrated oil shale ash filters (NH1; NH2).

From both horizontal flow filter 6 water samples (NH1a; NH1b, NH1c; NH1d; NH1e; NH1f and NH2a; NH2b; NH2c; NH2d; NH2e; NH2f) were also taken from perforated sampling pipes (piezo-meters) inside the filter to see the distribution of pollution inside the filters and predict possible clogging.

Periodical sampling of hydrated ash from special sampling pipes (6 per filter), that are placed inside the horizontal flow filters, is also conducted parallel to the water sampling, however, these results are not analysed and discussed in this thesis.

2.6. Analytical methods

The water samples from the inflow and outflow of all filters of the pilot systems were taken once a month during the period from September 2013 – March 2014.

In the experiment biological oxygen demand (BOD_7), chemical oxygen demand (COD) value, total nitrogen (TN), total phosphorus (TP) and total iron concentration was analysed in accredited laboratories Ltd. Tartu Veevärk and Estonian Environmental Research Centre. In the laboratories of University of Tartu ammonium-nitrogen (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), SO_4^{2-}, Ca^{2+}, Mg^{2+}, Li^+, K^+, Cl^-, F^-, BrO^{3-} concentrations (unit mg/L, with ion chromatograph IC1000) where measured. Concentrations of dissolved and total o-PO_4^{3-} were determined using spectrophotometer (mg/L). Total suspended solids (TSS), volatile suspended solids (VSS mg/L) and alkalinity (mg $CaCO_3$/L) were determined by author of this thesis. Also conductivity (μS/m), pH value and temperature (C°) were determined using portative devices. Results that are presented and discussed in current work were analysed using Microsoft Office Excel.

3. Results

3.1. System effectiveness

In this paragraph the pollutants removal efficiency and changes in the content of different contaminants in two parallel working filter systems is presented.

3.1.1. Pre-treatment and primary treatment

Reduction of organic matter and solids

The results show that during six-month period the inflow of organic matter content was really high when compared with typical municipal wastewater. For example the median inflow chemical oxygen demand (COD) and biological oxygen demand (BOD_7) have been 1026 mg O_2/L and 600 mg O_2/L respectively. The same goes with the total suspended solids (TSS) which inflow concentration was 260 mg/L. The COD, BOD_7, TSS and VSS content variability in time are also shown on Figure 2. During pre-treatment in 2 m^3 septic tank the COD, BOD, TSS and VSS value decreased by 10.0%, 6.0%, 32.9%, 34.5%, respectively.

The purpose of vertical flow (VF) filters in our system is to lower the organic matter and solids loadings to horizontal flow hydrated ash filters but not to eliminate them. However, the results show that the effectiveness of under-dimensioned VFs has been relatively good in terms of organic matter and solids. The removal efficiency of COD in VFs was 60% in NV1 and 38% in NV2, and removal efficiency of BOD_7 was 69% in NV1 and 42% in NV2. The reduction of suspended solids concentration was somewhat lower – TSS was removed by 45% in NV1 and 36% in NV2. The removal efficiency of volatile suspended solids (VSS) in vertical flow filters was 5% NV1 and 30% NV2. We can see, that the NV1 with more stable loading mode had on average considerably higher efficiency, especially in case of organic solids (expressed as VSS; Figure 2).

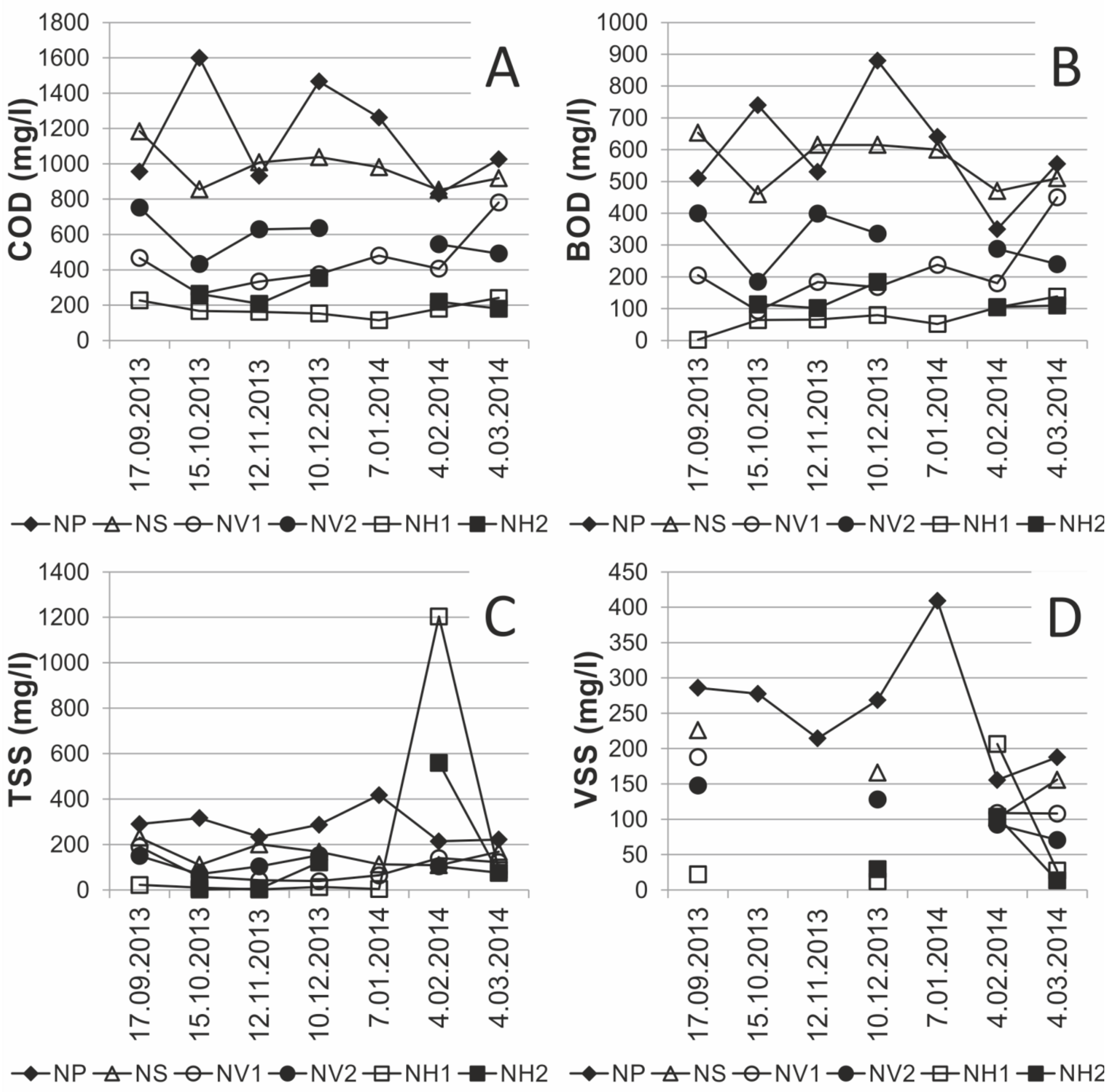

Figure 2. Removal of COD, BOD_7, TSS and VSS in Nõo experiment. The explanation of filters (NP, NS, NV1, NV2, NH1, and NH2) is described in the Materials and Methods. Second system (NV2+NH2) was resting for a month from 19th of December 2013 until 20th of January 2014.

Removal of nitrogen

In the effluent from the septic tank, most of the nitrogen was in the form of ammonia-nitrogen (NH_4-N) and the median concentration was 54 mg/L. Total nitrogen (TN) concentration from NS was 104 mg/L. The reduction of TN in vertical flow filters was rather low – 23% in NV1 and only 15% in NV2. The changes in concentrations of different forms of nitrogen in time are shown on Figure 3.

The results don’t show promising nitrification. It is probably caused by the fact that our vertical filters are under-dimensioned and the microbiological processes don’t have enough oxygen.

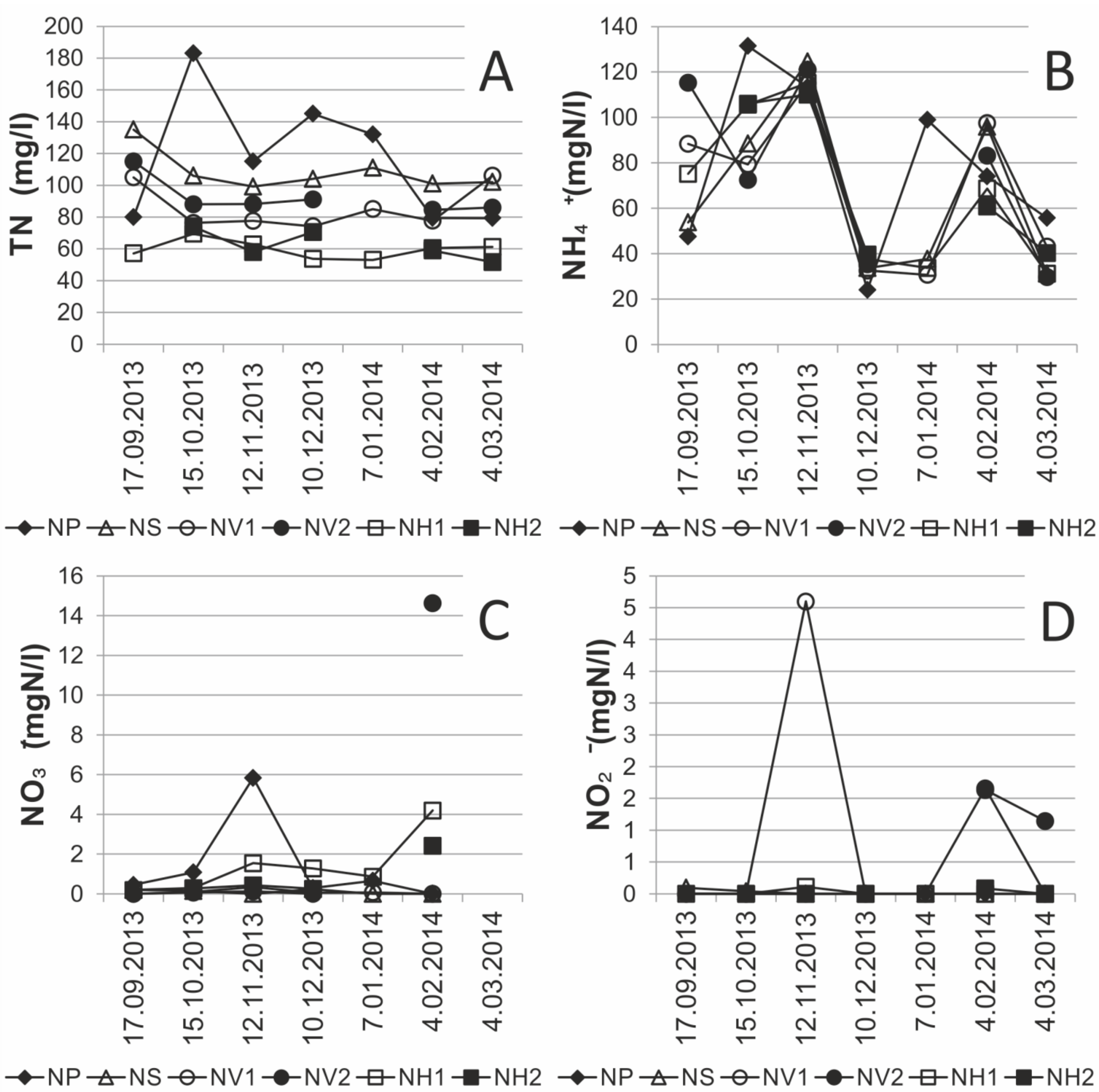

Figure 3. Changes in the content of different forms of nitrogen (TN, NH_4, NO_3, NO_2) in Nõo experiment. The explanation of filters (NP, NS, NV1, NV2, NH1, and NH2) is described in the Materials and Methods. Second system (NV2+NH2) was resting for a month from 19th of December until 20th of January 2014.

Changes in pH, alkalinity, temperature, conductivity, Ca and Mg

The median pH value of septic effluent (NS) was 7.9. The median outflow pH value in vertical flow filters filled with LECA was 7.36 in NV1 and 7.53 in NV2 (Fig. 4A). This shows that the properties of filter material (LECA) have no effect and the pH values stay neutral. The pH value also stays relatively the same during the 7 months period.

The alkalinity which describes the dissolution of of $CaCO_3$ in wastewater was low in the VF filters (Fig. 4B). The median alkalinity in NS effluent was 1405 (mg $CaCO_3$/L) and didn't change much in VF filters – (1403 mg $CaCO_3$/L in NV1 and 1451 mg $CaCO_3$/L in NV2). LECA material used in VF filters has no considerable impact on the alkalinity of the wastewater.

The median inflow concentration of calcium (Ca^{2+}) ions has been 59.8 mg/L and didn't change considerably in VF-s (Fig. 4C).

Temperature has been higher in the early autumn months (18°C in September) and lowering in the winter months (Fig. 4E). Also the conductivity has been higher in the autumn and lower in the winter (Fig. 4F). The Figure 4F shows that vertical flow filters have been low on conductivity and no changes occur monthly.

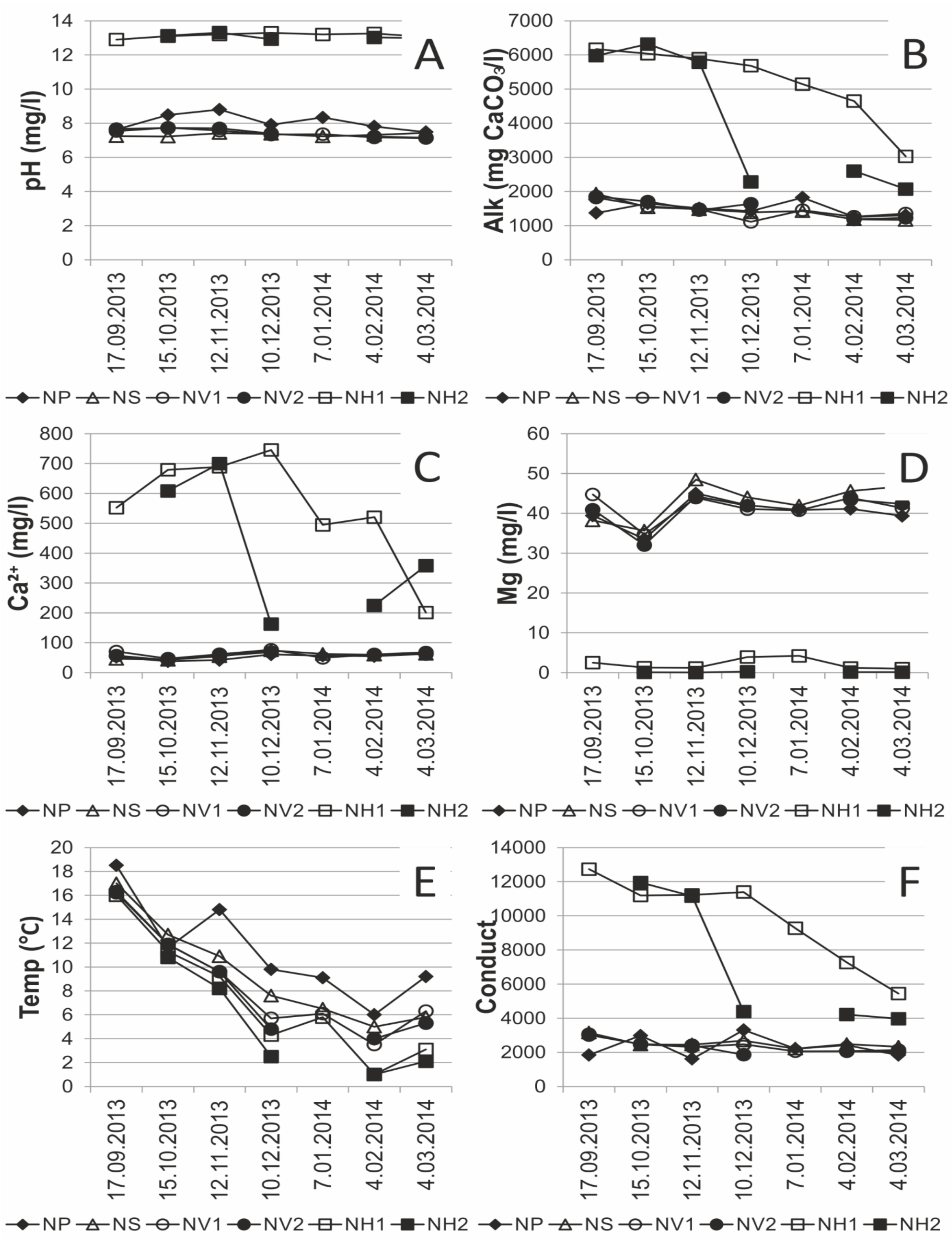

Figure 4. Changes in pH value, alkalinity, Ca^{2+}, temperature and conductivity in Nõo experiment. The explanation of filters (NP, NS, NV1, NV2, NH1, and NH2) is described in the Materials and Methods. Second system (NV2+NH2) was resting for a month from 19th of December until 20th of January 2014.

Removal of phosphorus

Most of the inflow phosphorus in wastewater was in the form of PO_4-P. The total phosphorus (TP) concentration of pre-treated wastewater that was pumped into our filter systems was very high; a median taken from NS was 25 mg/L. From the Figure 5A we can see that the inflow concentration of phosphorus (TP) in our experiment is highly variable. This could be because of the butchery wastewater and wastewater from carpet cleaning company that is irregularly discharged to the sewer system. The results also show that the median reduction of TP in septic tank effluent was only 4.8% and in vertical flow filters was not remarkable – 17% in NV1 and 8.5% in NV2. We can notice that most of the organic phosphorus is disintegrated to ortho-phosphates in VF filters (Fig. 5).

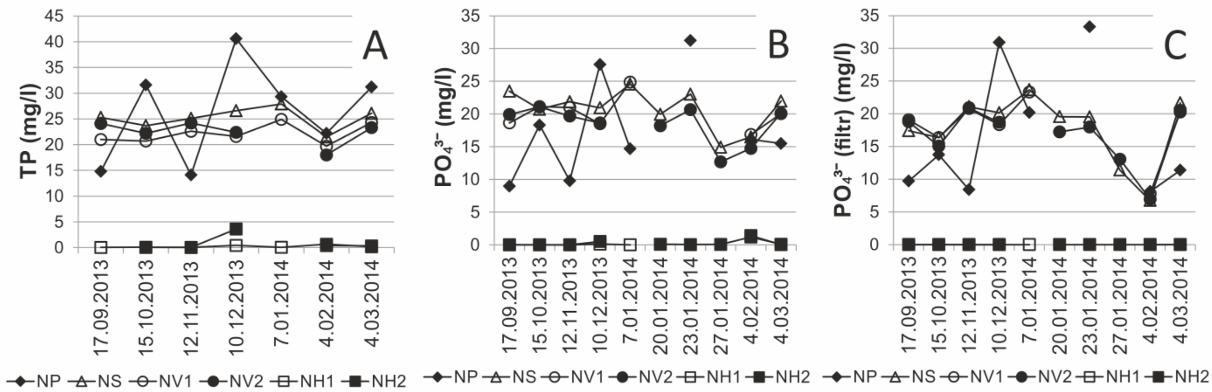

Figure 5. Removal of phosphorus (TP, PO_4^{3-}, and filtered PO_4^{3-}) in Nõo experiment. The explanation of filters (NP, NS, NV1, NV2, NH1, and NH2) is described in the Materials and Methods. Second system (NV2+NH2) was resting for a month from 19th of December until 20th of January 2014.

3.1.2. Changes in hydrated ash filters

Reduction of organic matter and solids

In our experiment, considerable amount of organic matter also enters to the horizontal flow (HF) ash filters with purpose to test the full capability of this material in P removal in unfavourable conditions. For example the median BOD_7 value of the inflow wastewater to the NH1 was 184 mg/L and to the NH2 312 mg/L (Fig. 2B). The reduction of BOD_7 in horizontal flow filters was 64% in NH1 and 54% in NH2. The median effluent BOD_7 values were 66 mg/L in NH1 and 110 mg/L in NH2; and COD values in NH1 167 mg/L and 219 mg/L in

NH2 (Fig. 2A). The BOD and COD outflow values are over the regulated limit value (shown in Table 2), however, much lower than expected from HF filters.

In horizontal flow filters the TSS was removed 75% in NH1 and 37% in NH2. The median outflow values from the horizontal flow filters were 17.3 mg/L in NH1 and 89 mg/L in NH2 (Fig. 2C), which shows that the result from second system was still over the regulated limit value (Table 2).

Removal of nitrogen

In our study the highest median reduction of TN was surprisingly achieved in NH2 filter (on average 30%). However, significant nitrogen removal in our experiment didn't happen. The median TN removal efficiency was approximately 40% in both filter systems. The median outflow values from the HF filters were 60 mg/L in NH1 and 58.9 mg/L in NH2 (Fig. 3A), which shows that the result from second system fit with the regulated limit value (Table 2).

Changes in pH, alkalinity, temperature, conductivity, Ca and Mg

As expected the pH values increased in our study in hydrated ash filters up to 13.0 (Fig. 4A). The outflow of hydrated ash filters shows a clear dependence on filter material properties. The HF outflow pH values have been relatively stable during the 6 months of experimentation.

The results show that also the alkalinity which describes the dissolution of carbonates in wastewater was higher in the effluent of HF ash filters (Fig. 4B). The alkalinity increased on average in HF ash filters from 1403 to 5415 mg $CaCO_3$/L in NH1 and from 1451 to 2600 mg $CaCO_3$/L in NH2. The Figure 4B also demonstrates the constant decrease in alkalinity of HF effluents in time.

We can see the same pattern of constant decrease with calcium (Fig. 4C). The median effluent value of Ca^{2+} was 552 mg/L in NH1 and 357.9 mg/L in NH2. However, on contrary magnesium is getting bound by hydrated ash and the effluent concentration is on average only 1.2 and 0.1 mg/L (median influent to HFs 41-42 mg Mg/L).

Removal of phosphorus with hydrated ash

During 6 months experimental period, the results show, that most of the phosphorus was removed in hydrated ash filters. The median efficiency of removing TP (median inflow TP concentration 29.3 mg/L) in ash filters was 99.7% in NH1 and 99.6% in NH2. The median outflow concentrations of TP were 0.07 mg/L in NH1 and 0.32 mg/L in NH2 and fit with the environmental regulation limits (Table 2). The results also show that when observing the HF effluents there have been no considerable differences between the efficiency of two parallel working hydrated ash filters in P removal.

The median inflow concentration of PO_4-P (i.e. unfiltered samples consisting of dissolved ortho-phosphates and particulate phosphates incorporated to solids) has been 20 mg/L. The median effectiveness of both filter systems in PO_4-P removal is similar: the removal efficiency of stable hydraulic loading regime (NV1+NH1) was 99.9% and in variable loading regime (NV2+NH2) it was 99.6%. However, from December we already noticed increased PO_4-P concentrations inside the NH2 filter (e.g. removal efficiency 69% in NH2f and 99% in NH1f). After the resting period of second filter system (from 19th of December 2013 until 20th of January 2014). The median removal efficiency of PO_4-P regained the same effectiveness as the first system (total 99.9% removal of PO_4-P). The median outflow PO_4-P values (unfiltered samples) were as low as 0.01 mg P/L (±0.53 mg/L) from NH1 and 0.07 mg P/L (±0.48 mg/L) from NH2.

Most of the inflow phosphates were in form of dissolved ortho-phosphates (median concentration 19 mg/L) and that is the key for having high phosphates precipitation capacity of hydrated ash. From the Figure 5B and 5C we can see that HF ash filters have high and stable PO_4-P and specially dissolved ortho-phosphates (i.e. analyses made from filtered samples; Fig. 5C) removal capacity after 6 months of operation. The median outflow dissolved ortho-phosphates concentration was on average 0.001 mg P/L for both filters.

3.2. Effect of pollutant loading on phosphates removal and changes inside hydrated ash filters

The experiment has lasted only for half a year and the first data analyses have been made. We saw that in this point of the experimentation (6 sampling events) we are not having enough data for full statistical analyses and therefore, in order to see whether there are first signs of some relationships between pollutant loading and phosphates removal, the trend line analyses were made. Furthermore, the distribution and extent of pollution inside hydrated ash filters during 6 months is determined.

3.2.1. Changes inside hydrated ash filters

The Figures 6 to 9 are showing the change inside hydrated ash filters during 6 months of experimentation (i.e. how the pollution has spread inside filters). The changes in distribution and extent of phosphates, calcium and pH value are observed.

By the time the experiment has been working just a month, we could see that PO_4-P has entered into the filters and high concentrations are seen in the first part (marked with A and B on the Figures 6-9) of the filters. The filtrated PO_4-P concentrations are slightly lower having not expanded in the filters as well as unfiltered PO_4-P samples have shown (Figures 6 and 7).

Calcium concentrations on the other hand have been higher in the end of the filters (i.e. further away from the inflow) and decreased in time. We could see that in NH1 (with stable hydraulic regime) Ca^{2+}concentrations are higher than in NH2 (with unstable hydraulic regime; Fig. 8). After the experiment has worked just for one month, the Ca^{2+} concentrations and pH values start to decrease in the inflow zone of the filters (marked with A and B). After 6 months period we can already see considerable differences in calcium concentrations and pH values inside the hydrated ash filters Fig. 9).

By December for filtered and unfiltered samples we saw higher PO_4-P concentrations inside both HF filters (Figures 6 and 7). The PO_4-P removal efficiency of NH2 had decreased to outflow PO_4-P concentration 0.5 mg/L and the outflow zone of the filter, sampling points marked with E and F on figures, had phosphates concentration of 8.9 mg/L and 5.6 mg/L, respectively. Furthermore, by December Ca^{2+} concentrations had lowered notably and therefore also pH values dropped down.

To test the effect of resting period on filter efficiency the second filter system NV2+NH2 had zero inflow from 19th of December 2013 until 20th of January 2014. The samples taken in January show that NH1 had maintained its good phosphorus removal efficiency and in NH2 (samples taken only from inside the filter) the calcium concentrations in the pore water of the filter started to increase again and therefore also pH values (see Fig. 8 and 9).

After restarting the inflow to the NH2 on 20th of January the samples were taken again in the beginning of February. From the results we can see that in the NH1 we still had high and stable phosphates removal capacity, however, the NH2 showed rapid increase of PO_4-P concentration inside the filter (Fig. 6 and 7). Yet, by March the phosphorus removal capacity of NH2 increased to the same level as in the NH1 showing only slight differences inside filters (Figures 6, 7 and 8).

Also, directly proportional relations could be seen between pH and PO_4-P and also Ca^{2+} and dissolved PO_4-P (i.e. filtrated samples). The substantial match draws out especially in the samples from inside of the HF filters. The trend line shows that the higher is Ca^{2+} concentration or pH value, the more efficient is the PO_4-P removal. It is again a confirmation that PO_4-P precipitation is related to the Ca content and pH value of the water (Table 6).

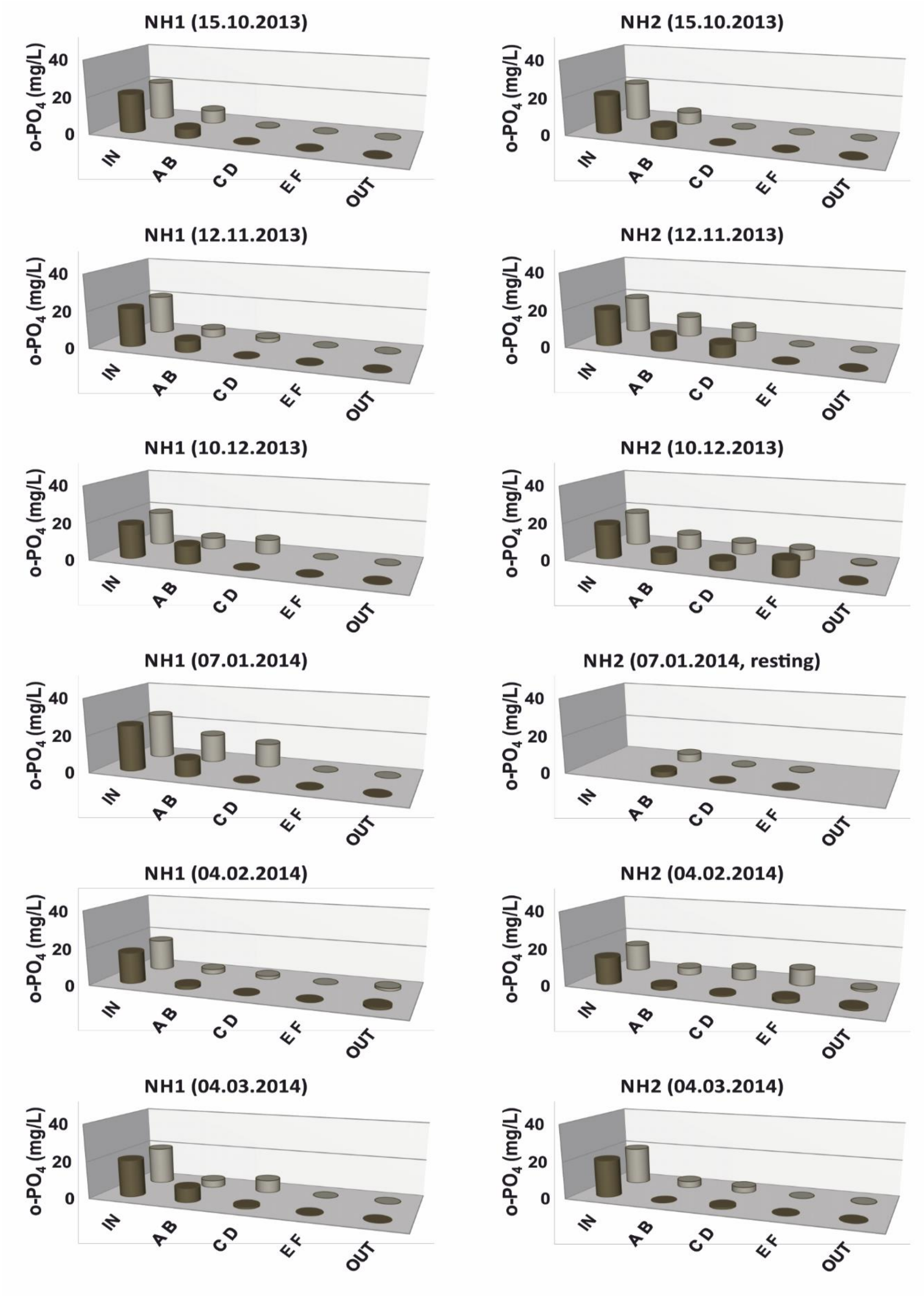

Figure 6. Changes in PO_4-P concentration (mg/L) inside the ash filters (NH1; NH2) during 6 month experimental period.

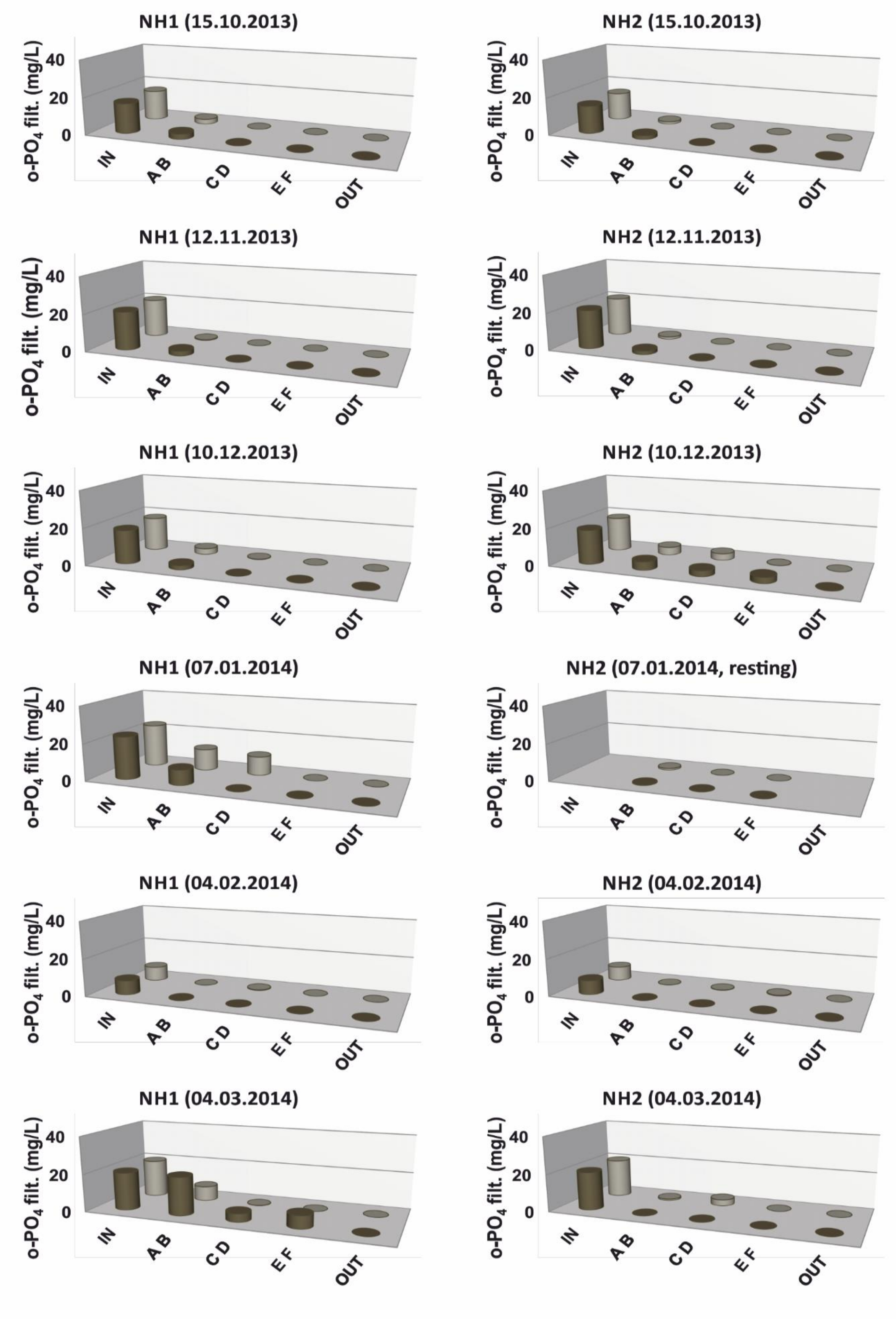

Figure 7. Changes in dissolved reactive PO_4-P concentrations (mg/L) inside the ash filters (NH1; NH 2) during 6 month experimental period.

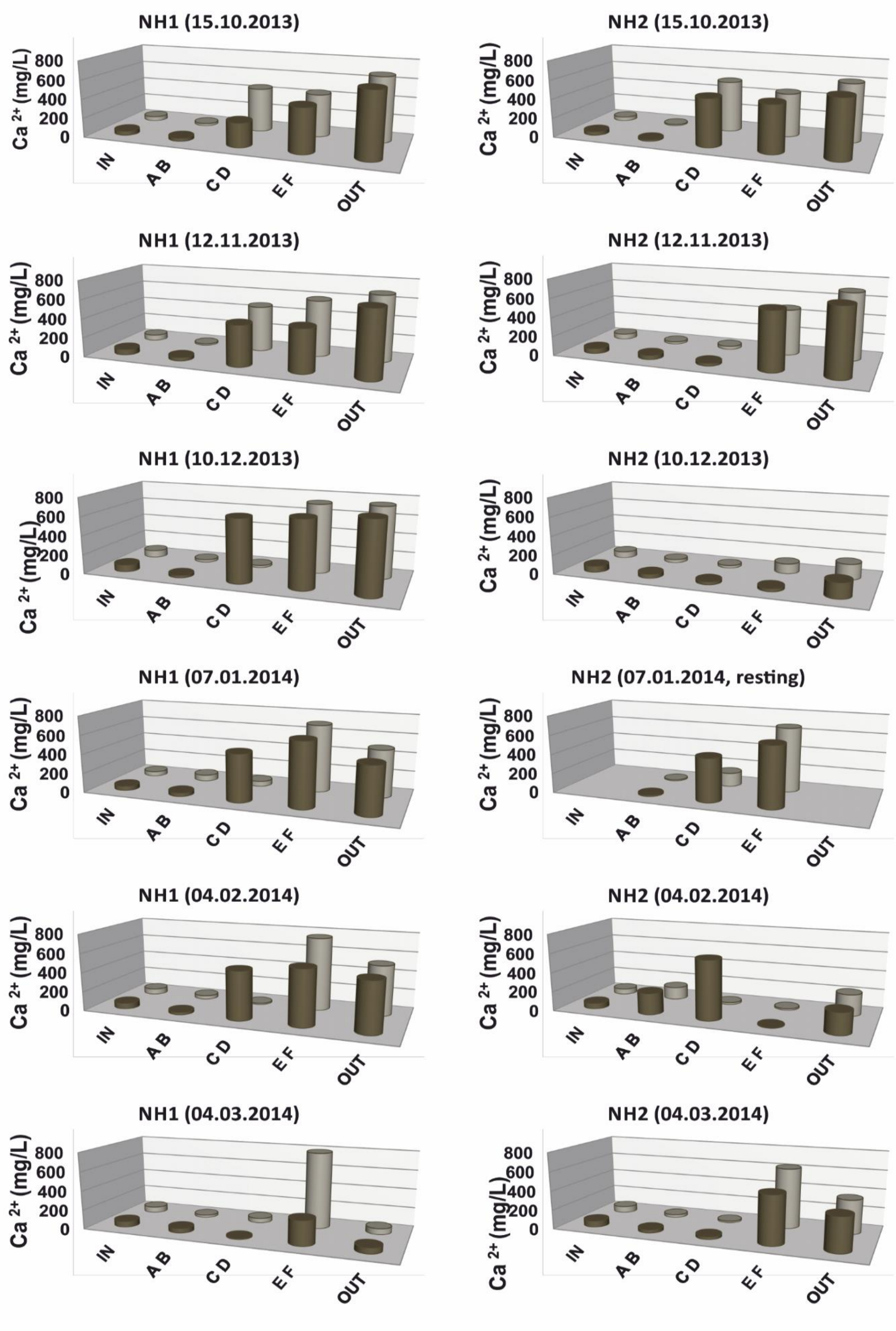

Figure 8. Changes in calcium concentration (mg/L) inside the ash filters (NH1; NH2) during 6 month experimental period.

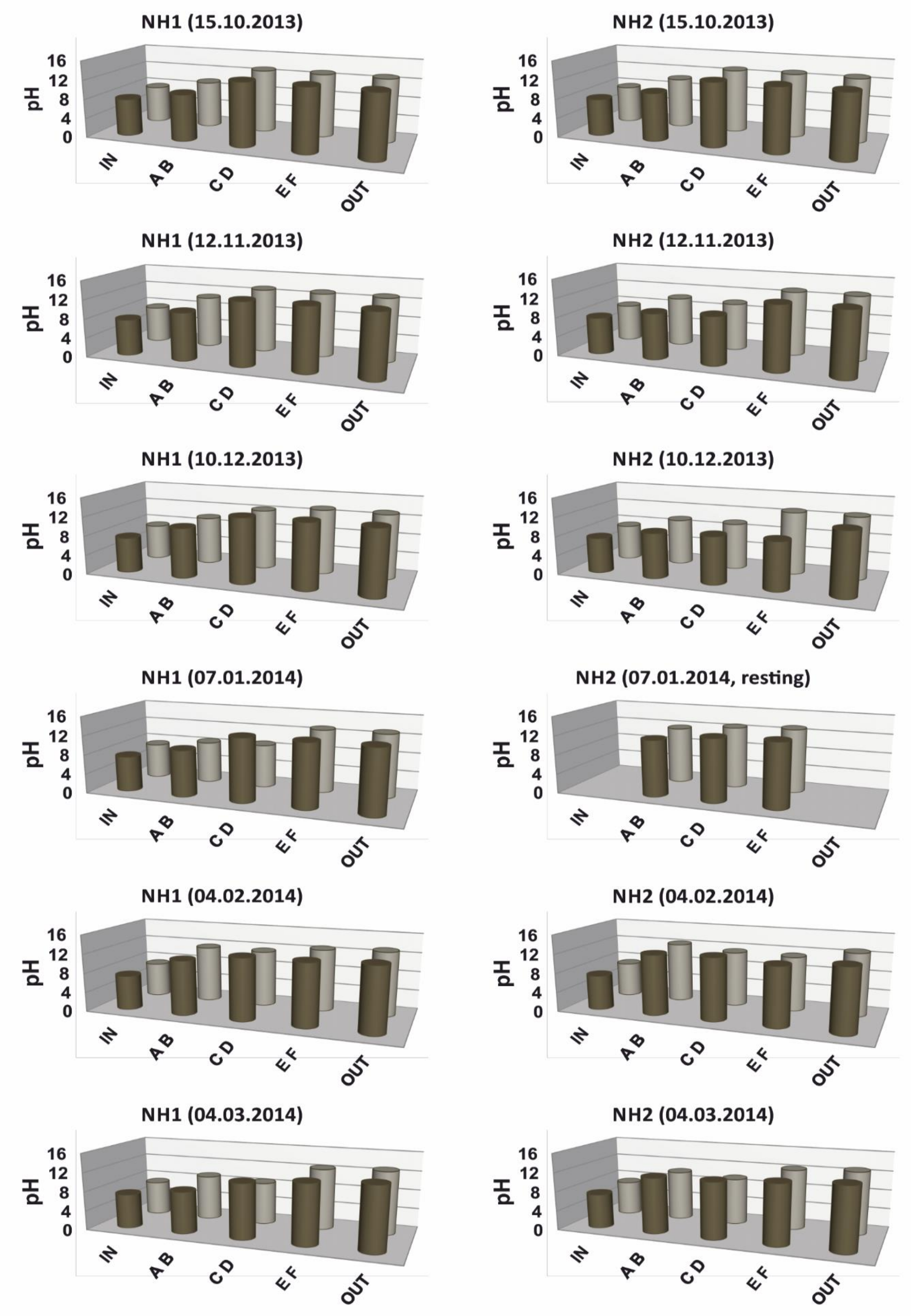

Figure 9. Changes in pH value inside the ash filters (NH1; NH 2) during 6 month experimental period.

3.2.2. Effect of pollutant loading on phosphates removal

The filter systems in our study were fed with an extremely high strength wastewater (Table 2). To understand, whether the organic pollution and solids have an effect on phosphorus removal, we made first comparisons between the COD, BOD_7, TSS, VSS, TN, NH_4 and TP concentration variations in time and dissolved PO_4-P (i.e. filtrated samples) concentration variations in time.

We could see slight relation between PO_4-P and COD, BOD_7, TN, TP, and Mg. The directly proportional graphs show that when some pollutant concentrations increased the PO_4-P value increases with the same rate and therefore the phosphates removal efficiency lowered. Most affected was the first zone of the filters (sampling points: NH1a, NH1b and NH2a, NH2b; see Tables 4, 5, 6). However, we are yet not having enough data (only 6 sampling events) to see good fit and correlations between pollutant loadings and phosphates removal in the hydrated ash filters. Despite that, we can see first changes inside the HFs and trends of relations between different pollutants.

5. Discussion

5.1. The efficiency of pre-treatment of septic tank and vertical flow filters

The influent to our experimental system was high strength wastewater with high organic matter and nutrients content (Table 2). The intention of this experiment is to test the full capacity of the hydrated ash in high pollution condition. Therefore, high organic loading rate was applied in order to observe its impacts on the P removal in HF ash filters. To achieve high pollutant loading rate to the HFs the pre-treatment phase (septic + VFs) was designed to be under-dimensioned.

The results show that the organic loading into our system differs from month to month– the COD, TN and TP inflow variations are seen on the Figures 2A, 3A and 5A, respectively. This could be caused by the special composition of the raw wastewater of the settlement caused by irregular butchery and carpet cleaning company wastewater inflow to the main sewer system.

As expected, in the septic tank the best removal efficiency was achieved in case of solids (median 33%, up to 73%), but no removal of o-PO_4^{3-} and only 4.8% removal of TP were present. According to different studies the average septic efficiency with municipal wastewater is for TSS more than 70%, for BOD_7 20-60%, and for TN and TP only 10-20 % (Kuusik, 1995, Bounds, 1997). For best removal in septic tank it is crucial to have optimal hydraulic retention time of one to two days. In our experiment the average retention time was about 2 days, however, the used inflow wastewater was untypically high strength and therefore more difficult to treat.

The aim of vertical flow filters is to achieve aerobic biological treatment of wastewater– usually degradation of organic matter and nitrification of ammonium-nitrogen. Typically VFs are used as primary treatment and are followed by other treatment steps, e.g. horizontal subsurface flow filters. In our experiment the VFs had the purpose to lower (yet not to eliminate) the organic matter, solids, nutrients loading to the following hydrated ash filters. Therefore, the VF filters of were under-dimensioned. The results showed that VFs had relatively good organic matter and solids removal efficiency, but poor nitrification rate. This can be explained by the fact that there exists a competition for space on the filter media and oxygen between the ordinary heterotrophic organism (OHOs) for BOD_7 removal and the autotrophic nitrifying bacteria for ammonia removal (Metcalf & Eddy, 2003). OHO have a faster growth rate and a higher yield coefficient implying that they would predominate in the filter, leaving no space and oxygen for nitrifying bacteria. Previous studies have shown that to initiate nitrification in a fixed film packing reactor, the effluent BOD_7 needed to be less than 30 mg/L and for complete nitrification it needed to be less than 15 mg/L (Metcalf & Eddy, 2003). In our experiment the average inflow BOD_7 to the VFs was as high as 600 mg O_2/L and probably all available oxygen was first handed used for mineralization of organic matter.

The process that is taking place in our VF filters with ammonium-nitrogen is ammonification, so that most of the nitrogen that exits the VFs is in the form of NH_4-N. Therefore, if our aim would be to support nitrification we would have to lower the organic and hydraulic loading rate to and increase the aeration rate of the VFs. One relatively easy solution for improving the efficiency of our VFs would be usage of recirculation of VF effluent back to the inflow with purpose to increase the aeration rate of the wastewater and to dilute the high strength influent with already treated effluent. Opposite to the carbon and nitrogen, phosphorus cannot be removed in treatment wetland and filter systems through metabolic processes. Phosphorus is removed in TWs by adsorption, precipitation and relatively small portion trough plant uptake. The sorption and precipitation of phosphorus are controlled by the properties of the filter material (e.g. content of Fe-, Al-, Ca-minerals, and porosity), the hydraulic parameters (loading rate, porosity of and retention time in material) and the physicochemical environment (Faulkner and Richardson, 1989; Kadlec and Knight, 1996; Zhu et al, 1997; Vymazal et al., 2000). In our vertical flow filters the used filter material (LECA) and hydraulically unsaturated conditions are not favouring phosphorus removal. This demonstrates the need for a separate treatment step with reactive filter materials in order to remove phosphates from the wastewater.

5.2. The efficiency of hydrated ash filter in phosphorus removal

In alkaline conditions, such as in hydrated ash, phosphates are bound with calcium and magnesium and precipitated as hardly soluble salts (Kaasik et al. 2008). The adsorption and precipitation are affected by the reaction and retention time between polluted water and filter material (Liira et al. 2009). Therefore, it is important to implement hydraulically saturated conditions and to use optimal retention time for hydrated ash filters.

The excellent phosphates removal of the hydrated oil shale ash filters was similar to the previous studies and was mostly based on active filtration of phosphates by formation of insoluble Ca-phosphates (Liira et al., 2009; Kõiv et al., 2010, Karabelnik et al., 2012). Unlike to column study done by Liira et al. (2009), who reported a decrease from 91% to 49% in P removal over a five-month period, in our experiment the TP removal efficiency (most of our TP was in form of dissolved ortho-phosphates) remained high throughout six-month period (99.6% removal of TP in NH1 and 98.6% in NH2 system).

In our study, the phosphorus removal rate in hydrated oil shale ash using high strength wastewater was even slightly higher than reported in previous studies (Liira et al., 2009, Karabelnik et al., 2012). This can be attributed to the high influent dissolved phosphates concentration and therefore highly P-saturated conditions in the pore water of the hydrated ash. Previous research has demonstrated that the higher is dissolved phosphates concentration in wastewater the higher is also the removal rate (Kõiv et al. 2010). The results of study carried on by Kõiv et al. (2010) show that the removal rate of phosphorus in hydrated ash filters depends significantly on the concentration of phosphates in solution. The removal efficiency is low (<50%) at low P concentrations (< 0.2 mg/L), and efficiency increases abruptly when the phosphates concentration is higher than 0.5 mg/L. Hinedi et al. (1999) and Plant and House (2002) show in their research, that at low P concentrations (< 20 mmol/L, i.e. 0.62 mg/L) the phosphorus in the calcite seeded system is co-precipitated with calcite by incorporating P ions into calcite crystal surfaces (Kõiv et al. 2010). At P concentrations exceeding 20 mmol/L, however, the calcite precipitation ceases and precipitation of the Ca-phosphate occurs at high oversaturation with respect to the stable hydroxyl-apatite phase (Plant and House, 2002).

Furthermore, the initial pH of hydrated oil shale ash filters used in the present study had an average value 13.1. This average value is slightly higher compared to those reported from previous experiments (average pH value from the hydrated oil shale ash filter effluent in experiment done by Kõiv et al. (2009) was 12.0 and in Liira et al. (2009) experiment 11.0), which could pose an additional reason for better performance observed here. This could be due to the slightly different composition (e.g. higher Ca dissolution rate) of the hydrated ash compared to the material used in previous study and/or the different fraction (more small size particles) and therefore bigger special surface area of current hydrated ash.

The results showed that all the magnesium that entered the hydrated ash filters was kept in the material and the outflow concentrations were really low (on average 1.2 mg/L in NH1 and 0.1 mg/L in NH2). Magnesium is known to inhibit the growth of the most stable Ca- phosphate crystalline formation (House, 1999), therefore, the effect of Mg on phosphates removal should be further studied. To address the problem of highly alkaline effluent of the hydrated ash filters entering environment there have been several studies demonstrating that high pH can be lowered by using polishing filters or other types of treatment steps. Liira et al. (2009) did show that the water treated with hydrated ash can be efficiently neutralized to pH 7-8 (that fits to the environmental regulations) by using a peat filter bed installed subsequent to the hydrated ash filter.

5.3. The effect of different hydraulic loading regime on P removal

The results show that in the end of the experiment during 6 months period when observing the overall efficiency (according to effluent values) of hydrated ash filters there has been no difference between two parallel working systems (NV1+NH1 and NV2+NH2) in PO_4-P removal during this six month period. However, when examining changes inside the ash filters we can see differences between the filters. From these results we can make first conclusions about the effect of different loading regime on the efficiency of filter material. As expected the stable and constant loading and retention time ensures also a better overall efficiency and slower saturation of filter material.

The one month resting period in for second filter hydrated ash filter NH2 has improved the median removal efficiency of PO_4-P (from 69% to 99.9%) in HF ash filter to the same level as in first filter NH1 (from 69% to 99.9%). Similar phenomena was found also in Kõiv et al., (2010) experiment where the median removal efficiency of TP in HF filters increased to 85.4% and 99.2% in the Väätsa and Tapa experiment respectively after the VF filters were switched off. Regeneration of P retention sites was demonstrated also in on-site experiment of Bird and Drizo (2010), where electric arc furnace steel slag filters were used. The increase in the phosphorus removal could be explained by the additional seeding effect at numerous new nucleation sites created by the formation of Ca-phosphate and probably authigenic calcite- crystallites. A similar effect was discovered by Adam et al. (2005) in small-scale box experiments for phosphorus sorption by Filtralite-P, where the increase in the P sorption capacities of the material after the resting periods was explained by the formation of the seeds of calcium phosphates. Also, probably the lack of inflow pollution during resting period gives the material extra time for the calcium dissolution; however, it seems that the NH2 had some sort of shock effect after restarting of the second system (results of February) that can be observed on Figures 6 to 9. Regeneration of P retention sites was demonstrated also in Bird and Drizo (2010) on-site experiment, where electric arc furnace steel slag filters were used. Therefore, we also recommend when treating high strength wastewater to ensure relatively stable hydraulic regime or otherwise alternate resting cycles should be integrated into the design of hydrated oil-shale ash filters systems for high strength content wastewater.

5.4. The effects of solids, organic matter, nutrients loading rates on phosphorus removal

Interestingly, the removal efficiency of phosphates in the hydrated ash filters is not considerably affected by the inflow wastewater composition after 6 month period. Although the organic matter and solids removal was good in the experimental systems, the analyses made while correlating organic matter, solids, nitrogen, main cations and anions, alkalinity and conductivity data with o-PO_4^{3-} didn't show any significant match. The results don't show good relations probably because of the lack of data. The data of only 6 samples is not enough to show good match between pollutants effects on phosphorus removal, we could see only the first trends.

On the other hand, comparing pH and Ca^{2+} with PO_4-P gave significant match. The inverse proportional trend line indicates that the higher the pH value and Ca^{2+} content in HF ash filters is, the lower is PO_4-P content and therefore the higher is phosphorus removal efficiency (Table 6). A significant correlation between increasing pH and P removal was found also in Nilsson et al. (2013) column experiment for Polonite (also Ca-rich reactive material) with wastewater of high BOD_7.

Significant match was seen also by comparing the data of Ca^{2+} and pH. This result proves again that PO_4-P precipitation is connected with the dissolved Ca^{2+} concentration and therefore pH of the water, and this is supported by other studies where calcareous filter materials were used (e.g. Liira et al., 2009, Kõiv et al., 2009, Nilsson et al., 2013).

5.5. Potential of clogging of hydrated ash

The clogging of a filters substrate material caused by development of biofilm has been identified as one of the biggest operational problems in similar to the on-site wastewater treatment systems (Bird and Drizo, 2010). According to McDowell-Boyer et al. (1986) clogging increases the possibility of straining within porous media, such as hydrated oil-shale ash in the present case. To prevent the clogging in subsurface flow TWs it is suggested that these systems could be intensified by recirculating the effluent to the front of the system or improving the aeration in case of vertical flow systems (Fonder and Headley, 2013).

Based on previous studies with hydrated oil shale ash (e.g. Liira et al., 2009; Kõiv et al., 2010) and relatively low inflow pollutant loading rates the clogging and saturation of material has never occurred. The estimated expected lifespan of the hydrated ash should be longer than two years (Liira et al., 2009). Yet, there has not been any studies conducted with main purpose to see the effect of high organic and solids loading rate on hydrated ash.

Current experiment should give a better understanding on main processes inside hydrated ash and show the effect of potential clogging with organic matter and solids. Hence, it is important to determine whether the high loading results in rapid decreased of filter efficiency and clogging of the material. Also, the clogging of distribution and other pipe systems can occur first handed and cause lot of problems, therefore, regular control and maintenance of the filter system is needed.

All information gained from this experiment should provide us with knowledge about the specific design parameters and restrictions when planning to implement hydrated ash as reactive filter material.

Conclusions

The results of this study described the effectiveness of hydrated oil-shale ash filters and demonstrate their potential for the treatment of high-strength municipal wastewater. During first six months of the experiment the inflow organic matter and nutrients content was really high when compared with typical municipal wastewater (e.g. median BOD_7 600 mgO_2/L, TN 100 mg/L, TP 29 mg/L and PO_4-P 15.5 mg/L). The under-dimensioned vertical flow LECA filters showed relatively good results in terms of organic matter and solids removal, but not in nitrification. This is probably caused by the fact that in our highly loaded vertical flow filters there is competition between different microbial communities for the space and oxygen.

We determined high efficiency for TP and PO_4-P removal in horizontal flow hydrated ash filters during the whole experiment (TP: 99.6% in NH1 and 98.6% in NH2; PO_4: 99.9% in NH1 and 99.6% in NH2), while also maintaining high pH values of the filter effluent (median pH 13.0). The median outflow PO_4-P values were as low as 0.01 mg/L (±0.53 mg/L) from NH1 and 0.07 mg/L (±0.48 mg/L) from NH2. We can conclude that six sampling times is not giving us enough data to see significant correlations between input pollutants and P removal. We could observe only the first trends.

During the first six months there was only few sign of clogging of the hydrated oil-shale ash, however, the distribution and drainage piping needed cleaning. Therefore regular control and maintenance of the filter systems is needed.

Based on this research so far, we recommend that when treating high-strength wastewater alternate resting cycles should be integrated into the design of horizontal subsurface flow hydrated ash filter systems. To promote nitrification, aeration increase is needed in vertical flow filters.

In order to see the impact of high organic, nutrient and solid loading rate on the removal of phosphates, the experiment has to continue and more data gathered. All information gained from this experiment should provide us with knowledge about the specific design parameters and restrictions when planning to implement hydrated ash as reactive filter material.

Summary in Estonian

Fosfori aktiiv-filtratsioon hüdratiseerunud põlevkivituha filtrites: erineva hüdraulilise viibeaja ja reostuskoormuse mõju

Maris Plado

Projekti "Fosforiärastustehnoloogiad märgalapuhastites: põlevkivituhasette filtersüsteemide omadused ja pikaajaline toimimine" raames käivitati 2013. aasta septembris Nõo reoveepuhasti juures välikatse, mis kestab 2015. aasta augustini. Käimasoleva välikatse eesmärgiks on leida sobilik spetsiaalselt fosfori-ärastusele orienteeritud puhastus-süsteem haja-asustuses paiknevatele majapidamistele, väikeasulatele, ettevõtetele jne. (reostuskoormus 5 kuni 500 IE). Katse hindab varasemate uurimustööde käigus efektiivseks osutunud hüdratiseerunud põlevkivituha pikaajalist fosfori sadestamise (Ca-fosfaadina) potentsiaali ning materjali eluiga kõrge reostuskoormuse korral.

Täismõõtmetes katse, mis imiteerib 5 IE suuruse reostuskoormusega reoveeallikat (nt. eramajapidamine), koosneb eelpuhastus etapist (2 m^3 septikust; NS) ja kahest paralleelselt töötavast pinnasfiltersüsteemist, mis erinevad ainult hüdraulilise režiimi poolest (see mõjutab reovee viibeaega filtris). Esmane reovee puhastus toimub vertikaalvoolulistest pinnasfiltrites (NV1 ja NV2, mõlema maht 3 m^3), milles on filtermaterjaliks erineva fraktsiooniga kergkruus. Sekundaarne puhastus toimub horisontaalvoolulistes pinnasfiltrites (NH1 ja NH2; mõlema filtri maht 8 m^3), mille täitematerjaliks on hüdratiseerunud põlevkivituhk. Esimene pinnasfiltersüsteem (NV1+NH1) on stabiilse hüdraulilise režiimiga (perioodiliselt iga 40 minuti tagant (0,55 m^3/d) ning teise pinnasfiltersüsteemi (NV2+NH2) korral imiteerib režiim ühepereelamu reoveeteket – hommikuti/õhtuti ja nädalavahetuseti on vee kasutus intensiivsem (5 päeva nädalas 0,4 m^3/d ja 2 päeva 0,9 m^3/d). Mõlema pinnasfiltersüsteemi hüdrauliline koormus on aga sama – 3,83 m^3/nädalas.

Käesoleva magistritöö eesmärkideks on:

- analüüsida hüdratiseerunud põlevkivituha P-ärastuse efektiivsust kõrge reostuskoormusega katses;
- kindlaks määrata eelpuhastuse ja esimese astme puhastuse roll orgaanilise aine ja teiste reoainete eemaldamises;
- hinnata erineva hüdraulilise režiimi mõju fosforiärastusele hüdratiseerunud tuhas;
- uurida kõrge reostuskoormuse mõju hüdratiseerunud tuha efektiivsusele ja jälgida reostuse levikut tuhafiltrites.

Antud uuringus kasutatakse sissevooluna kõrge reoainete sisaldusega olmereovett, mille keskmine BHT_7 on 600 mg O_2/L, üldlämmastik 100 mg/L, üldfosfor 29 mg/L ja fosfaatide sisaldus 15,5 mg/L. Eesmärgipäraselt allamõõtmeline (et garanteerida ainult osaline reostuse eemaldamine) vertikaalvoolulised kergkruusa filtrid näitasid üllatavalt häid tulemusi orgaanilise ja tahke aine eemaldamises, kuid jäid hätta ammoonium-lämmastiku nitrifikatsioonis. See on arvatavasti tingitud kõrgest sisendkoormusest vertikaalvoolulistesse filtritesse, mille tõttu toimub filtris konkurents ruumile ja hapnikule ning domineerivad on orgaanikat lagundavad mikro-organismid.

Hüdratiseerunud tuha fosfori (P) sidumise efektiivsus oli suurepärane mõlemas horisontaalvoolulises filtris. Üldfosfori sidumisefektiivsus oli keskmiselt 99,6% stabiilse viibeajaga filtris NH1 ja 98,6% varieeruva viibeajaga filtris NH2. Kuna enamus filtritesse sisenevast fosforist oli lahustunud fosfaatide kujul. Lahustunud PO_4-P sidumise efektiivsus oli tuhafiltrites kuue kuu jooksul stabiilselt 99,9% NH1-s ja 99,6% NH2-s ning keskmine väljavoolu PO_4-P kontsentratsioon oli mõlema süsteemi korral vaid 0,002 mg/L.

Samas, vaadates muutuseid tuhafiltrites seest võetud veeproovides, me näeme, et ebastabiilse koormusega filtris NH2 toimus kiiremini vee pH ja kaltsiumi kontsentratsiooni alanemine ja sellega seoses ka fosforiärastuse vähenemine. Plaaniline kuuajaline puhkepaus tunduvalt parandas NH2 fosfaatide sadestamise efektiivsust, sest vee seismine tuhafiltris intensiivistas kaltsiumi lahustumist ja põhjustas poorivee pH tõusu.

Antud tulemuste põhjal me järeldame, et stabiilne viibeaeg tagab parema efektiivsuse ning ebastabiilse koormuse korral on efektiivsust võimalik suurendada ja filtrit võimekust taastada pikemaid puhkepause kasutades.

Saadud tulemuste põhjal saame järeldada, et kuus proovivõtukorda ei andnud meile piisavalt informatsiooni kõrge reostuskoormuse mõju kohta tuhafiltritele, et näha märgatavat korrelatsiooni süsteemi sisenevate saasteainete ja fosfaatide ärastamise efektiivsuse vahel.

Loodetavasti edasise 1,5 aasta jooksul (katse kestab kuni august 2015) on selgemini ning statistiliselt usaldusväärselt näha ka erinevate reoainete mõju tuhafiltrite efektiivsusele, küllastumisele ning elueale. Projekti tulemused peaksid andma täpsemad teadmised hüdratiseerunud tuhafiltrite projekteerimiseks ja kasutamiseks.

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Supplementary data

Table 4. The direction of the relationship between different pollutants (COD, $BOD_{7,}$ TSS, VSS) concentrations (mg/L) towards dissolved PO_4-P (i.e. filtered sample) concentration. Directly proportional graph (marked with "↗") shows relation when one content increases another content increases at the same rate. Inversely proportional graph (marked with "↘") shows that as one concentration decreases the other one increase at the same rate. No relation between concentrations (marked with "→") means that there was no relation between two pollutants. The inflow pollution content was compared towards the dissolved PO_4-P contents inside the hydrated ash filter samples (marked with a, b, c, d, e, and f) and also towards the samples taken from effluents of the NH1 and NH2. The pollution content inside the ash filters were also compared with the dissolved PO_4-P contents inside the hydrated ash filter samples. The presented pollutants were on X-axis and dissolved PO_4-P was on Y-axis.

	COD in/PO_4 out	COD out/PO_4 out	BOD_7 in/PO_4 out	BOD_7 out/PO_4 out	TSS in/PO_4 out	TSS out/PO_4 out	VSS in/PO_4 out	VSS out/PO_4 out
NH1	→	→	→	→	→	→	→	→
NH1_a	↗	n/a	↗	n/a	→	n/a	→	n/a
NH1_b	↗	n/a	↗	n/a	→	n/a	→	n/a
NH1_c	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH1_d	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH1_e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH1_f	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH2	→	→	→	→	→	→	→	→
NH2_a	↗	n/a	↗	n/a	↗	n/a	↗	n/a
NH2_b	↗	n/a	↗	n/a	↗	n/a	↗	n/a
NH2_c	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH2_d	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH2_e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NH2_f	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table 5. The direction of the relationship between different pollutants (TN, NH_4-N, TP) concentrations (mg/L) towards dissolved PO_4-P (i.e. filtered sample) concentration. Directly proportional graph (marked with "↗") shows relation when one content increases another content increases at the same rate. Inversely proportional graph (marked with "↘") shows that as one concentration decreases the other one increase at the same rate. No relation between concentrations (marked with "→") means that there was no relation between two pollutants. The inflow pollution content was compared towards the dissolved PO_4-P contents inside the hydrated ash filter samples (marked with a, b, c, d, e, and f) and also towards the samples taken from effluents of the NH1 and NH2. The pollution content inside the ash filters were also compared with the dissolved PO_4-P contents inside the hydrated ash filter samples. The presented pollutants were on X-axis and dissolved PO_4-P was on Y-axis.

	TN in/PO_4 out	TN out/PO_4 out	NH_4 in/PO_4 out	NH_4 out/PO_4 out	TP in/PO_4 out	TP out/PO_4 out
NH1	→	→	→	↘	→	→
NH1_a	↗	n/a	↘	↘	↗	n/a
NH1_b	↗	n/a	↘	↘	↗	n/a
NH1_c	n/a	n/a	n/a	n/a	n/a	n/a
NH1_d	n/a	n/a	n/a	n/a	n/a	n/a
NH1_e	n/a	n/a	n/a	n/a	n/a	n/a
NH1_f	n/a	n/a	n/a	n/a	n/a	n/a
NH2	→	→	→	↘	→	→
NH2_a	↗	n/a	→	↘	↗	n/a
NH2_b	↗	n/a	↘	↘	↗	n/a
NH2_c	n/a	n/a	n/a	n/a	n/a	n/a
NH2_d	n/a	n/a	n/a	n/a	n/a	n/a
NH2_e	n/a	n/a	n/a	n/a	n/a	n/a
NH2_f	n/a	n/a	n/a	n/a	n/a	n/a

Table 6. The direction of the relationship between different pollutants (magnesium and calcium) and parameters (alkalinity, conductivity and pH) towards dissolved PO_4-P (i.e. filtered sample) concentration. Also, the direction of the relationship between Ca concentration (mg/L) and pH value is shown. Directly proportional graph (marked with "↗") shows relation when one content increases another content increases at the same rate. Inversely proportional graph (marked with "↘") shows that as one concentration decreases the other one increase at the same rate. No relation between concentrations (marked with "→") means that there was no relation between two pollutants. The inflow pollution content was compared towards the dissolved PO_4-P contents inside the hydrated ash filter samples (marked with a, b, c, d, e, and f) and also towards the samples taken from effluents of the NH1 and NH2. The pollution content inside the ash filters were also compared with the dissolved PO_4-P contents inside the hydrated ash filter samples. The presented pollutants were on X-axis and dissolved PO_4-P or pH were on Y-axis.

	Mg in/PO_4 out	Mg out/PO_4 out	Cond. in/PO_4 out	Cond. out/PO_4 out	Alc. in/PO_4 out	Alc. out/PO_4 out	Ca in/PO_4 out	Ca in/PO_4 out	pH in/PO_4 out	pH out/PO_4 out	Ca in/pH out	Ca out/pH out
NH1	→	→	→	→	→	→	→	→	→	→	→	↗
NH1_a	↘	↗	↘	↗	↗	n/a	↘	↗	↘	↘	↗	↘
NH1_b	↘	↗	↘	↗	↗	n/a	↘	↗	↘	↘	↗	↘
NH1_c	n/a	n/a	n/a	n/a	n/a	n/a	n/a	↘	n/a	↘	n/a	↗
NH1_d	n/a	n/a	n/a	n/a	n/a	n/a	n/a	↘	n/a	↘	n/a	↗
NH1_e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	→	n/a	→	n/a	↗
NH1_f	n/a	n/a	n/a	n/a	n/a	n/a	n/a	→	n/a	→	→	→
NH2	→	→	→	→	→	→	→	→	→	→	↗	↗
NH2_a	↘	↗	↘	↗	↗	n/a	→	↘	↗	↘	↘	↗
NH2_b	↘	↗	↘	↗	↗	n/a	↗	↘	↗	↘	n/a	↗
NH2_c	n/a	n/a	n/a	n/a	n/a	n/a	n/a	↘	n/a	↘	n/a	↗
NH2_d	n/a	n/a	n/a	n/a	n/a	n/a	n/a	↘	n/a	↘	n/a	↗
NH2_e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	↘	n/a	↘	n/a	↗
NH2_f	n/a	n/a	n/a	n/a	n/a	n/a	n/a	↘	n/a	↘	n/a	↗

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